Norwegian University of Life Sciences
Faculty of Science and Technology

Philosophiae Doctor (PhD)
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# Identification of efficient and affordable technologies for sustainable production of biodiesel from various bio-resources

## Identifisering av effektive og rimelige teknologier for bærekraftig produksjon av biodiesel fra forskjellige bioressurser

Shemelis Nigatu Gebremariam

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*- Dedicated to my beloved family*

"*Whoever dwells in the shelter of the Most High will rest in the shadow of the Almighty*"
Psalm 91:1

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# Summary

Population growth and a significant improvement in living standards in most parts of the world has resulted in an increasing energy demand. Fossil fuels are used for most of the world's energy demands. However, fossil fuels have been identified to be one of the main sources of greenhouse gas (GHG) and other environmental pollutants. Fossil fuels are increasingly more difficult to obtain to support the world's expanding economic activities. Therefore, the search for alternative renewable energy resources that could secure the world energy supply without imposing significant negative impact on the natural environment is inevitable. Biofuels are promising renewable energy alternatives to replace petroleum fuels. Among such biofuels is biodiesel, which is non-toxic and biodegradable and has low GHG emmisions compared to the fossil diesel. Biodiesel can be produced easily from various feedstock types using a number of different technologies. Homogeneous base catalyzed transesterification is the conventional way to produce biodiesel at an industrial scale. However, this catalyst technology requires oil feedstock with very high purity, such as edible oil. The high price of edible oil could increase the overall production cost so that biodiesel would not be economically competitive with fossil diesel. There are also food versus energy controversies. Consequently, the high cost of production has been the main constraint for wide spread use of biodiesel fuel. Since the cost of feedstock comprises more than 80% of the total biodiesel production cost, identifying a production process that could produce fuel grade biodiesel from low quality and cheap feedstock would be indispensable.

The primary objective of the present PhD thesis is, therefore, to identify technically efficient and economically affordable technologies for the production of fuel quality biodiesel from non-edible and cheap oil feedstock. In doing so, the thesis attempted to evaluate the techno-economic performances of some selected production technologies. In addition, in order to optimize the production processes, the thesis assessed the sensitivity of the production technologies towards the change in market values of inputs and outputs as well as the change in production capacity. The entire study is process simulation based using two-advanced software - Aspen Plus® and Super Pro®.

The present PhD thesis is based on seven scientific papers that are geared towards achieving the same objective as this thesis, as stated above. It is evident from the vast scientific literatures that there have been enormous amount of research undertaken on the production of biodiesel using different technological routes. Therefor, the approach that we

first considered was a review of the relevant literatures to provide an overview of the advantages and disadvantages of the main transesterification techniques for biodiesel production (**Paper I**). Categorized by their catalyst type, the technologies have been evaluated for their choice of feedstock as well as for their reaction conditions, which are required to efficiently convert the feedstock to biodiesel. A state of the art review of the available literatures has been undertaken to investigate the economics of biodiesel production (**Paper II**). This review was related to the determination and comparison of the total cost of investment, direct production costs as well as various system variables affecting profitability among different production technologies and production scales.

Two effective catalyst technologies (Sulfuric acid and Calcium oxide) were selected for further assessment of the techno-economic performances of the process alternatives (**Paper III**). Three complete process flows were designed using these catalysts separately and in combination. The sensitivity of the process alternatives were also analyzed for changes in market values of oil cost and biodiesel selling price. To have a base for optimizing the process, a comprehensive investigation of the effect of more market variables on the feasibility of the CaO catalyzed process has been carried out (**Paper IV**). This sensitivity analysis was performed over the market value of the price of biodiesel, glycerol, oil feedstock, alcohol, catalyst, and labor cost, equipment maintenance cost as well as a variation of local tax to test how these variables could affect the feasibility of the business.

In an extended study, the techno-economic performances of the different layouts of biodiesel production processes using sulfuric acid catalyst have been assessed (**Paper V**). Four different scenarios of sulfuric acid catalyzed biodiesel production processes have been simulated based on four different arrangements of operation units for major downstream processes. The sensitivity analysis was undertaken to investigate how Net Present Value (NPV) and Payback time could be affected by a change in market values of biodiesel selling price and oil purchasing cost. This could help to identify the most tolerant alternative to the global market fluctuations of the variables. Similarly, the techno-economic implications of the different process layouts and capacities of biodiesel production using a CaO catalyst has also been investigated (**Paper VI**). In this study, four scenarios of biodiesel production processes using a CaO catalyst have been designed based on the different possible arrangements of each unit procedure required to produce biodiesel from acidic oil. These four process scenarios have also been redesigned into two additional feedstock capacities (with a total of three feedstock capacities: 3106.34, 5177.23, and 7248.12 $kgh^{-1}$) to investigate the economic effect of variation of the oil feeding capacities. The latest catalyst technologies that are proved to be viable in converting non-edible oil to biodiesel are also included in the study (**Paper VII**). The catalyst studied are bulk CaO, enzyme, ionic liquid and nano CaO particle, for which the whole process flow has been designed to investigate techno-economic performances of the alternatives for production of fuel grade biodiesel from low quality feedstock.

# Sammendrag

Befolkningsøkning og en samtidig betydelig økning i levestandarden i de fleste områdene i verden har bidratt til et stadig økende behov for energi. Fossilt brennstoff dekker i dag mesteparten av verdens energibehov. Imidlertid er fossil brennstoff pekt på som en av de viktigste bidragsyterne til klimagassutslipp og global oppvarming, samt andre miljøforurensninger. Det er stadig vanskeligere å skaffe nok fossilt brennstoff for å sikre økonomisk utvikling i mange land, spesielt i Afrika. Derfor er det avgjørende at man finner alternative, fornybare energikilder som kan sikre verdens energibehov, uten samme betydelige negative innflytelse på miljøet som fossilt brensel. Bioenergi kan være lovende fornybare kilder for å erstatte oljebaserte energikilder. En av disse er biodiesel, som ikke er giftig, er nedbrytbar og har lave klimagassutslipp sammenlignet med fossile kilder. Biodiesel kan utvinnes fra mange typer biologisk materiale, ved hjelp av flere teknologier. Homogen base katalysert transesterifisering er den konvensjonelle måten å produsere biodiesel industrielt. Imidlertid krever denne katalysatormetoden en olje av meget høy kvalitet, slik som matolje. Høy pris på matolje hindrer biodiesel fra matolje i å kunne konkurrere prismessig med fossil diesel. I tillegg har man konflikten mellom mat og energiproduksjon. Som et resultat av dette, har høye produksjonskostnader vært det viktigste hinderet for utstrakt bruk av biodiesel. Siden prisen på biologisk material utgjør mer enn 80% av den totale kostnaden for biodieselproduksjon, blir det derfor nødvendig å identifisere en produksjonsprosess som kan produsere biodiesel av god nok kvalitet (‘fuel grade’) fra billig biologisk materiale av lav kvalitet.

Hovedproblemstillingen i denne doktoravhandlingen er derfor å identifisere effektive og økonomisk bærekraftige teknologier for å produsere ‘fuel quality’ biodiesel av ikke-spiselige og billige biologiske oljekilder. Gjennom dette har avhandlingen forsøkt å evaluere de tekno-økonomiske forutsetningene av utvalgte produksjonsteknologies. I tillegg har avhandlingen undersøkt hvor følsomme teknologiene er for endringer i markedsverdien av innsatsfaktorer og ytelse, så vel som endringer i produksjonskapasitet, i en søken etter å optimalisere produksjonsprosessen. Hele avhandlingen er gjort ved simuleringsstudier av prosessene basert på to dataprogrammer - Aspen Plus® and Super Pro®.

Avhandlingen består av syv vitenskapelige artikler som alle er rettet mot å oppnå det samme målet som avhandlingen som helhet, som er gjengitt tidligere. Vitenskapelig litteratur viserat det har vært utført en enorm forskningsinnsats innenfor produksjon av biodiesel,

gjennom bruk av forskjellige teknologier. Vi skrev først en oversiktsartikkel basert på relevant litteratur for å skaffe en oversikt over fordeler og ulemper av de viktigste transesterifiserings teknologiene for biodiesel produksjon (**Artikkel I**). Kategorisert etter katalysatoregenskapene, har teknologiene blitt evaluert i henhold til biologisk material, samt for forholdene de behøver for å få reaksjonene til å være optimale for å omdanne biologisk materiale til biodiesel. Vi har en oversiktsartikkel som har gjennomgått litteraturen for å sammenfatte hva som er økonomisk lønnsomt i forhold til biodieselproduksjon (**Artikkel II**). Denne oversikten var relatert til bestemmelse og sammenligning av de totale investeringskostnadene, direkte produksjonskostnader, så vel som forskjellige systemvariabler som kan påvirke lønnsomheten til ulike produksjonsteknologier og skala av produksjonen.

To effektive katalysator-teknologier (svovelsyre og kalsiumoksid, CaO) ble deretter valgt for nærmere studier av tekno-økonomisk karakter for prosessalternativene (**Artikkel III**). Tre komplette prosessflytskjema ble designet der man brukte disse katalysatorene hver for seg eller samtidig. Sensitiviteten til de ulike prosessalternativene ble også analysert med tanke på endringer i markedet for olje, og for salgsprisen på biodiesel. For å ha et utgangspunkt for optimalisering av prosessen, foretok vi en grundig undersøkelse av hvilken virkning de ulike markedsvariablene hadde på muligheten for å gjennomføre en katalysatorprosess ved hjelp av CaO (**Artikkel IV**). Denne sensitivitetsanalysen ble foretatt på markedsverdien ved hjelp av prisen på biodiesel, glycerol, olje, alkohol, katalysator, lønnskostnader, vedlikehold, så vel som lokalt skattetrykk, for å se hvordan disse variablene påvirket lønnsomheten.

I en utvidet analyse så vi på den tekno-økonomiske yteevnen til ulike produksjonssystemer ved å bruke svovelsyre som katalysator (**Artikkel V**). Fire ulike scenarier for biodieselproduksjon med svovelsyre ble simulert, basert på fire ulike sammensetninger av enhetene for produksjon for hovedprosessene nedstrøms. Sensitivitetsanalysen ble foretatt for å se på hvordan 'Net Present Value (NPV)' og 'Payback time' ble påvirket av endringer i markedet for verdien av biodiesel kostnaden ved kjøp av olje. Dette vil bidra til å identifisere de mest robuste alternativene med vekslende pris i et globalt marked. De tekno-økonomiske påvirkningene av ulike produksjonssystemer og kapasitet for biodieselproduksjon ved hjelp av en CaO-katalysator har blitt analysert ved samme metode (**Artikkel VI**). I denne studien har fire scenarier for biodiesel produksjon der

CaO ble brukt som katalysator, blitt utført basert på ulike mulige sammensetninger av hver produksjonsenhet, i den hensikt å produsere biodiesel fra syreolje (acidic oil). Disse fire prosess-scenariene har også blitt redesignet for ytterligere to matehastigheter for biomateriale (noe som gir totalt tre matehastigheter: 3106.34, 5177.23, og 7248.12 kgh$^{-1}$). Dette er gjort for å undersøke effekten på den økonomiske gevinsten når man endrer matekapasitet. Den nyeste katalysatorteknologien som har vist seg å være brukbar til å konvertere ikke-spiselig olje til biodiesel er brukt i den siste artikkelen i avhandlingen (**Artikkel VII**). Katalysatoren brukt her er bulk CaO, enzym, Ioniske løsninger og Nano CaO partikler, hvor hele prosessflyten er designet for å undersøke det tekno-økonomiske utbyttet av de ulike alternativene for produksjon av drivstoffklasse biodiesel fra biologisk materiale av lav kvalitet.

# List of Articles

### Paper I

Gebremariam SN, Marchetti JM. Biodiesel production technologies*: review. AIMS Energy*. 2017;5(3):425-57.

### Paper II

Gebremariam SN, Marchetti JM. Economics of biodiesel production: Review. *Energy Conversion and Management*. 2018;168:74-84.

### Paper III

Gebremariam SN, Marchetti JM. Techno-economic feasibility of producing biodiesel from acidic oil using sulfuric acid and calcium oxide as catalysts. *Energy Conversion and Management*. 2018;171:1712-20.

### Paper IV

Gebremariam SN, Marchetti JM. The effect of economic variables over a bio-refinery for biodiesel production using calcium oxide catalyst. DOI: 10.1002/bbb.2039; *Biofuels, Bioprod. Bioref.* (2019).

### Paper V

Gebremariam SN, Marchetti JM. Biodiesel production through sulfuric acid catalyzed transesterification of acidic oil: Techno economic feasibility of different process alternatives. *Energy Conversion and Management*. 2018;174:639-48.

### Paper VI

Gebremariam SN, Marchetti JM. Techno-economic performance of a bio-refinery for the production of fuel-grade biofuel using a green catalyst. *Biofuels, Bioproducts and Biorefining*. 2019;13:936-49.

### Paper VII

Gebremariam SN, Marchetti JM, Trine HE, Terfa MT. Techno-economic performance of bio-refineries for biodiesel production using different catalyst technologies. (Under evaluation in *Energies*).

## Additional scientific contributions

### Oral presentation

Gebremariam SN, Marchetti JM. Techno-economic feasibility of producing biodiesel from acidic oil using sulfuric acid and calcium oxide as catalysts. The 23rd International Congress of Chemical and Process Engineering, CHISA. August 25-29, 2018. Prague, Czech Republic.

Gebremariam SN, Marchetti JM. Techno-economic comparison of latest technological solutions for biodiesel production. The 27th European Biomass Conference and Exhibition, EUBCE. May 27-30, 2019. Lisbon, Portugal.

### Poster presentation

Gebremariam SN, Marchetti JM. The effect of economic variables over a biodiesel production plant using calcium oxide as a catalyst. The 26th European Biomass Conference and Exhibition, EUBCE. May 14-17, 2018. Copenhagen, Denmark.

Gebremariam SN, Marchetti JM. Biodiesel production through sulfuric acid catalyzed transesterification of acidic oil: Techno economic feasibility of different process alternatives. The 23rd International Congress of Chemical and Process Engineering, CHISA. August 25-29, 2018. Prague, Czech Republic.

Gebremariam SN, Marchetti JM. Study of the processing layout & capacity and their effect on the techno-economic performance of a biodiesel production process using CaO as catalyst. The 27th European Biomass Conference and Exhibition, EUBCE. May 27-30, 2019. Lisbon, Portugal.

### Conference proceeding publications

Gebremariam SN, Marchetti JM. The effect of economic variables over a biodiesel production plant using calcium oxide as a catalyst. The 26th European Biomass Conference and Exhibition, EUBCE. May 14-17, 2018. Copenhagen, Denmark.

Gebremariam SN, Marchetti JM. Study of the processing layout & capacity and their effect on the techno-economic performance of a biodiesel production process using CaO as catalyst. The 27th European Biomass Conference and Exhibition, EUBCE. May 27-30, 2019. Lisbon, Portugal.

Gebremariam SN, Marchetti JM. Techno-economic comparison of latest technological solutions for biodiesel production. The 27th European Biomass Conference and Exhibition, EUBCE. May 27-30, 2019. Lisbon, Portugal.

# List of abbreviations

| | |
|---|---|
| ASTM | American Society for Testing and Materials |
| CEPCI | Chemical Engineering Plant Cost Index |
| FFA | Free Fatty Acid |
| FoB | Fixed on Board |
| GHG | Green House Gas |
| HHV | High Heating Value |
| IRR | Internal Rate of Return |
| ISBL | Inside Battery Limits |
| IUPAC | International Union of Pure and Applied Chemistry |
| MSPII | Marshall & Swift Process Industry Index |
| NPV | Net Present Value |
| OECD | Organization for Economic Co-operation and Development |
| OSBL | Outside Battery Limits |
| ROI | Return Over Investment |

# Table of Contents

# 1. Introduction

## 1.1. General Introduction

According to the projection of the International Energy Outlook 2017 report, which is made under different scenarios, the world energy consumption will keep increasing due to population expansion and a change of living standards [1]. By 2040, more than 65% of the energy consumption will be from non-OECD countries, where more economic activities are sprouting [2]. For example, the average annual energy consumption increment (from 2012 - 2040) in Africa alone is expected to be 2.6% [2]. However, fossil fuels are still the dominant source of energy to supply the world energy demand [3]. Crude oil, coal, and gas are the main resources for the world energy supply, with consumption of oil based fuels having the larger share [4]. Based on the World Energy Outlook 2018 report [5], for the New Policies Scenario (NPS), the increasing demand for oil-based fuels between the years 2017 and 2040 is considerable. Such demand in developing economies grows by 18 million barrels per day, whilst demand in advanced economies drops by nearly 10 million barrels per day. There is also 3 million barrel per day growth in oil use in international aviation and shipping [5].

Even though the fossil fuel consumption in Ethiopia is at a lower level compared to most other countries, the trend of consumption is increasing due to population growth and expansion of economic activities [6]. Almost all of the fossil fuels used are imported and the annual import of petroleum products is absorbing more than one third of Ethiopia’s annual income from export [6]. Among the major sectors, transport has the highest fossil fuel use and diesel fuel is the used most with a daily average consumption of approximately 8 million liters [7]. The annual average growth of diesel fuel demand in Ethiopia, between 2012 and 2030, is estimated to be 4.7% [8]. The trend of this growth is the same on a global scale. For instance, the increase in global demand for diesel fuel alone is predicted to be 2.8 million barrel per day between 2017 and 2040 [5]. The International Energy Outlook 2016 [2] in particular, showed that for the next two decades, world fuel oil demand is concentrated in the transport sector and in which diesel (including biodiesel) fuel demand is expected to dominate, showing the largest gain (13 quadrillion Btu), which is about 36% of the total liquid fuel demand.

However, the use of fossil fuels is proved to be the main source of most GHG and environmental pollutants [9, 10]. The report from the World Energy Outlook 2018 indicated that there is a very little room for the development of fossil fuel projects without contradicting international objectives about climate change [5]. Moreover, fossil fuels are becoming scarce and it is unlikely that the ever-increasing world energy demand can be met by mainly using such limited resources. This urges the world to look for alternative energy resources, which are affordable, accessible, environmentally benign and sustainable. Biomass, being the most abundant and versatile energy resource, is the most suitable candidate to replace fossil fuels [11, 12]. Liquid fuels from biomass (biofuels) are promising fuel types to satisfy the world energy demand and at the same time, minimize the environmental effects of using energy resources at large. Biodiesel is one of the biofuels gaining attention due to its environmental and technical advantages over its counterpart – fossil diesel. Biodiesel is a renewable fuel produced from plant oil biomass and animal fat feedstock. It is non-toxic, biodegradable, and can be produced from various types of biomass resources in such a way that decentralized production schemes are possible on both small and large-scale capacities. Technically, it has a better lubricating characteristic that helps to reduce engine wear. In addition, its higher oxygen content favors complete combustion of the fuel and thus the amount of particulates released during combustion is very small [13].

Ethiopia is one of the sub-Saharan countries to devise a biofuel policy strategy to guide the associated demand towards sustainable development [14]. There is also strong initiative from the government to pave the way for the development of major biofuels such as bioethanol and biodiesel. The production of bioethanol is already in practice using the byproducts from three state-owned sugar factories [15]. However, the production of biodiesel is only at its infancy, where a number of national and international investors have been provided with land and investment licenses for the production of the major crops for biodiesel feedstock, such as *Jatropha curcas*, Castor and Palm tree. In the Ethiopian government strategy for biodiesel development, *Jatropha curcas* is the priority crop since it can be grown in arid climates (rainfall as low as 200 mm, mean temperatures of 20-25 degrees Celsius) and marginal soils to produce 1000 kg of oil per hectare [16].

The conventional way of producing biodiesel involves the use of homogeneous base catalyst like NaOH and KOH as well as high quality oil feedstock with an FFA content of less than 0.5% [3, 17]. Using such high quality oil as feedstock equates to an expensive overall production process and raises the issue of food versus energy controversies. Therefore, the use of biodiesel fuel as a replacement to fossil diesel is hindered by its higher production cost, which is usually attributed to cost of raw materials mainly oil feedstock [18, 19]. The way out from this problem suggests two-step solutions. The first one involves searching for alternative raw materials that are cheap and convenient for biodiesel production, while the second entails distinguishing the specific process technologies for effective conversion of the candidate cheap-feedstock type to biodiesel. The former considers characterization of various feedstock types based on their oil yield as well as the quality of the oil for production of fuel grade biodiesel. Whereas the later is about testing the different catalyst technologies if they are suitable for efficient conversion of the feedstock in question to biodiesel. In line with this, a number of studies have been done and various feedstock types, catalyst technologies and optimum reaction conditions have been assessed.

This thesis is focused on identifying economically affordable and technically efficient production technology options. This involves comparison of techno-economic performances among selected viable catalyst technologies as well as amongst different possible arrangements of the unit procedures required to produce fuel quality biodiesel using each type of catalyst. The economic feasibility assessment considers current market values of inputs and outputs in the Ethiopian market context.

## 1.2. Research Objectives

The drawbacks of using biodiesel as a substitute fuel to the fossil diesel is associated with its higher cost of production, from which the cost of feedstock forms the higher share. This invites the need to look for cheap, alternative feedstock as well as an efficient and affordable technology for efficient conversion of such feedstock to biodiesel. Within these aspects, numerous studies have been done; and based on their results, a number of cheap feedstock types and catalyst technologies are recommended. Therefore, further study on the techno-economic performances of the full process layouts using most of these catalyst technologies, which can convert cheap oil feedstock to biodiesel, would give clear picture on their feasibility for sustainable production of biodiesel fuel. In line with this, the research objectives of the present thesis includes:

(i) Assessment and identification of potential existing technologies for conversion of different feedstock types to biodiesel (**Paper I**);

(ii) Evaluation of the technical efficiency of the selected technologies (**Papers III, V, VI & VII**);

(iii) Assessment and determination of the affordability and economic feasibility of the selected technologies (**Papers II, III, V, VI, & VII**); and

(iv) Measurement of the sensitivity of the technologies towards the change in market values of inputs and outputs (**Papers III, IV, V, VI & VII**).

## 1.3. Organization of the thesis

The accomplishment of the objectives of the present thesis were addressed in each of the seven publications and the description about each article is presented as follows.

In **Paper I**, a state of the art review has been undetaken on the latest publciations related to the conversion of different oil and fat feedstock to biodiesel. More emphasis has been given on reviewing the effect of the main reaction conditions for an efficient production of biodiesel from different feedstock types as well as on summarizing the advantages and disadvantages of these major transesterification techniques. In addition, the feedstock characters suitable for efficient conversion using homogeneous and heterogeneous acid and base catalysts as well as enzyme catalysts have also been identified.

**Paper II** has focused on reviewing the research on the economics of biodiesel production, emphasizing on the methods of assessment and determination of total investment cost and operational costs, as well as on assessment of economically better catalyst technology and feedstock alternatives. It has also given emphasis on profitability of biodiesel production and the major system variables affecting economic viability among different types of production technology as well as different production scales.

**Paper III** accentuates on the techno-economic evaluation of biodiesel production using two catalyst technologies - sulfuric acid and calcium oxide. Accordingly, in this study, three alternative production processes using these two catalysts have been designed for techno-economic analysis: Sulfuric acid ($H_2SO_4$) catalyzed transesterification and esterification; Calcium oxide (CaO) catalyzed transesterification; as well as CaO catalyzed transesterification with pre-esterification using $H_2SO_4$. A conceptual simulation of the processes were designed using Super Pro and Aspen Plus software. Using the process flow sheets, a material balance for the total capacity of forty-one thousand tons of feedstock per year was done. Accordingly, the technical performances were evaluated in terms of the quantity and quality of biodiesel produced, amount and quality of glycerol produced, and the amount of biodiesel produced per raw material consumed. The economic competitiveness of the three different scenarios were compared based on parameters such as total investment cost, capital investment cost, operating cost, unit production cost, NPV, ROI, and gross margin. The economic effects of change of oil cost and biodiesel selling price were also analyzed using NPV as the main economic indicator.

**Paper IV** was focused on investigating the effect of some market variables of a biodiesel production considering a novel calcium oxide catalyzed transesterification process. A conceptual process simulation of the plant using Aspen Plus and Super Pro software was employed to carry on the economic scenarios and to evaluate the effects of selected variables such as prices of biodiesel, glycerol, oil, alcohol, catalyst, equipment maintenance, labor, as well as tax variation.

In **Paper V**, a homogeneous sulfuric acid catalyzed transesterification of acidic oil has been designed into four process scenarios based on four different downstream process routes. The conceptual design and simulation of these process alternatives have been carried out using Super Pro and Aspen Plus software. These process models were used to evaluate the techno-economic competitiveness of the four different scenarios. In the four process scenarios, all reactors for biodiesel production have been designed to have the same reaction conditions and the same amount of oil feedstock input. The difference between the scenarios was only in the arrangements and type of downstream process equipment required to get fuel grade biodiesel. The technical performances have been evaluated based on quality and quantity of products as well as the amount of biodiesel produced per feedstock consumed.

The specific economic parameters considered were unit production cost, NPV, IRR (after tax), and payback time.

In **Paper VI**, a calcium oxide catalyzed biodiesel production process has been proposed in four different scenarios based on different possible arrangements of the downstream processes. The process flow diagrams of the proposed scenarios were designed using Aspen Plus and Super Pro software. These process simulations were undertaken to evaluate the techno-economic performance of the process scenarios. Technical performance was evaluated based on the quantity and quality of the biodiesel and glycerol produced, the amount of biodiesel produced per amount of feedstock consumed, and the amount of other valuable byproducts. Similarly, the economic performance of the process scenarios has also been assessed using parameters such as total investment cost, unit production cost, NPV, IRR, payback time, and ROI. Each of these four scenarios were divided into two production capacity levels to investigate the effect of change in production capacity on the economic feasibility of the process alternatives.

**Paper VII** was focused on the techno-economic performances of four technological alternatives for the production of fuel grade biodiesel from non-edible oil resources. These alternative technologies include bulk CaO catalyst, enzyme catalyst, nano CaO catalyst and ionic liquid catalyst. The study was mainly based on process simulations designed using both Aspen Plus and Super Pro software. The quantity and quality of biodiesel and glycerol as well as the amount of biodiesel produced per amount of feedstock were the parameters used for evaluation of technical performances. The parameters for economic performances were total investment cost, unit production cost, NPV, IRR and ROI.

# 2. Research background

## 2.1. Biodiesel

The history of biodiesel fuel is commonly associated with Rudolf Diesel. He designed the original diesel engine to run on vegetable oil, with the first engine test on August 10th, 1893 in Augsburg, Germany [20]. Some scholars argue that E. Duffy and J. Patrick were the first to conduct the process of transesterification in 1853 to get fuel from fat [21]. Rudolf Diesel later demonstrated his prime engine model powered by peanut oil, a biofuel, receiving the "Grand Prix" at the World Fair in Paris, France in 1900 [20]. His engine was a single 10 feet iron cylinder with a flywheel at its base. During that time, it was thought that fuel from biomass would dominate and become as important as petroleum and the coal tar products. Nevertheless, until the 1970s petroleum oil embargo, many diesel engine manufacturers considered fossil diesel as the only acceptable fuel for diesel engine. This is because fossil diesel fuel was much cheaper to produce than the biomass alternatives, ignoring that in the years ahead it would bring high pollution costs. In the 1970s, the petroleum oil embargo caused many countries to look again at vegetable oil as a possible alternative fuel. Scientists from many countries rediscovered that straight vegetable oil could be used to run diesel engines; however, eventually the poor quality of the fuel spray, due to the thickness (viscosity) of the vegetable oil, caused damage to the engines. Many scientists then conducted experiments to convert the vegetable oil into biodiesel.

Biodiesel is defined as the monoalkyl esters of vegetable oils or animal fats. The use of biodiesel as a fuel has considerable environmental and technical benefits. The main advantages are associated with energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. It is readily available and renewable, and its use can reduce the dependency on imported petroleum fuels in countries like Ethiopia, where most of the oil fuel consumed is imported. The raw materials for biodiesel production can be found everywhere in such a way that decentralized production is possible from small to large-scale [22]. Therefore, biodiesel production can provide hundreds, or even thousands of jobs in rural or remote areas. More over, since biodiesel can be produced close to populated areas, it is the local community that benefits, as opposed to fossil fuels, which are usually produced offshore or in foreign countries by multinational corporations.

Biodiesel is a biodegradable fuel with a higher oxygen content and a higher cetane number than the fossil diesel, which leads to complete combustion and reduced emissions of CO and hydrocarbons [23]. This makes biodiesel cleaner and more environmental friendly. The oxygen content of biodiesel ranges between 10 to 12 weight percent (wt%). The variation is mainly due to the differences in the degree of oxygenation of the different feedstock and respective chemical compositions. When highly saturated oils are used as feedstock, the biodiesel would be more oxygenated, burns cleaner and be more stable. Biodiesel from vegetable oil sources has been recorded as having a cetane number range of 46 to 52, while the animal-fat based biodiesel's cetane number range from 56 to 60 [24, 25]. Biodiesel as a fuel is also known to have lower sulfur and aromatic content, which improves the air quality and increases the life-span of diesel engines [26].

The technical benefits of using this fuel are associated with its portability and capability in reducing engine wear. The higher flash point favors portability as it has lower risk of catching fire. The flash point of biodiesel exceeds 130°C, significantly higher than that of petroleum diesel which can be as low as 52°C [25]. The inherent lubricity of biodiesel fuel is the other favorable character, which minimizes engine wear.

However, there are also some demerits on the utilization of biodiesel as a fuel. The production cost with the current technologies used is high, for which around 80% of the production cost is attributed to the feedstock [27]. While biodiesel is cleaner than fossil fuels on average, it tends to produce slightly more nitrogen oxide (about 10% more) [28]. This causes increased pollution around big cities and fuel use centers, and contributes to the formation of smog and acid rain. The preliminary cause for the formation of NOx is attributed to the higher oxygen content of biodiesel. This is because the combustion of the oxygenated biodiesel would encourage complete combustion, which in return results in higher temperature of combustion. Thus, the higher the temperature the higher the formation of NOx compounds [28].

## 2.2. Biodiesel Production Technologies

A number of oil feedstock and their derivatives can be used as fuel for diesel engines. There are four major approaches to make such fuel from oil feedstock: 1) direct use or blending of oils, 2) thermal cracking or pyrolysis, 3) micro-emulsion, and 4) transesterification reaction.

Direct uses of vegetable oils have generally been considered not satisfactory and impractical for diesel engines. The high viscosity, acid composition, free fatty acid content, gum formation, polymerization during storage and combustion, carbon deposits and lubricating oil thickening are obvious problems [29]. In such cases, it is helpful to dilute vegetable oils with materials like diesel fuels, solvents or alcohols. The dissolution produces a reduction of the viscosity and of the density of the final mixture in comparison with the vegetable oil.

Pyrolysis refers to a chemical change caused by the application of thermal energy in the absence of air or oxygen, or by the application of heat in the presence of a catalyst, which results in cleavage of bonds and formation of a variety of small molecules. Pyrolysis typically occurs at temperatures above 430°C. The process produces gases, bio-oil, and a char depending on the rate of pyrolysis, which is related to temperature. Based on the operating conditions, the pyrolysis process can be divided into three subclasses: conventional pyrolysis, fast pyrolysis and flash pyrolysis [30]. Fast pyrolysis is the one used for production of bio-oil.

Among the physical properties of raw vegetable oil, which means that it is not used directly as fuel, is its viscosity. The formation of micro-emulsion is one of the potential solutions for solving the problem of vegetable oil viscosity [29]. According to the definition from the International Union of Pure and Applied Chemistry (IUPAC), micro-emulsion is dispersion made of water, oil, and surfactant(s) that is an isotropic and thermodynamically stable system with dispersed domain diameter varying approximately from 1 to 100 nm, usually in the range of 10 to 50 nm [31]. The components of a biodiesel micro-emulsion may include diesel fuel, vegetable oil, alcohol, and surfactant and cetane improver in suitable proportions. Alcohols such as methanol and ethanol are used as viscosity lowering additives, higher alcohols are used as surfactants and alkyl nitrates are used as cetane improvers [32].

Transesterification reaction is the most preferred amongst the four approaches mentioned above because it enables the use of diverse feedstock types for the production of a fuel highly resembling conventional diesel in quality. Through this method, oils and fats (triglycerides) are converted to their alkyl esters with viscosity similar to diesel fuel. Transesterification reaction can be catalyzed or non-catalyzed. The types of catalyst used for the transesterification process are usually either chemically like basic or acidic catalyst, or enzymatic such as lipases. However, there are also some less investigated but efficient ways to produce biodiesel through esterification of oils and fats such as those using nano catalysts and ionic liquid catalysts. The non-catalyzed transesterification is carried out only by using an alcohol at supercritical conditions where the alcohol, usually methanol, is at a temperature and pressure above its critical point, at which distinct liquid and gas phases do not exist [33, 34]. In the supercritical state, the dielectric constant of the alcohol is decreased so that two-phase formation of vegetable oil/alcohol mixture is not encountered and only a single phase is found favoring the reaction [35].

Each transesterification technique requires different feedstock characteristics. For example, some can handle feedstock with high FFA content where as others are very sensitive to even small amounts. Some production techniques have more advantages than the others at least with respect to i) cost of production, ii) minimum waste generation, and iii) high productivity among others. In addition, there are very important reaction conditions, which should always be optimized for efficient production of biodiesel. Among them, the most commonly studied are: molar ratio of alcohol to oil, type and amount of catalyst, reaction temperature, reaction time, reaction medium, type and relative amount of solvents.

### *2.2.1. Homogeneous acid catalyzed transesterification*

The acid catalyzed process is due to the reaction of a triglyceride (fat/oil) with an alcohol in the presence of acid catalyst to form esters (biodiesel) and glycerol. This method can produce biodiesel using a wide range of feedstock from low to high FFA content. Compared to the base catalysts, acid catalysts are usually recommended for production of biodiesel from feedstock with high FFA content. This is because the acid catalysts can also catalyze the esterification of the FFA to produce more biodiesel and water in addition to the transesterification of the triglycerides. This would enable the use of very cheap and low quality feedstock for biodiesel production, which could in return make this catalyst technology a potential candidate for the reduction of the total cost of biodiesel production.

However, the homogeneous acid catalyzed transesterification reaction requires longer time and higher temperature than the alkali catalyzed reaction [36]. It starts by mixing the oil directly with the acidified alcohol, so that transesterification and separation occur in a single step, with the alcohol acting both as a solvent and as esterification reagent [37]. In order to avoid the competitive formation of carboxylic acids, which reduce the yields of alkyl esters, the homogeneous acid catalyzed reaction should be carried out in the absence of water [38].

Sulphuric acid, sulfonic acid, and hydrochloric acid are the usual homogeneous acid catalysts, being sulphuric acid the most commonly used. One of the drawbacks of producing biodiesel using homogeneous acid catalyzed transesterification is that the amount of free glycerol in the biodiesel is higher than the maximum value allowed to satisfy the international standard - ASTM [39]. Another problem associated with using acid catalysts, in general, is the corrosion of equipment.

### *2.2.2. Homogeneous alkaline catalyzed transesterification*

The alkaline catalyzed transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol in the presence of alkaline catalysts such as alkaline metal alkoxides and hydroxides as well as sodium, calcium or potassium carbonates to form esters (biodiesel) and glycerol. Alkali catalyzed transesterification is much faster than acid catalyzed and it is less corrosive to industrial equipment and, therefore, it is the most often used commercially [40]. However, presence of water and the high amount of free fatty acid in the feedstock would result in the hydrolysis of the triglyceride to form more FFA as well as saponification of the FFA, respectfully. In this case, the reaction would be incomplete with subsequent formation of emulsion that could make separation of the glycerol very difficult [41].

The main disadvantages due to the presence of significant saponification reaction are the consumption of catalyst and increased difficulty in the separation process. The former reduces the amount of biodiesel product, whereas the later leads to high production cost. In addition to that, formation of water in the product will also inhibit the reaction. In this case, just like the water present in the oil feedstock, the one formed during saponification reaction will also hydrolyze triglyceride to form more FFA.

Generally, base catalysts have much higher catalytic activity than acid catalysts in the transesterification reaction; but are selectively suitable for deriving biodiesel only from refined oils with a low content of FFA, usually less than 0.5% [42]. This makes base catalyzed processes confined to the use of only high quality oil like vegetable cooking oil, which in turn makes it an expensive way to produce biodiesel while creating food versus energy controversy. However, if feedstock with a high FFA content has to be used for biodiesel production using homogeneous base catalysts, a separate additional reaction step should be considered in order to reduce the FFA content to the lower level, 0.5%. Usually the additional step involves acid catalyzed esterification reaction. This will enable us to choose among different feedstock types with higher FFA content. Nevertheless, this additional process makes it more complex in the instrumentation (because of the addition of esterification unit) than the sole alkaline - catalyzed process, thereby resulting in an increase in equipment and operating costs.

The efficient production of biodiesel using base catalyzed transesterification is not only dependent on the quality of the feedstock, it is also dependent on the crucial reaction operation variables such as alcohol to oil molar ratio, reaction temperature, rate of mixing, reaction time, type and concertation of catalyst and also on the type of alcohol used [43, 44]. Even though in theory, the stoichiometric ratio of alcohol (usually methanol) to oil is 3:1, in order to assist the forward reaction so that to get higher conversion, the concentration of the alcohol has to be increased. This is because; a lower amount of alcohol means slower forward reaction and less percentage of yield. Conversely, high alcohol amounts, beyond the optimum, interfere with the separation of glycerin due to an increase in solubility; the glycerin remaining in the solution drives the equilibrium backward, resulting in a lower yield of esters. This is due to the fact that the alcohol, with one polar hydroxyl group, can act as an emulsifier that enhances emulsions [43]. For example, the optimum molar ratio of methanol to oil for 90 - 97.5% conversion of vegetable oils into methyl ester is usually taken to be 6:1 [3, 45]. Sodium hydroxide, potassium hydroxide and sodium methoxide are catalysts usually used in base catalyzed transesterification. Sodium hydroxide is mostly preferable owing to its intermediate catalytic activity and at a much lower cost [46].

The relative concentration of catalysts required for maximum production is dependent on the type of feedstock used. For example, the alkaline catalyst concentration in the range of 0.5 – 1% by weight of the oil could result in 94 - 99% conversion of most vegetable oils into esters [41].

### *2.2.3. Heterogeneous catalyzed transesterification*

The use of homogeneous catalysts, especially base catalysts, causes difficulty in purification of the biodiesel product from by-product glycerol and requires wastewater treatment. As a result, the purity of the biodiesel produced using homogeneous base catalysts is usually compromised. To alleviate these problems, heterogeneous catalysts, usually solid base catalysts, are recommended. Solid base catalysts have many advantages, such as having mild reaction condition, easy separation, high activity and less contamination [47].

The use of heterogeneous catalysts, both in acid and base form, have the advantages of having easy and less costly separation as well as the possibility of reusing the catalyst. They are usually categorized as acid solids, where it is possible to catalyze free fatty acids' esterification and triglycerides' transesterification reactions; base solids, which are able to catalyze triglycerides' transesterification reaction; and bi-functional solids (acid-base character) which show the ability to simultaneously catalyze esterification and transesterification reactions [48].

The heterogeneous acid catalyst relatively requires high alcohol to oil molar ratio and has slower reaction rate [49]. Comparatively, heterogeneous base catalyzed transesterification reduces process stages and wastes, and enables easy catalyst separation and reuse [50]. The solid base catalysts, such as magnesium oxide (MgO), calcium oxide (CaO), strontium oxide (SrO), alkali and alkaline earth metal supported oxides, mixed metal oxides, and anionic resins have been engaged for biodiesel production [51]. Among these, calcium oxide is an extensively researched heterogeneous catalyst because it ensures high basicity, little solubility, it is easy and safe to handle, and above all it is economically cheaper as it can be produced from waste sources [51]. The preparation of the CaO catalyst from wastes follows a simple step involving calcination at a temperature of about 800 – 1000°C [52, 53]. Using such catalyst, a maximum conversion of 98% could be achieved with optimum reaction conditions at 5wt.% catalyst with respect to oil mass and alcohol molar ratio of about 6:1 [54].

### 2.2.4. *Enzyme catalyzed transesterification*

It is possible to use an enzymatic catalyst for biodiesel production due to its advantages, such as ease of saponification and purification, and no washing requirements nor neutralization [55, 56]. Enzymatic catalysts can also be applied on a feedstock with high FFA content and it can convert more of the oil into biodiesel. However, the problems associated with enzyme catalysts are the higher costs and longer reaction time [43]. Consequently, due to these two drawbacks, enzyme catalyzed transesterification method is infrequently used industrially. The enzymes that are usually found to be capable of catalyzing transesterification are the lipases. The lipase catalyzed transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol in the presence of lipase enzyme as a catalyst to form esters (biodiesel) and glycerol.

Lipases for their transesterification activity on different oils can be found from a number of sources. The attractive characteristics of lipases are its ability to utilize all mono, di, and triglycerides as well as the free fatty acids, high activity, reusability of immobilized enzyme, temperature and alcohol resistance. Some also argue that, biocompatibility, biodegradability and environmental acceptability of the biotechnological procedure when using lipase as a catalyst are the desired properties of this alternative biodiesel production method.

Enzymes are usually immobilized for better activity and stability. Selecting and designing the support matrix is important in enzyme immobilization [57]. In this respect, there are a number of ways to immobilize enzymes. These include cross-linked enzyme aggregates, microwave-assisted immobilization, click chemistry technology, mesoporous supports and most recently nanoparticle-based immobilization of enzymes [58]. Recently, the use of nanoparticles has emerged as a versatile tool for generating excellent support for enzyme stabilization due to their small size but large surface area [57], which results in better stability and activity of enzymes immobilized on such materials. In addition, nanoparticles strongly influence the mechanical properties of the material, i.e stiffness and elasticity, and provide biocompatible environments for enzyme immobilization [57]. However, during transesterification, the activity of immobilized enzyme is inhibited by methanol and glycerol, which are always present in the reacting mixture. The use of solvents, continuous removal of glycerol, stepwise addition of methanol are some of the ways to reduce the inhibitory effects thereby increasing the effectiveness of the process [59].

In general, process optimization in lipase-catalyzed transesterification, can be done at least through the screening of various commercial lipase preparations; pH tuning; immobilization; adjusting water content in the reaction media; adjusting the amount of enzyme used; and adjusting the temperature of the reaction [60].

### *2.2.5. Nano catalyzed transesterification*

There are a number of recent developments in catalytic conversion of oils and fats to biodiesel. Among them, biodiesel production using nano catalyst is more promising in terms of some advantages over the conventional acid/base catalysts. Nano catalysis involves the use of nanomaterials as catalysts for a variety of homogeneous and heterogeneous catalysis applications. Such catalysts have a high specific surface area and a high surface energy resulting in high catalytic activity. Generally, nano catalysts improve the selectivity of the reactions by allowing reaction at a lower temperature, reducing the occurrence of side reactions, higher recycling rates and energy recover [61]. In this respect, there are promising alternatives for efficient production of biodiesel from oils and fats as they have a high specific surface area and high catalytic activities eliminating the specific problem of mass transfer resistance associated with conventional catalysts [62]. In general, nano catalyzed transesterification is insensitive to FFA and water content, carried out at relatively low temperature and taking a short time. The catalyst can be reused multiple times, which provides cost benefits. However, it requires more alcohol for an effective yield and in some cases, preparation of appropriate catalysts is expensive [63].

### *2.2.6. Ionic liquids catalyzed transesterification*

Ionic liquids are organic salts comprising of anions and cations that are liquid at room temperature. The cations are responsible for the physical properties of ionic liquids (such as melting point, viscosity and density), while the anion controls its chemical properties and reactivity [64]. Their unique advantage is that while synthesized, they can be moderated to suit the required reaction conditions. Another great advantage of using Ionic liquids, specifically to catalyze transesterification for biodiesel production, is the formation of a biphasic system at the end of the reaction [65]. This biphasic system occurs because the ionic liquid, which is insoluble in the organic phase, remains in the aqueous phase along with the alcohol, the catalyst and the glycerol produced during the reaction [66]. This makes it very easy to separate the final products, because most of the top phase is biodiesel with very little amount of the alcohol. Simple vacuum evacuation of this very little amount of alcohol can then isolate pure biodiesel. The bottom phase contains alcohol, glycerol and ionic liquid. This bottom phase can then be rinsed with water for 3 to 4 cycles to separate glycerol with high purity [67, 68]. Among the different possible types of ionic liquids for catalysis of transesterification reaction for biodiesel production, those composed of 1-n-butyl-3-methylimidazolium cation are the most widely studied and discussed [69]. This is due to their synthesis being quite simple and cheap, and by controlling the synthesis it is also possible to control the purity of the materials formed. Generally, Ionic liquid catalysts have high catalytic activity, excellent stability and can also be easily separated and reused many times. However, it requires relatively more alcohol for effective yield and usually the production of ionic liquid is expensive.

### *2.2.7. Supercritical transesterification*

One of the approaches to overcome problems associated with poor immiscibility between the reactants as well as the technical problems caused by the use of catalysts is to use the supercritical methodology. Supercritical alcohol transesterification reaction takes place under high temperature and pressure. In this scenario, liquid and vapor phase are no longer confined under normal conditions and a single supercritical fluid phase is generated [43]. In the supercritical transesterification method, alcohol and triglyceride, which are immiscible liquids at room temperature, form a homogenous fluid. Accordingly, the reaction will be accelerated, as there is no mass transfer limitation under such conditions. Using this technique, the conversion of vegetable oils into biodiesel is performed in approximately 4 minutes [40]. Some authors recommend the use of a co-solvent to improve the conversion efficiency [70, 71]. In general, supercritical transesterification is insensitive to FFA and water content of the feedstock and thus enables the use of wider feedstock types, usually takes a shorter time and produces more fuel amount per feedstock mass. However, its requirement of a high temperature and pressure together with a larger amount of alcohol consumed during the reaction could make it economically unprofitable.

## 2.3. Economics of biodiesel production

The higher cost of the biodiesel production can be dramatically reduced by using alternative feedstock, which are cheaper such as Jatropha, Castor, Jojoba, and waste cooking oil, among others. However, the conventional homogeneous alkali catalyzed transesterification could not provide fuel quality biodiesel from these types of alternative feedstock due to the considerable FFA content, which could lead to the production of soap rather than biodiesel. There are a number of technologies available for the efficient conversion of oil and fat with a high FFA content into biodiesel. In fact, the possible ways to reduce the cost of biodiesel production (unit cost of production) include; improving productivity of the technologies (to increase yield), reducing capital investment cost and reducing the cost of raw materials. These demand a thorough execution of economic analysis among the available catalyst technologies as well as feedstock alternatives so that the best option, in economic terms, can be selected.

The total investment cost to produce biodiesel varies depending on a number of factors such as the type of technology chosen, the production scale (plant size), type and market price of raw materials used, among others. The total investment cost can be categorized into fixed capital investment cost and operating (working capital investment) cost. Fixed capital investment cost represents the capital necessary for the installation of process equipment with all auxiliaries, whereas operating cost considers raw materials cost, utility cost, labor dependent costs, facility dependent costs and other similar variable expenses.

### *2.3.1. Capital investment cost*

There are five known classifications of the methods to estimate capital investment cost in chemical processing industries [72]. These are order-of-magnitude estimates (class 5), study estimates (class 4), preliminary estimates (class 3), definitive estimates (class 2) and detailed estimates (class 1). The capital cost estimates using order-of-magnitude and study estimates are usually undertaken for preliminary feasibility analysis to compare process alternatives. Preliminary estimates and definitive estimates are employed to carry out a more accurate estimation of the capital cost on the profitable process alternative screened using class 5 and/or class 4. Eventually, detailed estimates is usually applied as the final detail estimation of all the costs associated with the construction of the new plant so that a construction decision can be made [72].

In order to get an overview of the economic feasibility of potential technological alternatives, the capital investment cost for biodiesel production is usually determined using the study estimate approach [27, 73, 74]. The major cost categories under capital investment cost are equipment and direct plant costs. Direct plant costs include those required for equipment installation, instrumentation, piping, electrical facilities, yard improvement, and auxiliary facilities, among others. There are different techniques to calculate the fixed capital investment cost for biodiesel production processes. In all of these techniques, the primary activity involves an estimation of total equipment cost, and the calculation of all other components of capital cost are based on that of equipment cost, either installed or purchase cost. Generally, in order to have an accurate estimation of the total investment cost, the full process needs to be designed. The selection of the equipment size, the construction materials and total amount and finally the material and energy balance of the entire process must be performed [75]. The most updated and accurate costs involved for each piece of equipment should be obtained from vendors and suppliers based on the current market needs. If such cost data are for different plant capacity and at different purchasing time, it is necessary to adjust the equipment purchasing cost based on the capacity of the equipment and purchasing time differences [72]. While scaling up or scaling down the equipment purchasing cost based on unit capacity of the equipment, cost relations like the six-tenth rule or the thirds power law described by Remer et al. [76] can be used. Similarly, cost indexes, such as Chemical Engineering Plant Cost Index (CEPCI) and Marshall & Swift Process Industry Index (MSPII) are two commonly used indexes to update the purchasing cost [72]. Such indexes are involved to account for price changes due to inflation or deflation.

The other approach to estimate the total equipment cost for specified production capacity involves the use of a formula for each type of equipment considered in the design to calculate the Fixed on Board (FoB) cost of the equipment. Apostolakou et al. [77] estimated the purchasing cost of a reactor constructed from a stainless steel with a volume from 0.1 up to 20m$^3$ using the following mathematical relationship $CV_R^O = 15000V^{.55}$; where $V$ stands for volume of the reactor. Accordingly, using such type of formula for each equipment considered in the process, the total purchasing cost could easily be determined.

There is also software for the estimation of equipment cost like the one developed by Peters and Timmerhaus [75]. This software is mainly applied to calculate the estimated purchasing cost of different equipment based on their specifications and parameters that designate the characteristics of each equipment. The parameters to be considered include the size, the material of construction, the power consumption, the output capacity and some process conditions. The estimate cost would then be determined when the latest Chemical Engineering Plant Cost Index and its date is taken into consideration. Other software for estimation of purchasing cost of all equipment involved in a given design are Richardson Construction Estimating Standards (now known as Cost Data Online) and Chemcost Capital Cost and Profitability Analysis Software. The later software enables the calculation of total installed costs using Installation Factors, to convert the supply cost of equipment into total installed costs. Total installed cost considers equipment purchasing cost plus costs for transport and associated insurance, cost of purchase tax as well as electricity and piping costs in some cases.

As indicated above, the total capital investment cost involves equipment purchasing cost as well as direct plant cost. The direct plant cost category includes direct expenses for labor and installation materials as well as indirect expenses such as transportation & associated insurance, purchase taxes, contingencies, contractor’s fee, construction overhead, and auxiliary facilities among others. For preliminary economic feasibility analysis of biodiesel production processes, the calculation of these direct plant cost categories can be performed based on the percentage allocation of the total equipment purchasing cost [78]. There are a number of approaches for the allocation of percentages of equipment purchasing cost for each cost category; among them are Peters and Timmerhaus method, Chilton method, and Holland method [79]. Peters and Timmerhaus method considers the purchasing cost of the equipment including delivery costs; the other cost categories mentioned up supra can be calculated using the percentage allocation of the equipment purchasing cost. This indicates different values of percentages of equipment purchasing cost for calculation of other investment cost categories.

In another approach, the total fixed investment cost can be divided into direct and indirect costs, both of which considering all possible physical structures required for construction of the process plant. The direct fixed investment cost considers financial resources allocated in the development of installations. These are subdivided into ISBL (Inside Battery Limits) and OSBL (Outside Battery Limits). ISBL include the financial resources required for equipment purchases, transportation, structural supports, insulation, paint, instruments, pipes, valves, electrical supplies and installation. All these expenses are directly related to the process. Whereas, the OSBL includes financial resources required for the development of the facilities outside the main processing area. These include investment for housing and auxiliary buildings, water treatment, and land acquisition for building the process plant among others.

Santana et al. [80], took the value of OSBL to be equal to 45% of the value of the ISBL. However, in another study, Van Kasteren et al. [81] took OSBL to be 20% of ISBL. For preliminary design and study cost estimates, the value of ISBL can be determined from the total equipment cost using Lang factor, especially for the major expansion of existing project [72]. The indirect cost, which includes other occasional costs is usually taken as 25% of the direct investment cost [80]. According to this holistic approach, therefore, the total investment cost can only be given in terms of ISBL. For example, the total investment cost is equal to 1.81 x ISBL if the OSBL is taken to be 45% of the ISBL.

### *2.3.2. Operating cost*

The operating cost of a biodiesel production process includes the expenses associated with raw materials, utilities, labor, repairs, maintenance, and depreciation among others. Raw materials mainly comprising of oil feedstock, catalyst, alcohol, washing water, and the like. The amount of raw materials required are dependent on the biodiesel production capacity of the process plant. Moreover, the material balance of the biodiesel production process is used as a reference to calculate the amount of raw materials needed to achieve the desired production capacity. Similarly, the utilities consumption are dependent on the type of process and type and size of equipment employed and it is usually estimated based on the energy balance of the process [82].

During the calculation of the total operating cost, the values for the cost of raw materials and utilities are typically based on the latest market prices. The labor cost estimation is entirely dependent on the type and number of labor required as well as the payment rate allocated for each labor type. The labor required can be estimated based on the number of workers required for the given plant capacity. The other cost categories included in operating costs, such as repair and maintenance costs, are usually taken as percentages of the operating cost. Whereas, depreciation cost is usually expressed in terms of percentage of equipment purchasing cost.

### *2.3.3. Alternatives to economize biodiesel production*

There are a number of studies performed to reduce the cost of biodiesel production to make it a more competitive fuel. Among the possible ways to reduce production costs are those that use cheaper catalyst alternatives [83, 84], as well as those that use technology with minimum overall energy input and faster transesterification reaction [54, 82]. Another viable option considers a technology that can produce fuel quality biodiesel from cheaper feedstock, since feedstock has the major share in cost of production [85, 86].

Most of the cheaper feedstock are waste oils, fats, or non-edible oil crops, which are usually associated with a higher amount of impurities, mainly FFA and water content. Higher FFA and water content of the feedstock jeopardizes the yield and quality of biodiesel, as there are side reactions with unwanted products. This, otherwise, demands the use of multiple chemical process steps or alternative approaches to produce biodiesel with better quality and yield, which in turn incur additional costs.

Acid catalyzed transesterification can esterify the FFA into biodiesel, which otherwise could be changed into soap in an alkali catalyst technology by consuming considerable amount of the catalyst, which also incurs extra investment for product separation and purification [43, 87]. However, acid catalyzed transesterification reaction is very slow, requires more alcohol, requires a larger reactor and the corrosiveness of the acid impose equipment deterioration. All of these do have cost implications. Comparatively, heterogeneous acid catalysts do have better economic performances among the acid catalyst technologies for that they can be easily separated and reused in the process cycle, are less corrosive, as well as have no washing steps required to purify the product [87]. In addition, the coproduct glycerol can be produced of a higher quality for higher market value. The other alternative is supercritical transesterification reaction as it has some technical advantages. It does not use catalyst so there is no additional step for pretreatment of the feedstock to minimize the FFA and it takes a shorter time to complete [49, 88]. However, it requires a high amount of alcohol and high reaction pressure and temperature, which incur considerable cost. The enzyme catalyzed transesterification reaction is also capable of producing fuel quality biodiesel from feedstock with a high FFA content, but the higher cost of the enzyme remains the main challenge for its industrial application. This implies that when a certain configuration of feedstock and production technology is selected for its low cost option, there should be a compromise between the cost reduced as well as the cost incurred. It is apparent that the cost reduced is due to the use of the cheaper configuration of feedstock and production technology whereas the cost incurred is usually due to additional steps and/or techniques for pretreatment of the low value feedstock, for product separation as well as for product quality improvement.

When large-scale production of biodiesel is considered, sustainable feedstock supply is the main issue. Currently, edible oil crops produced through large-scale agricultural systems are considered as the main supply to produce more than 95% of the world biodiesel product [89]. Nevertheless, enduring large-scale production of biodiesel from edible oil is not sustainable as there is clear controversy with crops for food, which also makes biodiesel an expensive fuel. In this regard, potential substitutes are non-edible oil crops, which can be produced at large scale at relatively cheaper price.

However, as far as alternative feedstock for a standard quality of biodiesel fuel are concerned, the price of the feedstock cannot be taken as the sole criterion to reduce the cost of biodiesel production. Rather, there should be a compromise between the price of the feedstock alternatives and the quality of the biodiesel produced from the alternatives in question. This is because the quality of the oil from such alternative feedstock may risk quality of the biodiesel produced. For example, one of the techniques to improve the quality of biodiesel produced from feedstock with high content of saturated fatty acid is using additives for improvement of the cold properties of the fuel [90]. Nevertheless, such quality improvement measures do have cost implications. Thus, the economic advantages of the alternative feedstock can be seen from perspectives of its low price as well as the impurities of the feedstock that may jeopardize the quality of the biodiesel, requiring expensive feedstock pretreatment and/or product quality improvement processes.

The economics of biodiesel production can also be seen among different technologies using the same feedstock. Some of the technologies do have economic advantages over the others usually due to having fewer unit operations, which in turn reduce the overall energy input and minimize the required investment. From another perspective, such economic advantages may also be due to the relative minimum cost of input materials usually catalysts. Using neat vegetable oil as feedstock, generally, the alkali catalyst technologies are the most cost effective, as there are fewer unit operations and less equipment and thus a relatively lower total investment cost compared to other potential alternatives. However, among the alkali catalyst technologies, heterogeneous ones are more cost effective than the homogeneous alkali catalysts due to reusability of the catalysts for a number of process cycles. The cheapest of all possible heterogeneous alkali catalysts is calcium oxide, which can be prepared from waste materials for a very low cost [91, 92].

## 2.4. Techno-economic performances

The techno-economic study of biodiesel production technologies are carried out to test the technical efficiency and economic feasibility of alternative technologies to choose the better performing option(s). The technical performances are usually determined through energy and material balance of the whole production process. In this way, the quantity and quality of the biodiesel and the glycerol are taken as the parameters to make a comparison among the technologies in question. The amount of biodiesel produced per amount of feedstock consumed is also another parameter in this approach.

The technological assessment can also be performed through evaluation of the technical benefits and limitations of the alternatives. These can include consideration of the number of process steps and the amount of equipment required to achieve a given quantity and/or quality of biodiesel. This depicts how complex, or simple, the whole production process might be.

The economic performance evaluation of a given biodiesel production plant is usually done following the assessment of its technical performance. This means, the plant size, optimized reaction conditions and estimated costs for goods and services have to be determined first, for possible comparison of the efficiencies of the process alternatives in terms of some selected economic parameters. There are a number of economic parameters to test if technically efficient production alternative is cost effective or not, given a specified market scenario. These include total investment cost, total annual operating cost, unit production cost, payback time, gross margin, NPV, ROI, and after tax IRR among others.

## 2.5. Simulation of chemical processes

Process simulation is used for the design, development, analysis, and optimization of technical processes such as chemical plants, chemical processes, environmental systems, power stations, complex manufacturing operations, biological processes, and similar technical functions. Process simulation is a model-based representation of chemical, physical, biological, and other technical processes and unit operations in software. Basic prerequisites are a thorough knowledge of chemical and physical properties of pure components and mixtures, of reactions, and of mathematical models, which in combination allow the calculation of a process in computers.

Process simulation software describes processes in flow diagrams where unit operations are positioned and connected by the product or the product streams. The software has to solve the mass and energy balance to find a stable operating point. The goal of a process simulation is to elucidate the fundamental mechanisms that control the process. Simulation can be used to forecast the future behavior of the whole system, and thus help to optimize the process based on the market. Process simulation always use models, which introduce approximations and assumptions but allow the description of a property over a wide range of reaction conditions that might not be covered by real data. Models also allow interpolation and extrapolation - within certain limits - and enable the search for conditions outside the range of known properties.

There are a number of available software for the simulation of biodiesel production process to assess the techno-economic performances of the different technological options. We have used Aspen Plus from Aspentech [93] and Super Pro from Intelligen Inc. [94] to design all the processes involved in all of the studies included in the present thesis. Aspen Plus is a powerful software in Chemical Engineering for chemical processes' optimization. The software includes a huge database of models and properties relevant to the thermodynamic, fluid and reaction engineering processes. It covers all major subjects of chemical engineering such as heat transfer, mass transfer, process calculation, and equipment design. In this study, Aspen Plus is used for energy and material balance because it is very specific in the selection of property methods, thermodynamic methods, and pure component parameters according to the character of the chemicals and the specific reactions involved in the processes.

Super Pro Designer is a valuable tool for engineers and scientists in process development, process engineering, and manufacturing. Super Pro provides, under a single umbrella, modeling of manufacturing and end-of-pipe treatment processes, project economic evaluation, and environmental impact assessment. The use of Super Pro in all of the studies, included in this thesis, is thus helpful for the economic analysis of the scenarios as the software is very convenient and flexible in acquiring meaningful cost data.

# 3. Result and discussion

The present thesis is focused on the identification of technically efficient and economically affordable technology for sustainable production of biodiesel from bio-resources. The entire study is based on process simulation using two of the latest commercial software, Aspen Plus and Super Pro. The design of the processes has taken some essential technical assumptions into account and the market values of inputs and outputs have also been considered based on Ethiopian market scenarios. In all of the process options studied, oil feedstock with 10% FFA content was considered because such feedstock character could represent most of the cheap feedstock available for possible reduction of the cost of biodiesel production. The optimum reaction conditions for each type of dominant chemical reaction involved in the studied processes is taken from literatures.

Throughout the entire study, the techno-economic performances of the different catalyst technologies for biodiesel production have been investigated. Comparisons have been made between the catalyst technologies as well as among the different process layouts of a given catalyst technology, which are designed based on the difference in the arrangement of the downstream processes.

Among the various catalyst technologies for biodiesel production, the most studied ones and the latest technical options from literature were provided due emphasis. The catalysts studied in the present thesis include bulk calcium oxide, sulfuric acid, enzyme, ionic liquid, and nano calcium oxide catalysts.

## 3.1. Techno-economic performance of biodiesel production using CaO & $H_2SO_4$ catalysts

In **Paper III**, the techno-economic feasibility of biodiesel production from acidic oil using sulfuric acid and calcium oxide catalysts have been investigated. Three process models were designed: Model I - Homogeneous sulfuric acid catalysis; Model II: Heterogeneous calcium oxide catalysis; and Model III: Heterogeneous calcium oxide catalysis with sulfuric acid pre-esterification. The flowsheets of the three process models are shown in **Paper III**, as **Figure** 2, 3, & 4, respectively.

The technical efficiency was assessed based on the quality and quantity of products through material balance and the affordability was assessed based on the total investment cost, operating cost, return over investment (ROI), gross margin, and net present value (NPV).

According to the results, all the models guarantee a potential to produce biodiesel with the required quality. It is possible to get more than 99% pure biodiesel in all of the process models studied. These results are in agreement with similar studies in literature [80, 95, 96]. **Table 1** indicates some significant technical aspects of the three process models for comparison.

**Table 1**. Technical aspects of the process models studied

| | Model I | Model II | Model III |
|---|---|---|---|
| Capacity (Thousands ton/year) | 41 | 41 | 41 |
| Process Temperature (°C) | 55 | 75 | 55&75[a] |
| *Input stream (Kg/h)* | | | |
| Oil feedstock | 5177.23 | 5177.23 | 5177.23 |
| Alcohol | 1646 | 2341 | 3285 |
| Sulfuric Acid | 109 | - | 117 |
| *Output Streams* | | | |
| Biodiesel (kg/h) | 5187 | 5132 | 5308 |
| Glycerol in biodiesel (wt. %) | 0.06 | 0.0014 | 0.07 |
| Performance[b] | 1 | 0.99 | 1.03 |
| Glycerol (kg/h) | 500 | 505 | 501 |
| Glycerol Purity (%) | 76 | 99.8 | 76 |
| Ethanol recovered (%) | 52 | 67.5 | 76 |

[a] *55°C was in reactor number one and 75°C was in reactor number two*

[b] *amount of biodiesel produced per amount of feedstock used*

Model III gives the higher amount of biodiesel whereas Model II produces the least. This is because in Model II a considerable amount of the FFA is consumed by saponification reaction, which could otherwise be converted into fatty acid ethyl ester (FAEE). In Model III, the pre-esterification reaction could provide additional FAEE, increasing the amount of biodiesel produced throughout the whole process. Model II showes the minimum performance by producing 0.99 metric ton of biodiesel for each metric ton of oil feedstock used, but it could still be taken as standard achievement. In all of the models, the use of distillation column for biodiesel purification could help to produce a high quality product to meet the ASTM standards. For instance, the higher percentage of glycerol is about 0.07%wt.

in the biodiesel from Model III, which is still far below the maximum allowable amount (0.24%wt.) according to the ASTM standard [97]. Higher amount (505 kg/h) and better quality (99%) of glycerol is attained in Model II. This is mainly because the catalyst is heterogeneous (with higher density difference) making the separation process very effective in producing a high amount and high quality of glycerol [98, 99]. This result is in agreement with some results from literature [100, 101].

Economically, the performances of the process models are different. As shown in **Table 2**, the most expensive alternative is Model I. In this alternative, the dominant reaction is the acid catalyzed transesterification reaction. Acid catalyzed transesterification is a very slow reaction [102, 103] and due to this it requires a larger volume to attain a equivalent production rate with its counterparts, such as alkali catalyzed transesterification. Therefore, in this scenario, Model I requires a larger volume reactor in order to accomodate comparable input delivery rate with the two other models. Such larger reactor volume resultes in higher equipment purchasing cost, higher facility dependent costs as well as a very high amount of utilities required to run the process. Model II is the cheapest alternative. The dominant reaction in this model is the CaO catalyzed transesterification reaction. This reaction is relatively fast, it only takes 2h to attain more than 97% conversion [104], favoring the alternative to have relatively smaller reactor volume. In addition, the use of CaO heterogeneous catalyst enables to have less process steps required to attain a comparable production amount and quality with respect to the two other models. Model II, has total investment cost of 4.8 million US$, which is 31% less than that of Model III and 37% less than that of Model I.

**Table 2**. Total capital investment cost for each model for comparison (thousand US$)

| Capital cost category | Model I | Model II | Model III |
|---|---|---|---|
| Direct Fixed Capital Cost | 4,437 | 1,963 | 3,715 |
| Working Capital | 3,064 | 2,765 | 3,078 |
| Startup & Validation Cost | 222 | 98 | 186 |
| Total Capital Investment Cost | 7,723 | 4,827 | 6,978 |

As shown in **Table 3**, the unit production cost variation among the studied Models is considerable, with maximum variation of 0.11 US$/kg. Moreover, these calculated unit production cost values are more or less in agreement with similar studies using different catalyst technologies and feedstock types [77, 82, 105]. For instance the unit production costs calculated by Karmeeet al.[82], using three catalyst technologies (base, acid and lipase) to produce biodiesel from waste cooking oil, were in a range of 0.75 US$/kg up to 1.048 US$/kg. In this thesis, the maximum unit cost of production is 0.886 US$/kg in Model I and the minimum is 0.779 US$/kg in Model II.

Model I can take a longer time to payback the investment and has the second minimum NPV at 7% interest rate. It is also more expensive to produce biodiesel using Model I and Model III than Model II. Model II is found to be the better alternative in terms of economic performances. Even though the amount of biodiesel produced is the least, Model II shows positive NPV, higher ROI and minimum payback time. However, Model I and III have poor economic performances, which could be indicated by a negative NPV for the same optimum market values of inputs and outputs applied for the three Models.

**Table 3**. Economic performances of the models studied

| | **Model I** | **Model II** | **Model III** |
|---|---|---|---|
| Feedstock Capacity (kg/year) | 41,003,662 | 41,003,662 | 41,003,662 |
| Annual Biodiesel Production (kg/year) | 41,115,414 | 40,644,750 | 42,115,566 |
| Total Investment cost (US$) | 7,723,101 | 4,827,041 | 6,978,211 |
| Annual operating cost (US$) | 36,426,905 | 31,664,441 | 36,095,266 |
| Total Annual Revenue (US$) | 34,342,293 | 33,305,116 | 33,187,279 |
| Unit Production Cost (US$/kg) | 0.8860 | 0.7791 | 0.8571 |
| Net Unit Production Cost (US$/kg) | 0.8034 | 0.6867 | 0.7240 |
| Unit Production Revenue (US$/kg) | 0.8353 | 0.8194 | 0.7880 |
| Gross Margin (%) | 3.81 | 16.19 | 8.12 |
| Return Over Investment, ROI (%) | 15.63 | 75.09 | 28.36 |
| Payback Time (year) | 6.4 | 1.33 | 3.53 |
| Net Present Value at 7% (US$) | -19,345,239 | 7,051,638 | -30,424,382 |

There is a wider gap in economic performance among the Models studied. This in turn invited further investigation into the sensitivity of the technologies towards the possible fluctuation of market values of the input and output variables. In this respect, the effects of two main market variables (oil cost and biodiesel price) have been tested to investigate how the economic feasibility of process alternatives could be affected by change of cost of these variables. The economic parameter used to test the effect of the market variables was the NPV. It denotes the present value of net cash inflows generated by a project minus the initial investment on the project. It is one of the most meaningful measures of capital budgeting in a project because it considers time value of money.

The percentage share of cost of oil feedstock from total raw material cost is 85% for Model I, 81% for Model II and 74% for Model III. As shown in **Figure 1,** below, the tendency of change of NPV with oil feedstock purchasing cost is the same for Model I and II, with a little change for Model III. In addition, among the three models, Model III shows more sensitivity to the change in oil feedstock cost, particularly above 0.480 US$/kg. For instance, a 0.02 US$/kg change in oil feedstock cost would result in a decrease in NPV of 7.5 Million US$ for Model III, 4.9 Million US$ for Model II and 5.8 Million US$ for Model I. In Model III, oil feedstock price above 0.490 US$/kg would make the business unprofitable. For Model I, the maximum oil cost that could still make the business profitable is 0.509 US$/kg. Accordingly, Models I and III are the least dependable alternatives for sustainable production of biodiesel. However, Model II shows more tolerance to fluctuation of oil cost, enabling to accommodate relatively expensive feedstock, up to 0.590 US$/kg, and make the business profitable with a positive NPV.

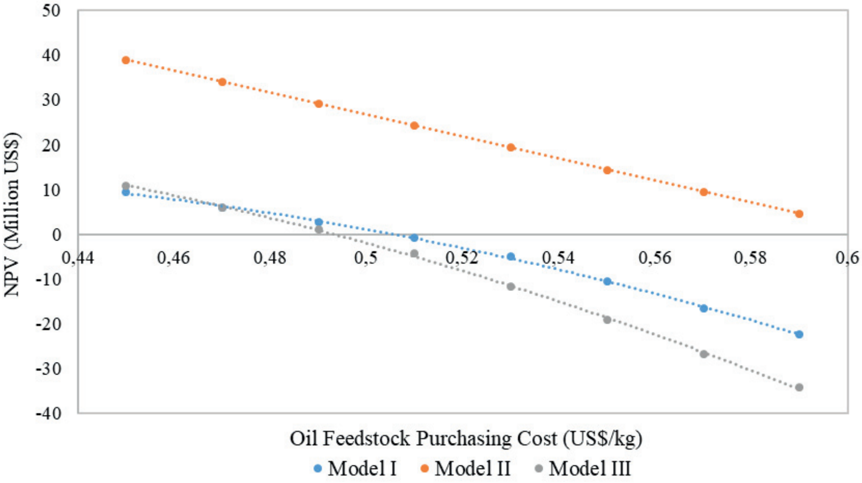

**Figure 1.** Effect of change of oil cost on NPV for Model I, Model II & Model III

In terms of the effect of biodiesel selling price, it is indicated in **Figure 2** that Models I and II have the same tendency in the change of NPV due to a change in biodiesel selling price. Whereas, Model III has a little difference in tendency of change of NPV, demonstrating a higher variation, particularly below 0.870 US$/kg of biodiesel. Because of this, Model III is the most sensitive to a decrease in the selling price of biodiesel. The minimum price, below which the business would be unprofitable, is 0.865 US$/kg for Model III and 0.853 US$/kg for Model I. Model II has more tolerance to market fluctuation of the selling price of biodiesel up to the minimum value of 0.754 US$/kg.

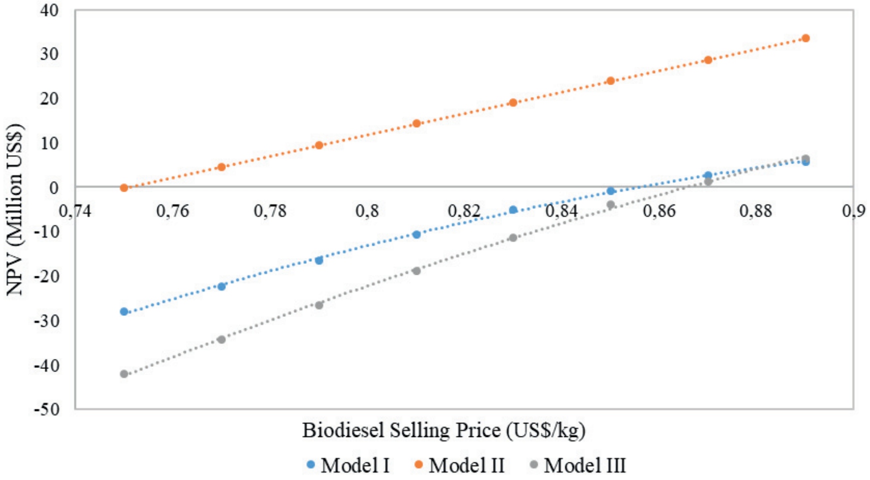

**Figure 2**. Effect of change of biodiesel selling price on NPV for Model I, Model II & Model III

In order to accurately review the performances of each catalyst technology, there should be further investigation on the techno-economic performances of the different process layouts using the two catalyst technologies, CaO and sulfuric acid. These investigations could help to evaluate the relative performances of the different process alternatives, which can be designed based on possible arrangements of the downstream processes required for production of fuel quality biodiesel, while using each catalyst technology. Accordingly, in section 3.2, the techno economic performances of four process scenarios using sulfuric acid catalyst have been assessed **(Paper V)**. Whereas similar study for CaO catalyst have also been done in **Paper VI** and shown under section 3.3.

## 3.2. Techno-economic performance of process layouts for biodiesel production using $H_2SO_4$ catalyst

In **Paper V**, the techno-economic feasibility of biodiesel production through sulfuric acid catalyzed transesterification has been investigated. In this study, the production of fuel quality biodiesel using a homogeneous sulfuric acid catalyzed transesterification of acidic oil is designed into four process scenarios based on four different downstream process routes. The process flowsheets of the alternatives are indicated in **Paper V**, as **Figure** 3, 4, 5, & 6.

All four of the process scenarios are found to be technically feasible ways to produce biodiesel at the required quality in accordance with ASTM standards. The technical performance results, such as biodiesel purity, glycerol purity and the amount of biodiesel and glycerol produced per amount of feedstock used, are in agreement with those reported in other studies [39, 82]. However, there is still a comparable difference among the scenarios in terms of these technical performances. For instance, scenarios II & III show better performance regarding the amount of biodiesel produced per amount of feedstock consumed. For scenario III, this is due to the double reactor configuration designed to improve the overall conversion of the oil into biodiesel. Whereas for scenario II, the higher performance might be due to the arrangement of the downstream processes, where ethanol recovery is performed after catalyst neutralization as well as biodiesel purification is undertaken using distillation just after the glycerol separation by decanting. Such process arrangement helps to minimize the amount of biodiesel lost during biodiesel purification and waste separation through distillation. Conversely, the least performance is recorded in scenario IV, where, during separation of the unreacted oil from the biodiesel in the second distillation process, considerable amount of the biodiesel could also be removed together with the unreacted oil. This might be due to the higher temperature of the reboiler required to separate the mixture of biodiesel and glycerol from the unreacted oil. Accordingly, the difference in the amount of biodiesel produced among the scenarios could range up to 341 kg/h. This value specifically indicates the product difference between scenario II and IV. In all of the scenarios, the biodiesel purity achieved is about 99.99%. This is mainly because of the fractional distillation employed to further purify the biodiesel after different arrangement of glycerol and calcium sulfate separation processes. As the main byproduct, glycerol could also be obtained at a higher quality because a number of separation processes are employed in each scenario. Apparently, the higher glycerol product is recorded in scenario III, where two consecutive reactors are designed for higher conversion percentages. The purity of ethanol recovered in each scenario is the same. However, the amount recovered in scenario III is slightly less than the rest because a little more is consumed due to the second reactor.

A good quality calcium sulfate could be produced from all the scenarios with almost the same quantity. In all of the scenarios, the separation of the calcium sulfate is made using a centrifugal decanter as it is efficient in separating the solid calcium sulfate from the rest of the components. Calcium sulfate, as the second byproduct, can be used as a soil conditioner and if further calcined at required temperature, it can also be used in making tiles, wallboard, and various plasters among others [106]. **Table 4** shows summary of technical performances of the studied process scenarios.

**Table 4.** Summary of technical performances of the process scenarios

| Technical performance indicators | Process scenarios with respective technical performances | | | |
|---|---|---|---|---|
| | **Scenario I** | **Scenario II** | **Scenario III** | **Scenario IV** |
| Annual Biodiesel production (kg/year) | 40,798,942 | 41,834,559 | 42,407,420 | 39,702,122 |
| Annual Glycerol production (kg/year) | 4,018,719 | 4,018,719 | 4,067,549 | 4,018,719 |
| Annual $CaSO_4$ production (kg/year) | 1,195,301 | 1,195,301 | 1,195,301 | 1,195,301 |
| Biodiesel purity (%) | 99.998 | 99.990 | 99.990 | 99.990 |
| Glycerol purity (%) | 96.20 | 99.98 | 99.95 | 99.86 |
| $CaSO_4$ purity (%) | 97 | 97 | 97 | 97 |
| Biodiesel produced per oil feedstock consumed (wt./wt.) | 0.995 | 1 | 1 | 0.968 |

Economically, scenario III is the most expensive alternative, as shown in **Table 5**. This is mainly because of the double reactor scenario (Figure 5 in Paper V), which is supposed to improve the oil conversion efficiency and get more biodiesel produced. Because as the number of equipment increased, there would be an associated increase in the total equipment, labor, and utility cost. Even though this double reactor scenario could produce more biodiesel and glycerol compared to others, the overall economic performance result indicated that it is not an economically feasible alternative.

**Table 5.** Summary of the economic performances of the studied process scenarios

| Economic performance indicators | **Scenario - I** | **Scenario - II** | **Scenario - III** | **Scenario - IV** |
|---|---|---|---|---|
| Total capital investment cost (US$) | 22,359,405 | 21,865,163 | 31,542,376 | 21,869,629 |
| Total equipment purchasing cost (US$) | 4,372,471 | 4,346,531 | 6,477,990 | 4,271,634 |
| Direct Fixed Capital (US$) | 18,021,578 | 17,521,523 | 26,699,684 | 17,605,966 |
| Working Capital (US$) | 3,436,748 | 3,467,564 | 3,507,708 | 3,383,365 |
| Total Annual operating cost (US$) | 44,081,688 | 44,262,764 | 47,811,814 | 43,353,794 |
| Total annual raw material cost (US$) | 23,805,788 | 23,805,788 | 23,805,788 | 23,805,788 |
| Labor dependent cost (US$) | 469,543 | 475,200 | 627,943 | 463,886 |
| Facility dependent cost (US$) | 6,026,595 | 5,867,002 | 8,928,640 | 5,887,610 |
| Laboratory, Quality Control &Analysis (US$) | 140,863 | 142,560 | 188,383 | 139,166 |
| Utility cost (US$) | 13,528,900 | 13,862,214 | 14,151,061 | 12,967,345 |
| Annual revenue from Biodiesel (US$/year) | 46,917,850 | 48,090,537 | 48,752,243 | 45,641,805 |
| Annual revenue from Glycerol (US$/year) | 417,323 | 417,323 | 422,206 | 417,323 |
| Annual revenue from $CaSO_4$ (US$/year) | 153,173 | 153,173 | 153,173 | 153,173 |
| Total Annual Revenue (US$/year) | 47,488,346 | 48,661,033 | 49,327,622 | 46,212,301 |
| Unit production cost (US$/kg biodiesel) | 1.0805 | 1.0580 | 1.1274 | 1.0920 |
| NPV at 7% (US$) | 4,268,069 | 8,761,177 | -7,556,647 | 3,076,566 |
| ROI (%) | 19.02 | 22.19 | 12.47 | 18.01 |
| After tax IRR (%) | 9.92 | 12.73 | 2.89 | 9.14 |
| Gross Margin (%) | 8.92 | 10.92 | 4.72 | 8.17 |
| Payback time in years | 5.26 | 4.51 | 8.02 | 5.55 |

At optimum market values of goods and services, scenario III provides a very high unit cost of biodiesel production, negative NPV and higher payback time, implying that the biodiesel fuel should be sold at a high price to achieve some profit; making this alternative economically unattractive. Comparatively, scenario II is the least expensive alternative and the second scenario in providing more biodiesel. Even though it has the same type and number of equipment with scenario IV, the arrangement of the equipment in scenario II could provide more biodiesel, making the alternative better in its economic performances through increasing the revenue. Due to the process arrangement, glycerol is decanted out before the biodiesel is purified using a distillation column and thus the amount of biodiesel lost during glycerol separation is minimized. In addition, this process arrangement favors scenario II to have relatively less utility requirement because the reboiler in the distillation column works at relatively lower temperature compared to the one in scenario IV, which has the same type of equipment as well as the same process arrangement until the separation of the calcium sulfate byproduct. This decreases the over production cost. In terms of the economic terms, scenario II indicates higher NPV, less payback time and minimum unit production cost. Scenarios I and IV are the third and fourth alternatives respectively, in terms of their economic performances. Both show positive NPV, signifying that they are still feasible in the given market values of inputs and outputs.

In terms of the total capital investment cost, scenario III is the highest again because of the double reactor situation, which increases the equipment purchasing cost and the associated utility, installation and instrumentation costs. Among the other scenarios, scenario I is the second most expensive mainly due to larger volume of distillation column required to recover the excess ethanol before glycerol and calcium sulfate separation. Similarly, such larger column volume results in higher equipment, utility, instrumentation, and installation costs among others. Because of the higher amount of biodiesel and glycerol produced, the superior revenue is recorded in scenario III, whereas scenario II shows the second larger revenue. Having the lower investment cost and second larger revenue, scenario II is the better alternative in terms of achieving lower unit production cost, higher ROI, and lower payback time.

We have also evaluated the sensitivity of the process scenarios towards the change in market values of oil feedstock and biodiesel prices. The economic indicators used to show the sensitivity of the businesses to changes in prices of the market variables are NPV and payback time. Accordingly, scenario III is the least dependable alternative for sustainable biodiesel production business. In this scenario, an increase in oil cost by 0.1 US$/kg could result in additional 4 years of payback time. At higher oil purchasing costs, above 0.53 US$/kg, the payback time would be beyond the lifetime of the project, making the alternative very sensitive to change of the oil purchasing cost. Comparatively, scenario II indicates more tolerance to change in oil purchasing cost, in which the same price change (0.1 US$/kg) could increase the payback time by about 1.9 years. **Figure 3** shows the effect of change of oil feedstock cost on the payback time.

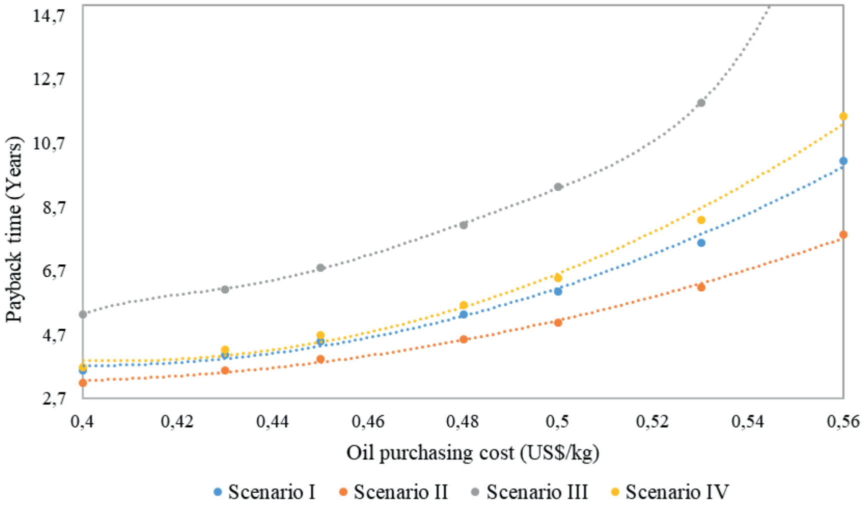

**Figure 3:** Effect of change of oil purchasing cost on payback time among the alternative scenarios

The negative NPV attained in scenario III, as shown in **Figure 4**, clearly suggests that the alternative is not economically feasible at even medium cost of oil feedstock (above 0.435 US$/kg). Consequently, feedstock has to be purchased at minimum cost (less than 0.43 US$/kg) in order to be profitable using scenario III. The other least dependable option is scenario IV. It is unprofitable at a moderately higher cost of oil feedstock (above 0.49 US$/kg). Comparatively, scenario II could provide positive NPV at higher cost of oil feedstock (up to 0.535 US$/kg), making it a more economically dependable alternative for sustainable biodiesel production business.

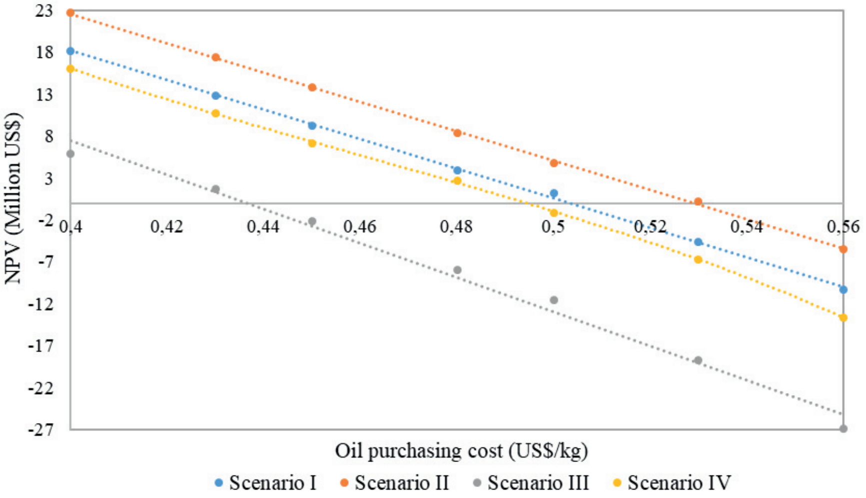

**Figure 4**: Effect of change of oil purchasing cost on NPV among the alternative scenarios

In terms of the effect of change of biodiesel selling price, scenario III is the most sensitive. Biodiesel price lower than 1.08 US$/kg would make the project's payback time to go beyond its lifetime, making it less practical. The next sensitive alternative is scenario IV, which also requires a biodiesel selling price of more than 1.14 US$/kg for its feasibility. Comparatively, scenario II is found to be the most tolerant to a considerable change in the market values of biodiesel selling price, allowing to consider minimum biodiesel price (up to 1.1 US$/kg) within the feasibility domain. **Figure 5** indicates the effect of change of biodiesel selling price on payback time.

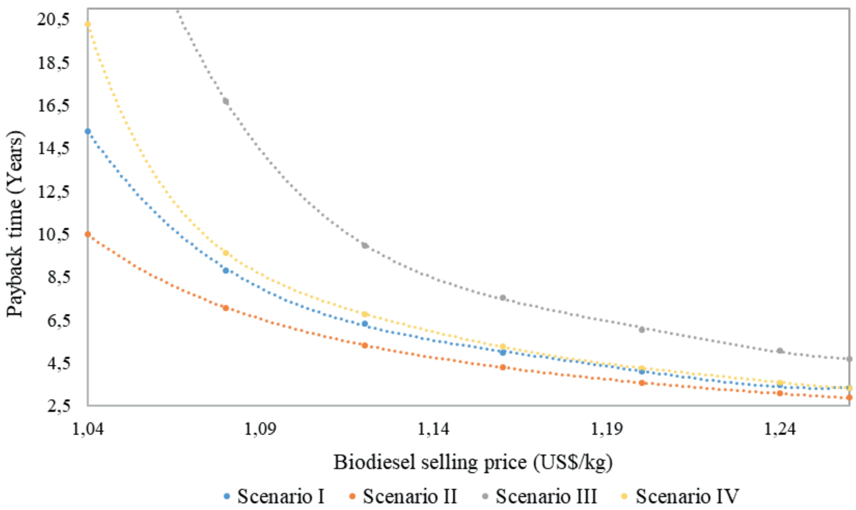

**Figure 5:** Effect of change of biodiesel selling price on payback time among the alternative scenarios

As shown in **Figure 6**, the trend of change of NPV with change in biodiesel prices is the same for all scenarios. However, among them scenario III is found to be more sensitive and achieves no profit to the business even if the biodiesel price is at 1.19 US$/kg. The next less dependable alternative is scenario IV, which indicates negative NPV starting from medium values of the biodiesel selling price (lower than 1.14 US$/kg). Scenario II is the better alternative in this respect, providing positive NPV even at lower values of biodiesel selling price (about 1.1 US$/kg).

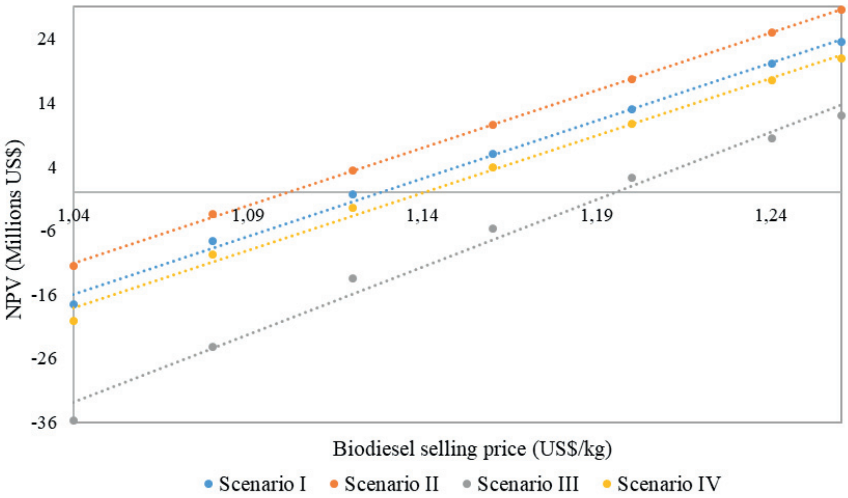

**Figure 6:** Effect of change of biodiesel selling price on NPV among the alternative scenarios

### 3.3. Techno-economic performance of process layouts for biodiesel production using CaO catalyst

Similar to what has been done in **Paper V** for sulfuric acid, in **Paper VI**, the techno-economic performance of a bio-refinery for the production of fuel-grade biodiesel using CaO catalyst was investigated. Four alternative process scenarios have been designed considering the various options of the downstream process units, which are required to produce fuel-grade biodiesel from acidic oil using CaO as a catalyst. It is assumed that the differences in the arrangement and type of these unit procedures would result in a change in their techno-economic efficiencies. The designed flowsheets of these four process scenarios are indicated in **Paper VI** as **Figure** 2, 3, 4 & 5.

In general, the technical performance of the scenarios, in terms of the amount of biodiesel per amount of oil feedstock as well as the quality of the products, are in agreement with the results found in other studies [39, 80]. The numerical values of the performance parameters from this study are indicated in **Table 6**.

**Table 6:** Numerical values of technical performance parameters

| Scenarios | Biodiesel | | Glycerol | | Recovered ethanol | | Performance * |
|---|---|---|---|---|---|---|---|
| | *Amount (kg/h)* | *Purity* | *Amount (kg/h)* | *Purity* | *Amount (%)* | *Purity* | |
| **I** | 5132 | 99.99 | 496 | 99 | 67.5 | 96.4 | 0.99 |
| **II** | 5347 | 99.80 | 505 | 76 | 75.8 | 98.6 | 1.03 |
| **III** | 5117 | 99.99 | 496 | 99 | 67.5 | 96.4 | 0.98 |
| **IV** | 5256.6 | 99.90 | 507.8 | 99 | 66.7 | 96.4 | 1.02 |

** Biodiesel amount per oil amount*

A higher biodiesel production amount is achieved in scenario II (5347 kgh$^{-1}$) and the lowest is in scenario III (5117 kgh$^{-1}$). In scenario II, the higher biodiesel amount is due to pre-esterification of the acidic oil to reduce the FFA content. This helps to omit the saponification reaction and produce an additional amount of biodiesel through the esterification of FFA. The second highest biodiesel amount is in scenario IV (5257 kgh$^{-1}$), which is actually due to the presence of a double reactor to achieve a greater conversion of oil to biodiesel. Even though all of the scenarios reached an acceptable level of biodiesel purity, scenarios II and IV accomplished this without additional purification processes, unlike scenarios I and III. The maximum purity in scenario IV is mainly due to the double reactors converting most of the oil, reducing the amount of unreacted oil in the biodiesel, and also due to the subsequent double centrifuges to efficiently separate glycerol and calcium soap from the biodiesel. Similarly, the absence of saponification together with the use of a short-cut distillation column for biodiesel purification could help to attain greater purity in scenario II. The former would help to avoid calcium soap impurity whereas the latter could efficiently separate the unreacted oil from the biodiesel. However, in scenarios I and III, the last unit procedures are additional process steps for further purification of the biodiesel product to meet the fuel quality standard. This could definitely incur additional costs and make the processes economically unattractive.

As shown in **Table 7**, the amount of glycerol product is relatively higher in scenarios II and IV. However, the glycerol product from scenario IV is 2.8 kgh$^{-1}$ higher than that from scenario II. This is because the double reactor phenomenon in scenario IV encourages the conversion of more oil to biodiesel and glycerol. The purity of the glycerol is also lower in scenario II, where a considerable amount of calcium sulfate impurity is found due to the sulfuric acid neutralization reaction in the second reactor. There is also another economically valuable byproduct – calcium soap from scenarios I, III, and IV. Calcium soap can be used as a feed supplement for dairy cattle and other ruminants [107].

**Table 7:** Impurities percentage in the biodiesel from each scenario and their respective maximum allowable amount as per ASTM

| **Scenarios** | **Biodiesel Purity (Mass %)** | **Percentage of impurities in the biodiesel product from each scenario** | | | |
|---|---|---|---|---|---|
| | | *Glycerol* | *Water* | *Triolein* | *Calcium soap* |
| I | 99.99 | 0.002 | 0 | 0 | 0 |
| II | 99.80 | 0.07 | 0 | 0 | 0 |
| III | 99.99 | 0.002 | 0 | 0.012 | 0 |
| IV | 99.90 | 0.04 | 0 | 0.06 | 0 |
| **Max. allowable due to ASTM** | | **0.25** | **0.05** | **0.2** | **5 ppm (0.0005%)** |

The results of the economic analysis indicate that the process scenarios could have significant difference in their performances. The numerical values of the economic performance parameters for each process scenario are shown in **Table 8**.

**Table 8:** Results of economic performance of each process scenario

| **Economic Parameters** | **Process Scenarios** | | | |
|---|---|---|---|---|
| | I | II | III | IV |
| Total Investment Cost (US$) | 5,611,537 | 7,541,684 | 5,346,045 | 6,165,411 |
| Annual operating cost (US$/year) | 32,620,354 | 36,562,306 | 32,422,148 | 32,380,476 |
| Annual credit (US$/year) | 4,311,526 | 6,396,949 | 4,416,524 | 3,965,946 |
| Total annual revenue (US$/year) | 32,620,938 | 34,042,058 | 32,409,485 | 33,323,059 |
| Unit production Cost (US$/kg) | 0.8025 | 0.8617 | 0.800 | 0.7770 |
| Unit production revenue (US$/kg) | 0.8025 | 0.8023 | 0.7997 | 0.7997 |
| Gross Margin (%) | 13.22 | 11.39 | 13.59 | 14.73 |
| ROI (%) | 52.81 | 36.81 | 56.26 | 55.04 |
| Payback time (year) | 1.89 | 2.72 | 1.78 | 1.82 |
| IRR, after tax (%) | NA | NA | NA | 11.64 |
| NPV (US$) | -3,324,238 | -27,234,609 | -3,307,283 | 2,297,909 |

Scenario II records a higher total investment cost, whereas scenario III is the cheapest among the process alternatives. This high cost of total investment in scenario II is due to the cost of equipment as it has three reactors such as for pre-esterification, acid neutralization, and biodiesel production. The higher the equipment cost, the higher would be the direct costs associated with equipment such as installation, auxiliary costs, and instrumentation costs as well as cost of utilities. The higher cost of raw materials, due to a larger amount of ethanol (for pre-esterification and transesterification) and additional catalyst (sulfuric acid for esterification) may also be the other reason for the high investment costs in scenario II. Even though scenario II could show a higher annual revenue, because of more biodiesel product, its unit production cost of biodiesel is higher than its unit production revenue. This results in negative NPV, a longer payback time, and less IRR and ROI, making the process economically unfeasible. Similarly, in scenario III the unit production revenue is slightly less than the unit production cost. In scenario I, the unit production revenue is almost equal to the unit production cost. These two options therefore have a negative NPV and are economically unproductive at the given market prices of inputs and outputs. Scenario IV is the most promising and techno-economically feasible production process. Even though it has the second highest investment cost, the unit cost of biodiesel production is well below the unit production revenue. Therefore, it has a positive NPV, a higher percentage of IRR and ROI, and a relatively shorter payback time.

The effect of production capacity on the economic feasibility of the four process scenarios has also been investigated. Unit production cost, payback time, and NPV have been used as the main parameters to assess the economic effect of such variation in production capacity.

**Figure 7** shows that scenario II gives higher values of unit production cost for all production capacities considered. The production cost changes only slightly (about 0.04 US$kg$^{-1}$ or 4.6% change) when the production capacity is changed from 3106.34 to 7248.12 kgh$^{-1}$. For the same change in production capacity, scenario IV indicates a greater reduction from its already low unit production cost (about 6.5%). This makes scenario IV more economically feasible at higher production capacities when it is compared to scenario II. Scenarios I and III show almost the same pattern in the change of unit production cost due to the change in production capacity. Scenario I indicates a 7.3% decrease whereas scenario III indicates a 5.8% decrease in unit production cost when production capacity is changed from

3106.34 to 7248.12 kgh$^{-1}$. However, scenario IV has the lowest unit production cost for all the alternative production capacities considered.

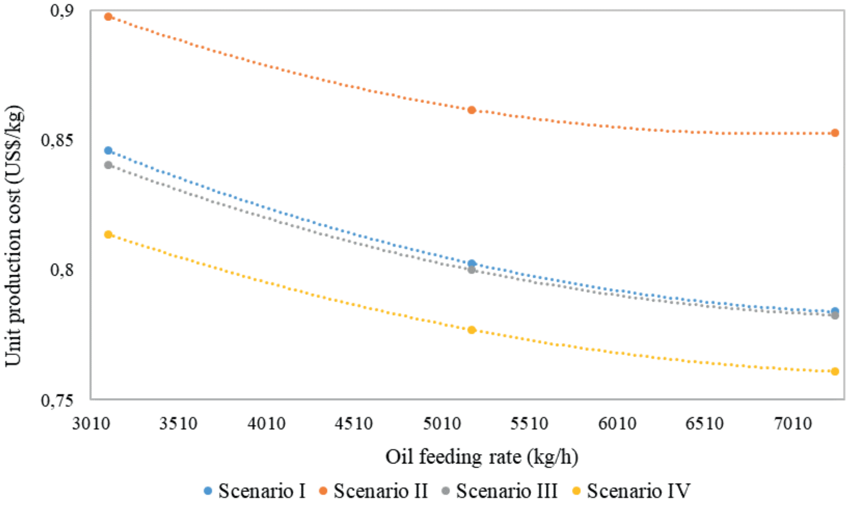

**Figure 7**. Effect of change of biodiesel production capacity on unit production cost

As indicated in **Figure 8**, scenario II has the longest payback time compared to the other scenarios. However, it indicates a 4.7% increament in payback time for a production capacity change from 3106.34 to 7248.12 kgh$^{-1}$. The trend line in the graph is not the direct mathematical representation of the change; rather it is to “connect the dots” and indicate the tendency of the change of the payback time with respect to production capacity. In comparison, scenario IV, could attain a 5.5% increament in payback time for the same change in production capacity. For scenarios I and III, the change pattern is more or less the same, with scenario I indicating a slightly higher reduction in payback time for larger production capacities.

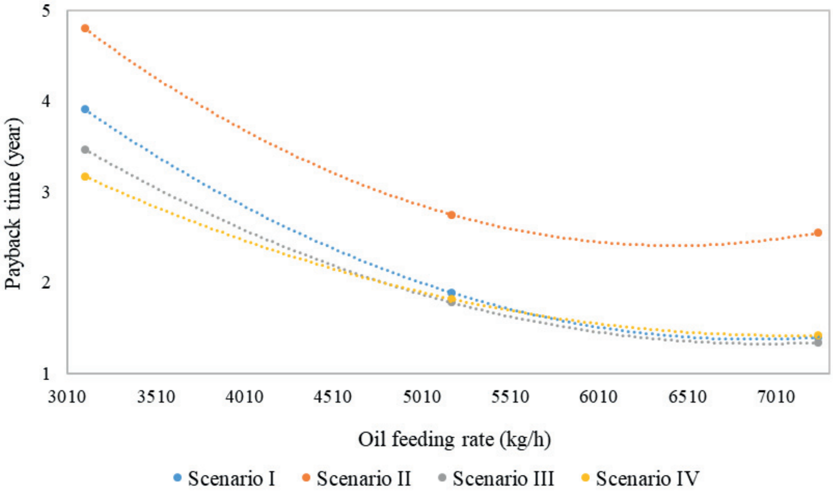

**Figure 8**. Effect of change of biodiesel production capacity on payback time

**Figure 9** shows the effect of the change of biodiesel production capacity on the NPV for all of the four process scenarios. For scenarios I, III and IV, the higher the production capacity the more feasible the business would become in terms of positive NPV. Furthermore, for scenario IV, the production business could be economically feasible at relatively lower production capacities of about 4600 kgh$^{-1}$ and above. However, for scenarios I and III the business can only be profitable when the oil-feeding rate is above 6260 and 6050 kgh$^{-1}$, respectively. Scenario II is more sensitive to change in production capacity, with a more negative NPV even with maximum production capacity. This could be due to the required increament in the number of equipment units for the reactors to accommodate the feedstock when the feeding rate is increased. This is because in scenario II, three reactors are designed. In addition, two of the reactors are made of stainless steel because the reactions involve sulfuric acid. This causes the cost of these reactors to escalate as their capacity increases. This increase in equipment units and/or size results in higher equipment costs, utility costs, labor costs, and other equipment-associated costs such as auxiliary costs. Consequently, the total investment cost and operational cost increases resulting in cash outflows exceeding the cash inflows as production capacity increased. It is clearly evident in the graph that for scenario II, the tendency of the response is different from that of the other scenarios.

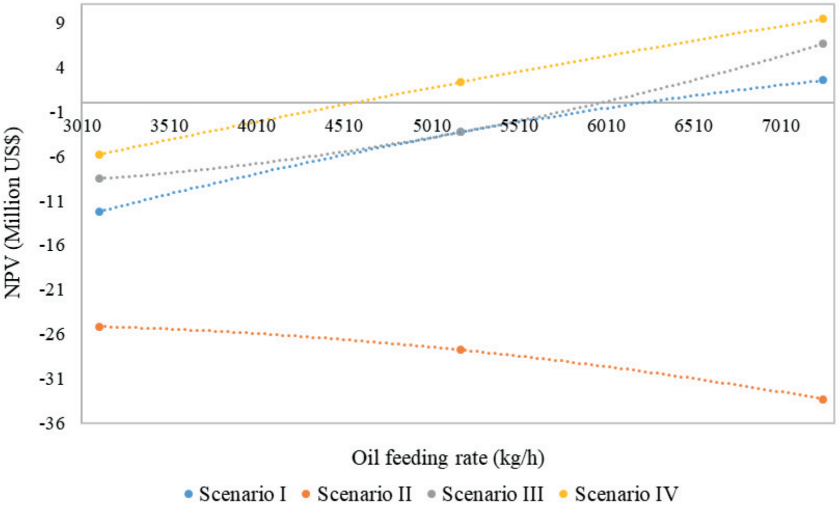

**Figure 9**. Effect of change of biodiesel production capacity on NPV

In addition to the techno-economic performance evaluation in **Paper VI**, further investigation on the effect of the changes of market values of more variables on the economic feasibility of biodiesel production using CaO catalyst has been carried out in **Paper IV**. In this study, price ranges have been set for biodiesel, glycerol, acidic oil feedstock, ethanol, CaO catalyst, labor cost, local tax and maintenance cost to gauge how the payback time and NPV change are affected by these eight market variables.

The NPV increases linearly as the biodiesel selling price increases. The payback time decreases in as the selling price of the biodiesel is increasing. At the lower range of biodiesel selling price, the increase in the sales price causes a very large response on the payback time, which tends to slow as the price gets higher above about 0.81 US$/kg. **Figure 10** displays that a fractional increase in the biodiesel selling price would bring considerable change in the NPV. With optimum production conditions, this analysis has indicated that selling the biodiesel with a price below 0.775 US$/kg is not profitable.

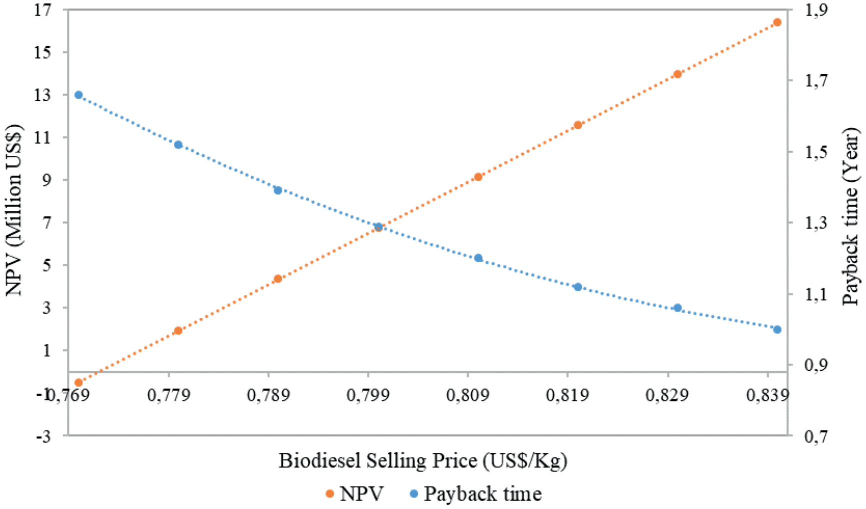

**Figure 10**. Effect of change of biodiesel selling price on NPV and payback time

In this particular study, the amount of glycerol produced with 87.8% purity is approximately 9.8% of the total production of biodiesel. Therefore, it is worth considering the glycerol for market. A price range of 0.05 US$/kg up to 0.18 US$/kg has been adopted in order to investigate how payback time and NPV could change. **Figure 11** indicates that the payback time is changing inversely with the glycerol-selling price. Whereas the NPV increases with increasing glycerol price. A 0.05 US$/Kg increase in the glycerol price would make a 1.21 Million US$ change on NPV. However, the effect of the glycerol price on the payback time is not directly reflected, such as in the case of biodiesel price, indicated above. An increase in the price of glycerol by 0.12 US$ (a three fold increment) could only decrease the payback time by 0.15 years but results in an increase of the NPV by about 2.88 Million US$ (an 11 fold increment). Without considering the glycerol for market (with zero value of glycerol price), the production process could become unprofitable with a negative NPV.

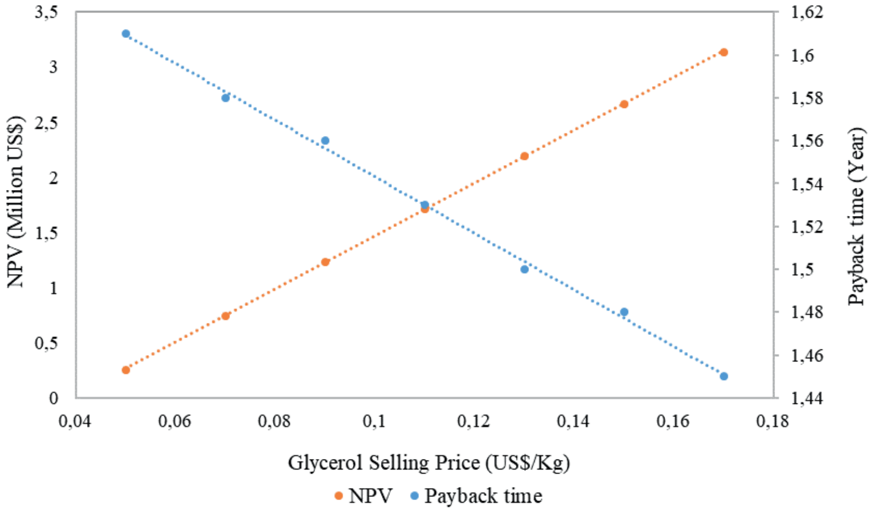

**Figure 11.** The effect of change of glycerol selling price on Payback time and NPV

As it is depicted in **Figure 12,** the NPV shows a strong response to a change in the cost of oil feedstock. Moreover, an increase in oil feedstock purchase cost by about 0.1 US$/kg (from 0.45 up to 0.55 US$/kg) could result in a decrease in NPV of about 24,502,000 US$, whereas the payback time increment is only about 6 months. A feedstock cost of 0.59 US$/Kg and above could make the business unprofitable with a negative NPV. The payback time increases sharply as the oil price is increased above 0.5 US$/Kg. An increase in the oil price by 0.09 US$/Kg when the oil feedstock price is above 0.5 US$/Kg could increase the payback time by 3.32 years. In this case, one can say that the oil price can have more profound effect on the profitability of the business than the other two market variables.

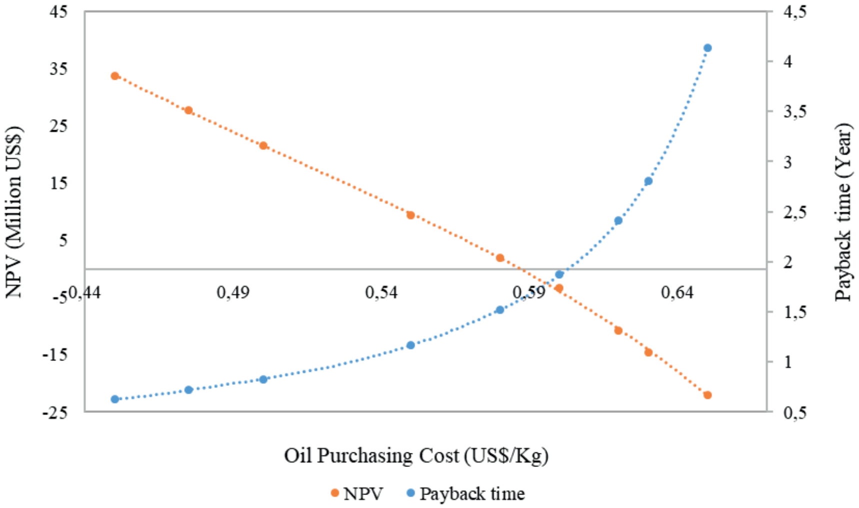

**Figure 12.** The effect of change of oil purchasing cost on Payback time and NPV

As it can be seen from **Figure 13**, the change in the NPV due to an increase in the cost of ethanol is very high. An increase in the cost of ethanol by 0.05 US$/kg could decrease the NPV by 5.54 million US$. A strong effect is observed when the cost of ethanol is increased beyond around 0.25 US$/kg. The maximum cost of ethanol for a profitable production process is approximately 0.31 US$/kg. However, since more alcohol is used in this process than the stoichiometric amount, the excess ethanol, which is recovered in the process, could be reused. This can help to reduce the effects of the purchase cost of alcohol on the profitability of the business over time.

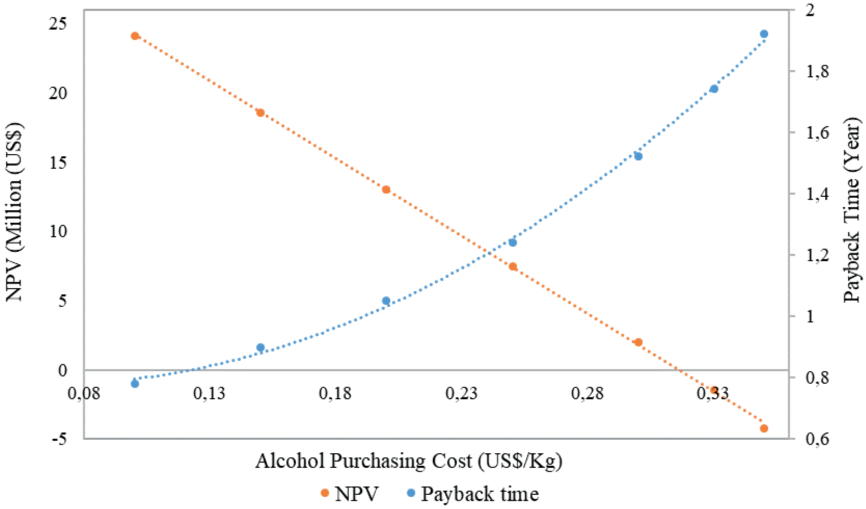

**Figure 13**. The effect of change of Alcohol purchasing cost on Payback time and NPV

**Figure 14** displays that the whole process could be insensitive to considerable change in cost of catalyst, because, even at higher cost of the catalyst, the NPV from the project is in the positive range. However, this small effect of change of catalyst purchasing cost is more profound on NPV than payback time. An increase in cost of catalyst by 0.1 US$/kg could result in reduction of the NPV by about 140,000 US$. However, the effect of the change in cost of catalyst on the payback time of the project is not that much significant. A catalyst price change from 0.08 to 0.3 US$/kg does not show considerable change in payback time.

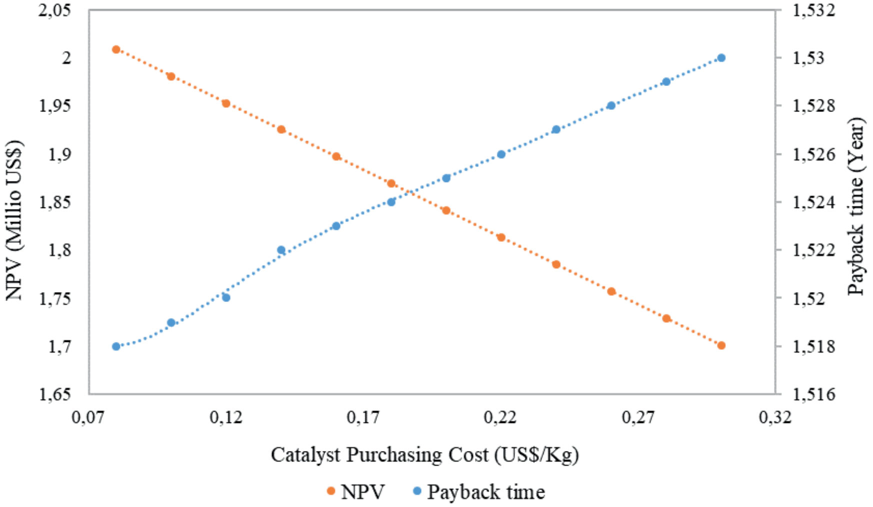

**Figure 14**. The effect of change of catalyst purchasing cost on Payback time and NPV

As shown in **Figure 15**, even with maintenance costs at a higher percentage of equipment purchasing cost, about 45%, the business could still be feasible with around 1.2 Million US$ NPV and 1.5 years increment in payback time. Therefore, the effect of equipment maintenance cost is insignificant. This indicates that better equipment maintenance can be achieved without compromising the profitability of the business to sustain the productivity of the project for longer time.

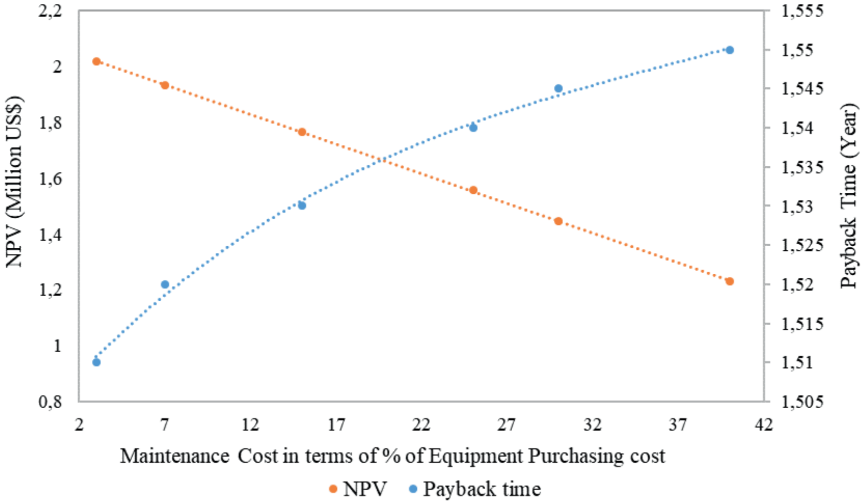

**Figure 15**. The effect of change of equipment maintenance cost on Payback time & NPV

Compared to the cost of materials and the prices of the products, the labor cost has a medium effect on the feasibility of the business, which could be more evident in terms of NPV than the payback time. The total basic rate (the sum of basic rates for supervisor, operator and reactor operator) above 100 US$/h could make the business unprofitable. In another expression, an increase in 15 US$/h of the basic rate payment for labor could reduce the NPV by around 982,000 US$, but comparatively in a very insignificant extension of the payback time. **Figure 16** demonstrates the effect of the variation of labor cost on NPV and payback time of the process.

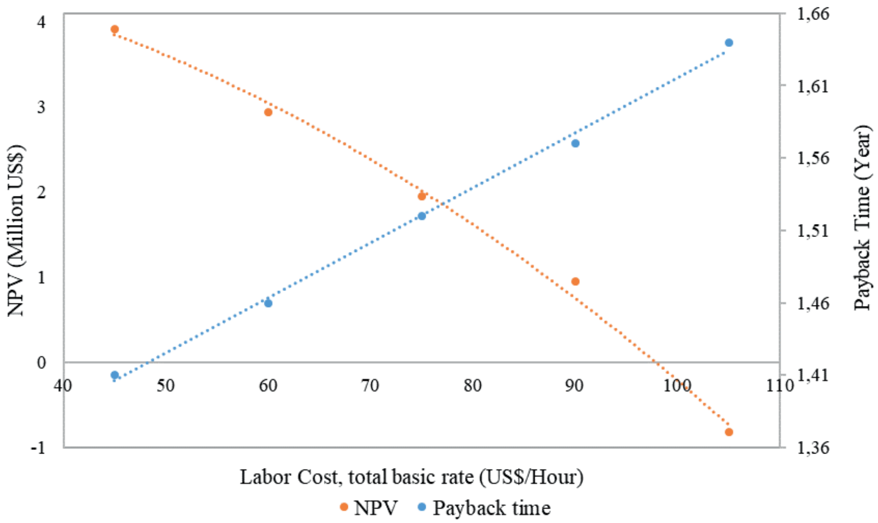

**Figure 16**. The effect of change of Labor cost on Payback time and NPV

As indicated in **Figure 17**, the effect of the tax variation on the NPV is straightforward. An increase in local tax amount by 175,612 US$ (10% Direct Fixed Cost (DFC)) could decrease the NPV by 1,073,000 US$ (a 35% decrease in the NPV). This effect is reflected less in terms of the payback time, because a 200% increment in tax amount could add only about 0.2 years to the project payback time. In general, it is possible to see that the production process could not be feasible at higher tax amounts.

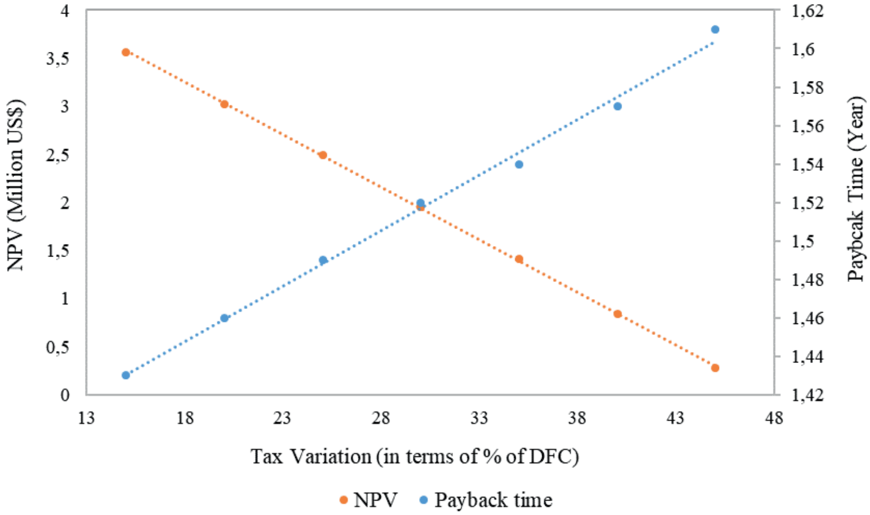

**Figure 17**. The effect of Tax variation on Payback time and NPV

## 3.4. Techno-economic performances of biodiesel production using latest catalyst technologies

The techno-economic performances of the four latest catalyst technologies for biodiesel production have been evaluated in **Paper VII**. The catalyst technology options studied are *Technology option I*: Enzyme catalyzed transesterification and esterification; *Technology option II*: Bulk CaO catalyzed transesterification; *Technology option III*: Ionic liquid catalyzed transesterification; and *Technology option IV*: Nano-CaO catalyzed transesterification. The process flowsheets for each technology option are indicated in **Paper VII**, as **Figures** 1, 2, 3 & 4, respectively**.**

All the process options are capable of providing fuel grade biodiesel and high quality glycerol; proving that the catalysts used, together with the unit procedures involved in separation and purification of the crude biodiesel, could attain a high quality product. Accordingly, the biodiesel from all technology options fulfil the ASTM standards for biodiesel fuel quality. However, there is a slight variation in the amount of biodiesel and glycerol produced. In terms of biodiesel product, technology option IV has the highest performance with about 98.98 kg/h product variation from the least performing one - option III. This is mainly due to the high catalytic activity of the nano CaO particles, which favors high conversion of the oil into biodiesel within a relatively short reaction time. It might also be due to the fact that the occurrence of saponification reaction using Zinc doped nano CaO particles is negligible [108], which also minimizes the chances of the catalyst being used by the FFA in the process of saponification. Relatively, the lowest performance in terms of biodiesel product is indicated in ionic liquid catalyst option. This is due to the lower conversion percentage achieved in the given optimum reaction conditions taken from literature [109].

Similarly, the higher glycerol production amount is attained in technology option IV, with product variation of 23.43 kg/h glycerol from the least performing option III. This is again due to the variation in the achievement of oil conversion percentage according to the required optimum reaction conditions. Consequently, option I and IV do have, relatively, the highest performance in terms of the amount of biodiesel produced per amount of feedstock consumed. **Table 9** indicates the relative technical performances of the technology options studied.

**Table 9:** Summary of technical performances of the technology options

| Indicators | Technology options | | | |
|---|---|---|---|---|
| | Option I | Option II | Option III | Option IV |
| Biodiesel amount (kg/h) | 5191.26 | 5132.16 | 5103.64 | 5202..62 |
| Biodiesel quality (% mass) | 99.9 | 99.9 | 99.9 | 99.9 |
| Glycerol amount (kg/h) | 507.47 | 503.06 | 489.98 | 513.41 |
| Glycerol quality (% mass) | 99 | 99 | 99 | 99 |
| Performances (biodiesel/oil) | 1 | 0.991 | 0.986 | 1 |
| *Impurities in biodiesel** | | | | |
| Glycerol (% mass) | 0.11 | 0 | 0.01 | 0.00 |
| Triolein (% mass) | 0 | 0 | 0 | 0 |

**The maximum allowable amount of impurities according to ASTM, are Glycerol 0.25% mass and Triolein 0.20% mass*

The catalysts from all of the technology options can be recovered and reused. This would help to reduce a considerable amount of money, which could be spent to purchase extra catalysts. The other advantage of the processes is that in all of the process options, except technology option II, there is no waste produced. In option II, the waste stream is composed of calcium soap and unreacted oil, which can be further purified for economic benefits. The unreacted oil from technology option I and III can be recycled directly to the processes, whereas the one from technology option IV should pass through a treatment step before it is reused to reduce the FFA content. This is because the unreacted oil from this process is composed of FFA, which is left unreacted in the Nano catalysis process.

Technology option I is the most expensive alternative, mainly due to the very high cost of the enzyme, Novozyme 435. Even though this catalyst can be reused for more than 200 times [110] and the process can give the second higher biodiesel product, the higher total investment cost of the option makes it uneconomically feasible for production of biodiesel fuel. The higher production cost in option I is also attributed to its relatively larger reactor volume required due to longer reaction time. Due to the larger equipment volume, the higher would be the costs of equipment, facilities and utilities.

The second most expensive option is technology option III. Its total investment cost is almost half of that of option I and 37% higher than the lowest option, which is option II. This is mainly because of second largest volume of reactors required due to longer reaction time as well as the additional centrifugal decanter required to separate the catalyst. The larger and the more equipment we use, the higher the utility cost and the other costs associated with the equipment. Technology option II has the least total capital investment cost because it requires smaller equipment sizes due to minimum reaction time and the catalyst involved is the cheapest among the catalyst options studied.

Even though technology option IV is the second cheapest option, the higher cost of the Nano CaO catalyst could still make it economically infeasible at the optimum market values of inputs and outputs considered. Similarly, option III is also economically infeasible at the current market prices of inputs and outputs. However, for the optimum market values of inputs and outputs considered, option II is found to be the most feasible option with positive NPV, lower unit production cost, higher IRR, ROI and Gross margin. **Table 10** summarizes the economic performances of the technology options.

**Table 10:** Summary of the economic performance of the technology options

| Economic performance parameters | Catalyst technology options | | | |
|---|---|---|---|---|
| | Option I | Option II | Option III | Option IV |
| Total capital investment cost (US$) | 13,200,448 | 4,608,642 | 6,319,464 | 4,744,425 |
| Total equipment purchasing cost (US$) | 1,629,303 | 432,295 | 674,025 | 403,033 |
| Direct Fixed Capital (US$) | 6,716,375 | 1,781,747 | 2,778,061 | 1,682,115 |
| Working Capital (US$) | 6,148,254 | 2,737,807 | 3,402,499 | 2,978,204 |
| Total Annual operating cost (US$) | 71,304,387 | 31,224,324 | 39,050,943 | 33,824,494 |
| Total annual raw material cost (US$) | 66,706,623 | 29,372,952 | 36,670,506 | 32,010,394 |
| Labor dependent cost (US$) | 624,549 | 364,320 | 390,343 | 364,320 |
| Facility dependent cost (US$) | 3,376,225 | 889,148 | 1,396,347 | 844,949 |
| Laboratory, Quality Control &Analysis (US$) | 187,365 | 109,296 | 117,103 | 109,296 |
| Utility cost (US$) | 299,626 | 378,608 | 366,644 | 385,535 |
| Annual revenue from Biodiesel (US$/year) | 32,087,761 | 31,704,748 | 31,529,636 | 32,140,209 |
| Annual revenue from Glycerol (US$/year) | 1,607,422 | 1,594,245 | 1,552,758 | 1,627,161 |
| Total Annual Revenue (US$/year) | 33,695,184 | 33,298,993 | 33,082,394 | 33,767,370 |
| Unit production Revenue (US$/kg) | 0.8186 | 0.8192 | 0.8184 | 0.8194 |
| Unit production cost (US$/kg biodiesel) | 1.7323 | 0.7681 | 0.9660 | 0.8208 |
| NPV at 7% (US$) | -349,847,116 | 9,736,266 | -57,834,235 | -3,217,935 |
| ROI (%) | 26.11 | 84.66 | 71.48 | 103.69 |
| After tax IRR (%) | NA | 32.73 | NA | NA |
| Gross Margin (%) | 13.79 | 17.53 | 20.19 | 21.93 |
| Payback time in years | 3.83 | 1.18 | 1.4 | 0.96 |

We have also performed a sensitivity analysis of the technology options towards change in market values of oil purchasing cost, biodiesel selling price and catalyst-purchasing cost. The effects have been evaluated in terms of NPV.

The trend at which the technology options respond towards the change in oil purchasing cost is almost similar. However, option I is found to be economically infeasible for all ranges of the oil purchasing cost considered. For option III, the maximum cost of oil feedstock has to be about 0.39 US$/kg, beyond which the option would be economically infeasible. Option II is found to be more tolerant to the market variation of oil cost. It can still be economically feasible up to 0.59 US$/kg of oil purchasing cost. In comparison, option IV is also the second most tolerant to market fluctuations of oil purchasing cost. Nevertheless, it can be economically feasible for oil purchasing cost less than 0.51 US$/kg. **Figure 18** indicates the effect of the change in market values of oil purchasing cost on NPV of the technology options.

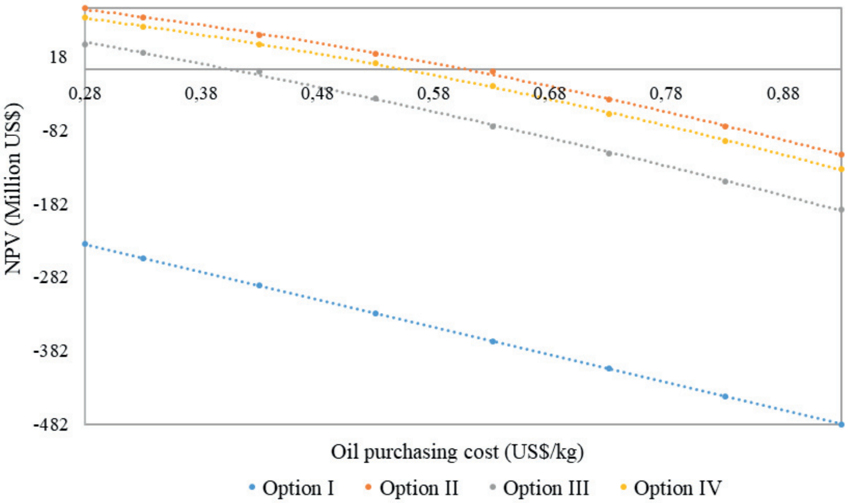

**Figure 18.** Effect of change of Oil purchasing cost on NPV for option I, option II, Option III and option IV

The changing trend of the technology options towards the variation of the market values of biodiesel price is almost similar. Option I is unprofitable at the considered ranges of biodiesel selling prices. For this option to be economically feasible, the biodiesel needs to be sold at a very high price (1.8 US$/kg), which would be very difficiult to achieve. Conversely, technology option IV can be economically feasible at almost half of this price (0.97 US$/kg). This demonstrates that the production of biodiesel fuel using technology option I should be subsidized in order to make the fuel economically competitive with fossil diesel in the market. For the biodiesel selling price range considered, option II is found to be more tolerant to the possible fluctuation of biodiesel price and can still be economically feasible at a biodiesel price as low as 0.77 US$/kg. **Figure 19** indicates the effect of a change of biodiesel selling price on NPV of the technology options.

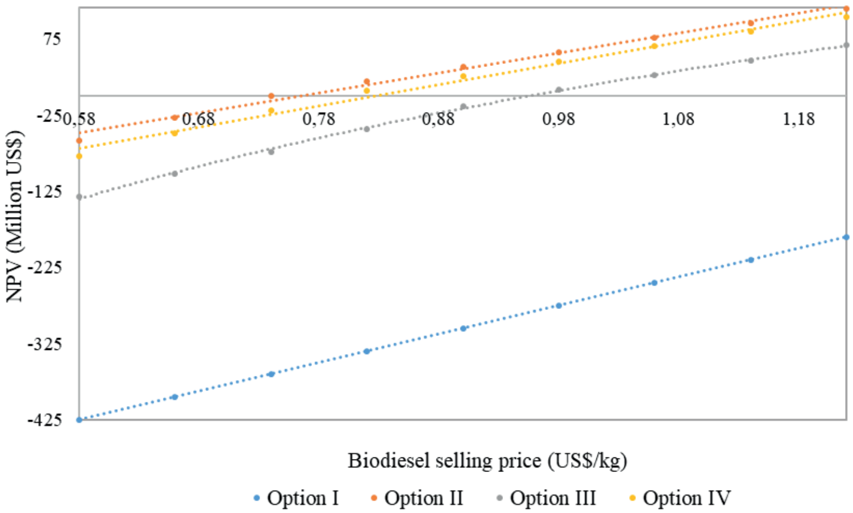

**Figure 19.** Effect of change of Biodiesel selling price on NPV for option I, option II, Option III and option IIV

The entire techno-economic comparison is among these four catalyst technologies. Thus evaluating the effect of the market values of the four catalyst types could give reasonable ground for selecting the technology option that is more tolerant to fluctuating costs of materials in the market. The trend at which the NPV changes with the catalyst cost is almost the same for all technological options. However, some get negative NPV at very low cost values and some at relatively higher values. For instance, option I could still be economically feasible for about 61 US$/kg cost of enzyme catalyst. This is mainly due to its higher reusability, which could reduce the overall cost of the catalyst. Nevertheless, this higher price, indicated here, is not enough to buy the very expensive enzyme catalysts, especially immobilized ones [110]. This demands more investigation on enzyme catalysts, which could be produced for a cost as low as 60 US$/kg while possessing the same catalytic performance as indicated here. Option III is the most sensitive towards a change in the value of catalyst purchasing cost. It is economically feasible for a catalyst cost of less than 4.1 US$/kg. Option IV gets its negative NPV for a catalyst cost of more than 5 US$/kg. The cheapest catalyst is the bulk CaO catalyst in option II. It can be produced from waste like eggshell, crab shell, and river snail shell among others. The cheap cost of and higher reusability of the CaO catalyst makes option II more tolerant to possible fluctuations of catalyst purchasing cost in the market. It gets its negative NPV from a catalyst cost of more than 7 US$/kg, which seems to be far from its current market value. **Figure 20** shows the effect of change of catalyst purchasing cost on NPV of each technology option.

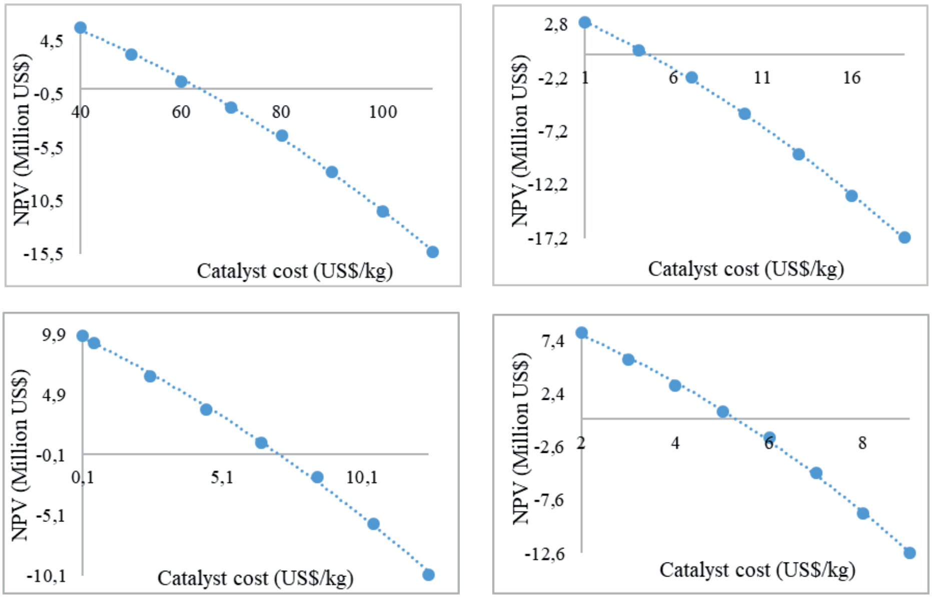

**Figure 20**. Effect of change of catalyst purchasing cost on NPV of each production technology option

# 4. Conclusion

The present thesis attempted to identify efficient and affordable technologies for sustainable production of biodiesel from cheap bio-resources. In doing so, the approach involves the evaluation of different convenient technologies for the efficient conversion of oil feedstock to biodiesel, measurement of the techno-economic performances of various process scenarios using different catalyst technologies and process layouts, as well as assessment of the effect of market variables on the economic performances of the different process scenarios.

Among the methods to change fat and oil to biodiesel, the most convenient one is the transesterification reaction. There are a number of techniques used to carry out transesterification of fat/oil for biodiesel production, each one requiring specific feedstock property and optimum operating conditions for efficient production of biodiesel. In **Paper I**, the state of the art review of the latest studies on the conversion of oil/fat feedstock to biodiesel has been carried out to make a comparison between the different possible technologies. The technologies studied include homogeneous and heterogeneous alkali catalyzed transesterification, homogeneous and heterogeneous acid catalyzed transesterification, enzyme catalyzed transesterification, nano particles catalyzed transesterification and supercritical transesterification. From the review of the different work, it was concluded that acid, enzyme and heterogeneous base (like CaO) catalyzed as well as supercritical transesterification processes are capable of producing biodiesel from low value and cheap feedstock, which has high FFA content. This could bring advantages by way of a reduction in the cost of biodiesel production because more than 80% of biodiesel production cost is due to cost of feedstock. From another point of view, irrespective of its type, the hetrogeneousity of a catalyst could bring a benefit to easily recover it for multiple reuse, which could also result in a considerable reduction of biodiesel production cost. The conventional homogeneous alkali catalyzed transesterification process could not provide biodiesel from feedstock with high FFA content. This is due to the saponification reaction far more dominating the transesterification reaction. The only disadvantage of the acid catalyst technologies is associated with its requirement of higher reaction temperature. In addition, especially when we use homogeneous acid catalysts, there might be corrosion issues depending on the type of the materials that the equipment is made from. Even though the enzyme catalyst technology revealed high performance in converting acidic oil/fat into biodiesel, the very high cost of the catalyst could make the production process economically infeasible. Similarly, the supercritical transesterification option has higher investment due to the requirement of higher pressure and temperature conditions. Thus, any attempt to reduce the cost of biodiesel production should consider the different possible catalyst technologies in combination with feedstock alternatives, while investigating the various possible process alternatives.

The review on the economics of biodiesel production in **Paper II** concludes that the cost of raw materials, especially the cost of feedstock, accounts for most of the cost of biodiesel production, irrespective of the technology type. Thus, the economic feasibility of biodiesel production processes is largely affected by the cost of feedstock. This demands the requirement for cheaper feedstock types, such as non-edible oil plants, waste cooking oil and animal fats. The problem with these low cost feedstock types is their higher amount of impurities. While using the conventional base catalyzed process, the presence of the higher FFA and water content in the feedstock demands the use of additional pretreatment as well as product separation and purification units in order to produce quality biodiesel fuel, which complies with ASTM standards. This in turn incurs a considerable amount of money to the total manufacturing cost. Therefore, to be profitable in biodiesel production, there should be a compromise between cost reduction, due to using cheaper feedstock, and the cost incurred due to additional steps and/or techniques for pretreatment of the low value feedstock, product separation and product quality improvement. Among the conventional technologies, the acid catalyzed transesterification reaction is the most cost effective to produce fuel grade biodiesel from cheaper feedstock with higher FFA content. Acid catalysts can catalyze both esterification and transesterification reactions without feedstock pretreatment steps. This economic feasibility is manifested by a lower total manufacturing cost, and a lower biodiesel breakeven price. Heterogeneous acid catalysts do have an additional advantage of reusability, resulting in less steps required for product separation and purification, and the production of high purity glycerol. These advantages have economic implications, making heterogeneous acid catalysts a good choice to reduce unit cost of biodiesel production. There are a number of catalyst alternatives prepared from wastes and cheap materials. Such cheap materials include eggshell, scallop waste shell, crustacean shells, bio-char from coconut shell, Kraft lignin and pyrolyzed sugar among others. These type of catalysts are cheap and most of them are reusable. CaO is one of the catalyts made the most from such cheap resources and it is very well known for effective conversion of low value oil feedstock to biodiesel. Least cost and reusable catalysts would bring considerable economic advantages through reducing manufacturing cost and improving throughput per unit time.

The economic feasibility of a biodiesel production process could be largely dependent on the type of catalyst technology involved. In **Paper III**, the techno-economic performance analysis of biodiesel production from acidic oil was carried out for three production technologies using two catalyst types, sulfuric acid and CaO. The first two models used each catalyst separately, whereas the third model involved the two catalysts together.

The process model, which uses the two catalysts together (Model III) could provide a higher amount of biodiesel product, whereas the CaO catalyst option (Model II) had a relatively low amount. At optimum production conditions, the biodiesel yield variation between the Model III and II could produce up to 176 kg/hr. The purity of the biodiesel produced from all technological alternatives studied is in line with the quality requirement of ASTM. Model II could produce high quality glycerol, as it used heterogeneous catalyst. Whereas, in Models I and III, the quality of glycerol produced is less due to the presence of $CaSO_4$. Model I produced less amount of glycerol compared to the other two models.

Economically, Model II is the superior alternative process scoring better results in all of the parameters. It shows lower unit production cost, shorter payback time, and a higher NPV at 7% interest rate, to mention a few. In terms of the sensitivity of the process models towards a change in market values of oil feedstock cost and biodiesel selling price, Model II is also found to be more tolerant than the two other models.

In **Paper IV**, further investigation of the effect of more market variables on the economic feasibility of the CaO catalyzed process option has been carried out. Accordingly, it was indicated that the cost of oil feedstock has a strong influence on the profitability of the business along with alcohol cost, biodiesel price, glycerol price, labor cost, tax variation and equipment maintenance cost, consecutively. The effect of change of equipment maintenance cost is found to be the least, providing the chance to increase the amount of cost allocated for routine maintenance activities to sustain the productivity of the process as much as possible. It was also determined that the minimum selling price of biodiesel for its profitable production is 0.775 US$/Kg (775 US$/ton). This price is relatively in agreement with biodiesel selling price forecasted in FAO-OECD Agricultural Outlook 2016 – 2025.

The techno-economic performances of four different process layouts using sulfuric acid catalyst have also been evaluated in **Paper V**. All of the four designed process scenarios are capable of producing fuel grade biodiesel and could also provide high quality calcium sulfate and glycerol byproducts for additional income. Scenario III, with double reactor, shows better technical performance with very low economic feasibility. In addition, scenario III is found to be the most sensitive alternative to change in market values of inputs and outputs. Comparatively, scenario II is the cheapest alternative. It also indicates good technical performance and provides a competitive amount of glycerol byproduct. In terms of sensitivity to a change in market values of inputs and outputs, scenario II is more tolerant than the other scenarios. Scenarios I and IV are relatively technically less efficient. In addition, scenario IV is the second most expensive alternative as well as the second most sensitive alternative towards a change in market values of inputs and outputs.

In **Paper VI**, similar performance assessments have also been performed for the other four process options using CaO catalyst. The process options have been designed based on four different arrangements of the downstream unit procedures, which are required to produce fuel grade biodiesel from acidic oil. All of the four process scenarios could provide fuel-quality biodiesel in accordance with the ASTM standards. In scenarios I and III, better quality biodiesel could be achieved with additional process steps considered to further purify the biodiesel. In general, in terms of overall technical performance, scenario IV is superior. It could attain biodiesel purity of 99.9%, provide the second highest amount of biodiesel (more biodiesel produced per amount of oil feedstock), and provide the highest amount of glycerol, which would also be of a higher quality. It could also provide another valuable byproduct – calcium soap, which might add an economic benefit to the process. The economic performance evaluation indicated that scenario II is not economically feasible due to the high investment cost, which results in a unit production cost that would be higher than revenue. This effect is more pronounced at higher production capacities. Comparatively good economic performance is indicated by scenario IV. However, at lower production capacity, scenario IV is not economically feasible. A production capacity with an oil feeding rate of more than 4600 kg/h could make scenario IV more dependable in terms of economic returns.

In addition to the two effective catalyst options, CaO and $H_2SO_4$, four latest catalyst technologies were also investigated for their techno-economic performances while producing fuel quality biodiesel from low value cheap feedstock (**Paper VII**). These catalyst technologies include enzyme, bulk CaO, ionic liquid and nano CaO catalysts. All of the studied catalyst options revealed competitive technical performances with almost the same amount of biodiesel produced using the same amount of oil feedstock. Economically option I is not feasible mainly due to the very high cost of the enzyme catalyst and larger volume of reactor. The second most expensive option is technology option III. Option II is the most efficient in economic terms as it attains higher positive NPV, higher IRR, higher Gross margin, higher ROI and minimum total capital investment cost. In technology option I the enzyme catalyst must be bought for less than 60 US$/kg for the process to be economically feasible. Option II is found to be the most tolerant towards the change in the market values of biodiesel price, oil cost and catalyst cost. It indicates profitability at a biodiesel price as low as 0.74 US$/kg, oil purchasing cost as high as 0.70 US$/kg and catalyst cost as high as 7 US$/kg.

# 5. Future perspectives

The main catalyst technology options considered in the whole study includes bulk CaO, $H_2SO_4$, enzyme (Novozyme 435), ionic liquid (Brønstade acidic ionic liquid), as well as Zink doped nano-CaO particles. These catalyst technologies are selected based on their own specific advantages over the conventional alkali catalyst for efficient production of biodiesel from low cost feedstock. However, there are also a number of other potential catalyst technologies for effective conversion of feedstock with high FFA content into biodiesel. Since this study alone could not investigate everything in this regard, in the future similar studies need to be undertaken by including the other potential catalyst technologies.

Among the studied catalyst technologies, biodiesel production process using bulk CaO catalyst has, more or less, found to be technically efficient and at the same time economically feasible. However, since this study is based entirely on simulation, just for a study estimate as a preliminary assessment, a thorough investigation is required, for example using a small pilot project, to further ensure the viability of the technology option for industrial application.

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# PAPERS

# Paper I

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*Review*

# Biodiesel production technologies: review

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**Abstract:** Biodiesel is a fuel with various benefits over the conventional diesel fuel. It is derived from renewable resources, it has less emission to environment, it is biodegradable so has very limited toxicity and above all its production can be decentralized so that it could have a potential in helping rural economies. However, there are also some worth mentioning challenges associated with production of biodiesel. Among them repeatedly mentioned are the cost of feedstock and the choice of convenient technology for efficient production of the fuel from diverse feedstock types. There are four main routes by which raw vegetable oil and/or animal fat can be made suitable for use as substituent fuel in diesel engines without modification. These are direct use or blending of oils, micro-emulsion, thermal cracking or pyrolysis and transesterification reaction. Due to the quality of the fuel produced, the transesterification method is the most preferred way to produce biodiesel from diverse feedstock types. Through this method, oils and fats (triglycerides) are converted to their alkyl esters with reduced viscosity to near diesel fuel levels. There are different techniques to carry out transesterification reaction for biodiesel production. Each technique has its own advantages and disadvantages as well as its own specifically convenient feedstock character. There are also some very important reaction conditions to be given due attention in each of this techniques for efficient production of biodiesel, such as molar ratio of alcohol to oil, type and amount of catalyst, reaction temperature, reaction time, reaction medium, type and relative amount of solvents, among others. This review is meant to investigate the main transesterification techniques for biodiesel production in terms of their choice of feedstock character as well as their determinately required reaction conditions for efficient biodiesel production, so that to give an overview on their advantages and disadvantages.

**Keywords:** Biodiesel; Transesterification; Acid catalyzed; Base catalyzed; Enzyme catalyzed; Supercritical

## Abbreviations

| | |
|---|---|
| ASTM | American Society for Testing and Materials |
| FAME | Fatty Acid Methyl Ester |
| FFA | Free Fatty Acid |
| GHG | Green House Gas |
| IEA | International Energy Agency |
| IUPAC | International Union of Pure and Applied Chemistry |
| OECD | Organization for Economic Co-operation and Development |

## 1. Introduction

The U.S Energy Information Administration, in its International Energy Outlook 2016 report, indicated that the world total energy consumption is significantly increasing. In this report, the worldwide energy consumption is projected over the 28 year period from 2012 to 2040 as shown in Figure 1.

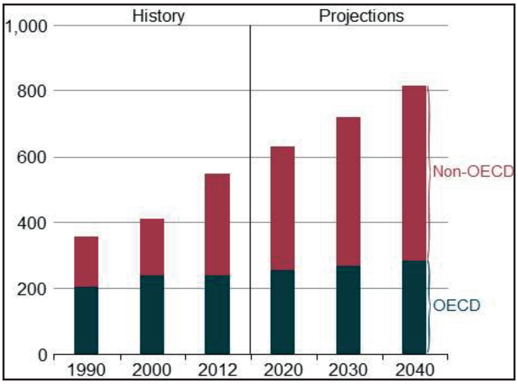

**Figure 1.** World energy consumption from 1990 up to 2040 in quadrillion Btu [1].

This projection specified that much of the growth in energy consumption is expected from non-OECD countries, where strong economic growth and expanding populations lead the increase in world energy use.

As countries develop and living standards improve, energy demand grows rapidly. For instance, in nations experiencing fast-paced economic growth, their life style changed and more economic activities emerge demanding more and more energy.

Crude oil, coal and gas are the main dominant resources for world energy supply [2]. However, most argue that demand for renewables would increase owing to limited reserve of the conventional fuels, which jeopardize the energy security issue, as well as for the environmental benefit of using renewables as alternative energy supplies.

According to the IEA Medium Term Renewable Energy Report 2015, the renewable energy share in the total world energy consumption is expected to have at least 26% increment by 2020 [3]. And the International Energy Agency, world energy outlook 2013 [4], particularly showed that, for the next two decades, world fuel oil demand is concentrated in transport sector and in which, diesel fuel demand is expected to dominate by 5.5 million barrel per day as shown in Figure 2.

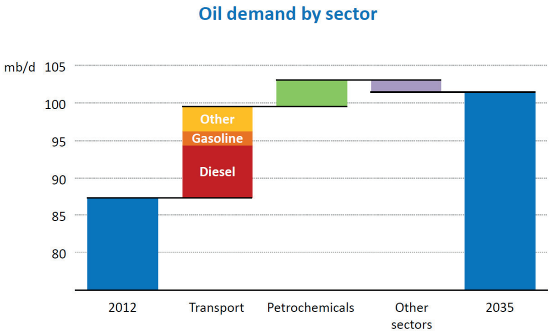

**Figure 2.** Oil demand by sector between 2013 and 2035 [4].

As it can be seen from Figure 2, diesel fuel use is expected to be the main to get the highest score in increment in oil demand for the years to come. This indicates there is more practical opportunity in working towards substituting the conventional diesel fuel with biodiesel so that attaining the required demand without causing negative consequence to our environment.

In accordance with this, the awareness of energy issues and environmental problems associated with burning fossil fuels has globally encouraged many researchers to investigate the possibility of using alternative sources of energy instead of oil and its derivatives. Among them, biodiesel seems very interesting for several reasons.

The invention of the vegetable oil fueled engine by Sir Rudolf Diesel dated back in the 1900s, however, full exploration of biodiesel only came into light in the 1980s as a result of renewed interest in renewable energy sources for reducing greenhouse gas (GHG) emissions, and alleviating the depletion of fossil fuel reserves. Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats and alcohol with or without a catalyst [5–9].

Biodiesel is highly biodegradable and has minimal toxicity. It has almost zero emissions of aromatic compounds and other chemical substances that are destructive to the environment. It has a small net contribution of carbon dioxide ($CO_2$) when the whole life-cycle is considered (including cultivation, production of oil and conversion of oil to biodiesel); and its production can be decentralized so that it could have significant potential for improvement of rural economy [5,10].

Compared to diesel fuel, biodiesel produces no sulfur, less carbon monoxide, less particulate matters, less smoke and hydrocarbons emission and more oxygen. More free oxygen leads to the complete combustion and reduced emission [11,12].

Vegetable oil and/or animal fat can be converted to fuel for diesel engine through four major possible ways: direct use or blending of oils, micro-emulsion, thermal cracking or pyrolysis and transesterification reaction. Among these methods, the most preferred one is transesterification reaction. Transesterification reactions enables the use of diverse feedstock types to produce a fuel highly resemble to conventional diesel in quality. Through this method, oils and fats (triglycerides) are converted to their alkyl esters with viscosity similar to diesel fuel.

Transesterification reaction can be catalyzed or non-catalyzed. The catalysis of transesterification is usually either chemically like base catalyzed transesterification and acid catalyzed transesterification, or using enzyme catalysts like lipase-catalyzed transesterification. However, there are also some less investigated but efficient ways to produce biodiesel through esterification of oils and fats such as those using Nano catalysts and ionic liquid catalysts. The non-catalyzed transesterification is carried out without any catalyst only by using an alcohol at supercritical conditions where the alcohol, usually methanol, is at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist [13,14,15]. In the supercritical state, the dielectric constant of alcohol is decreased so that two-phase formation of vegetable oil/alcohol mixture is not encountered and only a single phase is found favoring the reaction [16].

Each transesterification technique requires different feedstock character. For example, some can handle feedstock with high FFA content where as others are very sensitive to even small amount. Some esterification techniques are more advantages than the others at least with respect to cost of production, or minimum waste generation, or high productivity and the like. In addition, there are some very important reaction conditions, which should always be optimized for efficient production of biodiesel. Among them the very commonly studied are: molar ratio of alcohol to oil, type and amount of catalyst, reaction temperature, reaction time, reaction medium, type and relative amount of solvents.

Accordingly, in this paper, more emphasis is given on reviewing the effect of the main reaction conditions for an efficient production of biodiesel from different feedstock types as well as on summarizing the advantages and disadvantages of these major transesterification techniques.

## 2. Oil and Fat as Fuel in Diesel Engines and Biodiesel Production Technologies

The dominant technologies, which enable us to use oil and fat feedstock types as fuel in diesel engines, are usually described as direct use or blending of oils, micro-emulsion, pyrolysis and transesterification. Transesterification being currently mentioned by various researchers as the most preferable due to better quality of fuel produced [17,18,19].

### *2.1. Pyrolysis*

Pyrolysis refers to a chemical change caused by the application of thermal energy in the absence of air or oxygen, or by the application of heat in the presence of a catalyst, which results in cleavage of bonds and formation of a variety of small molecules. Pyrolysis is conducted at temperature range of 400–600 °C. The process produces gases, bio-oil, and a char depending on the rate of pyrolysis. Based on the operating conditions, the pyrolysis process can be divided into three subclasses: conventional pyrolysis, fast pyrolysis and flash pyrolysis [20] as shown in Table 1. Fast pyrolysis is the one used for production of bio-oil.

This liquid fraction of the thermally decomposed vegetable oil, bio-oil, is likely to approach diesel fuel properties and characteristics. Ma et al. [21] mentioned that the chemical compositions (heavy hydrocarbons) of the diesel fractions produced by catalytic cracking of copra oil and palm oil stearin were similar to fossil fuels. The process was simple and effective compared with other cracking processes according to them.

According to Ma et al. [21] pyrolytic chemistry is difficult to characterize because of the variety of reaction paths and the variety of reaction products that may be obtained from the reactions that occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids.

In another study, Mahanta et al. [22] mentioned that pyrolyzate (product of pyrolysis) from any feedstock type has lower viscosity, flash point, and pour point than petroleum diesel fuel and equivalent calorific values. In addition, the cetane number of the pyrolyzate is lower. According to them, the pyrolyzed vegetable oils contain acceptable amounts of sulfur, water and sediments and give acceptable copper corrosion values but unacceptable quantities of ash, carbon residual and pour point.

**Table 1.** Classification of pyrolysis methods with differences in temperature, residence time, heating rate, and major products [20].

| Method | Temperature (°C) | Residence Time | Heating rate (°C/s) | Major products |
|---|---|---|---|---|
| Conventional/slow pyrolysis | Med-high (400–500) | Long 5–30 min | Low 10 | Gases<br>Char<br>Bio-oil (tar) |
| Fast pyrolysis | Med-high (400–650) | Short 0.5–2 s | High 100 | Bio-oil (thinner)<br>Gases<br>Char |
| Ultra-fast/flash pyrolysis | High (700–1000) | Very short < 0.5 s | Low 10 | Gases<br>Bio-oil |

Abbaszaadeh et al. [23] also reported that biodiesel fuel produced through a pyrolysis process or known as bio-oil is suitable for diesel engines; however, low-value materials are produced due to the elimination of oxygen during the process. Undesirable properties that sometimes restrict the application of biodiesel produced through this process are low heating value, incomplete volatility, and instability [24]. But, in another view, Singh and Singh [25], mentioned that thermal pyrolysis of triglycerides has several advantages such as lower processing cost, simplicity, less waste, and no pollution.

Another disadvantage of pyrolysis is the need for distillation equipment for separation of the various fractions. Also the product obtained is similar to gasoline containing sulphur which makes it less ecofriendly [26].

The equipment for thermal cracking and pyrolysis is expensive for modest throughputs. In addition, while the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. It produces some low value materials and, sometimes, more gasoline than diesel fuel [21].

### *2.2. Micro-emulsification*

Among the physical properties of raw vegetable oil, which makes it to be not directly used as fuel, is its viscosity. Ma et al. [21] pointed out that, the formation of micro-emulsion is one of the potential solutions for solving the problem of vegetable oil viscosity.

According to IUPAC definition, micro-emulsion is dispersion made of water, oil, and surfactant(s) that is an isotropic and thermodynamically stable system with dispersed domain diameter varying approximately from 1 to 100 nm, usually 10 to 50 nm [27].

The components of a biodiesel micro-emulsion include diesel fuel, vegetable oil, alcohol, and surfactant and cetane improver in suitable proportions. Alcohols such as methanol and ethanol are used as viscosity lowering additives, higher alcohols are used as surfactants and alkyl nitrates are used as cetane improvers [28].

Mahanta et al. [22] reported that micro-emulsion can be made of vegetable oils with an ester and dispersant (co-solvent), or of vegetable oils, and alcohol and a surfactant and a cetane improver, with or without diesel fuels. All micro-emulsions with butanol, hexanol and octanol met the maximum viscosity requirement for diesel fuel. The 2-octanol is an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil [29].

Micro-emulsions can improve spray properties by explosive vaporization of the low boiling constituents in the micelles. Micro-emulsion results in reduction in viscosity, increase in cetane number and good spray characters in the biodiesel. According to Srivastava and Prasad [30], short term performances of both ionic and non-ionic micro-emulsions of aqueous ethanol in soybean oil was nearly as good as that of NO. 2 diesel fuel, in spite of the lower cetane number and energy content. NO. 2 diesel fuel is a fuel with distillation temperature of 640 degrees Fahrenheit at the 90% recovery point and meets the specifications defined in ASTM Specification D 975 [31].

However, as indicted by Parawira [32], continuous use of micro-emulsified diesel in engines causes problems like injector needle sticking, carbon deposit formation and incomplete combustion.

### *2.3. Dilution/Blending*

Direct uses of vegetable oils have generally been considered not satisfactory and impractical for both direct and indirect diesel engines. The high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating oil thickening are obvious problems. In another view, Ma et al. [21], pointed out that oil deterioration and incomplete combustion are the two severe problems associated with the direct use of vegetable oils as fuels.

In such cases, it is helpful to dilute vegetable oils with such materials as diesel fuels, solvent or ethanol. Dilution results in reduction of viscosity and density of vegetable oils. Bilgin et al. [33] indicated that the addition of 4% ethanol to diesel fuel increases the brake thermal efficiency, brake torque and brake power, while decreasing the brake specific fuel consumption. They also argued that since the boiling point of ethanol is less than that of diesel fuel, it could assist the development of the combustion process through an unburned blend spray.

In their review of biodiesel production methods, Ma et al. [21] mentioned that, the viscosities of 50/50 (winter rapeseed oil and diesel) and 70/30 (whole winter rapeseed oil and diesel) blends were much higher (6–18 times) than NO. 2 diesel. According to them, a blend of 70/30 winter rapeseed oil and NO. 1 diesel fuel (A light distillate fuel oil that has distillation temperatures of 550 degrees Fahrenheit at the 90% recovery point and meets the specifications defined in ASTM Specification D 975 [31]) was used successfully to power a small single-cylinder diesel engine for 850 h. No adverse wear and no effects on lubricating oil or power output were noted.

## *2.4. Transesterification*

Transesterification is the main convenient method to produce biodiesel from oil and fat feedstock types, which chemically resembles petroleum diesel. Through this method, oils and fats (triglycerides) are converted to their alkyl esters with reduced viscosity to near diesel fuel levels. This product is thus a fuel with properties similar to petroleum based diesel fuel, which enable it be used in existing petroleum diesel engines without modifications. Generally, transesterification is a reversible reaction, which simply proceeds essentially by mixing the reactants usually under heat and/or pressure. However, if some kind of catalyst is added to the reaction, it will be accelerated. The simplest chemical reaction for transesterification of triglycerides is presented in Figure 3.

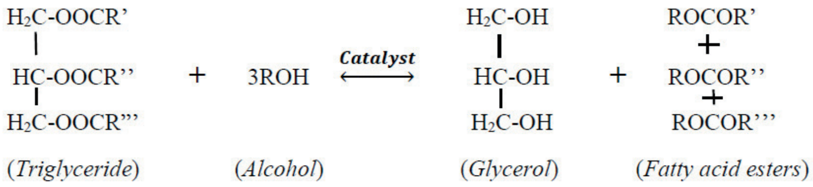

**Figure 3.** The general chemical reaction depicting transesterification of triglycerides [18].

There are a number of ways to produce biodiesel through transesterification. The general schematics diagram for these possible ways is shown in Figure 4.

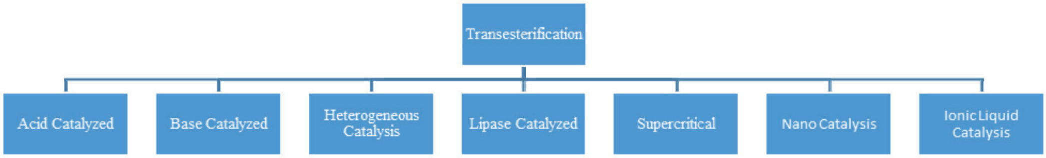

**Figure 4.** Schematic depicting major transesterification process types.

All of the catalytic transesterification processes involve the reaction of a triglyceride (fat or oil) with an alcohol in the presence of some catalyst to form esters and glycerol. A triglyceride has a glycerin molecule as its base with three long chain fatty acids attached. The characteristics of the oil/fat are determined by the nature of the fatty acids attached to the glycerin. The nature of the fatty acids can in turn affect the characteristics of the biodiesel [34].

A successful transesterification reaction for efficient biodiesel production is signified by easy and effective separation of the ester and glycerol layer after the reaction time. The heavier, co-product, glycerol can be purified for use in other industries, e.g. the pharmaceutical, cosmetics etc.

### 2.4.1. Homogeneous acid catalyzed transesterification

Acid catalyzed transesterification was the first method ever in history to produce biodiesel (ethyl ester) from palm oil using ethanol and Sulfuric acid [35].

The acid catalyzed process is due to the reaction of a triglyceride (fat/oil) with an alcohol in the presence of acid catalyst to form esters (biodiesel) and glycerol. Specially, this method is convenient and economically viable in producing biodiesel from oil or fat resources with high free fatty acid content. However, the acid catalyzed reaction requires a longer reaction time and a higher temperature than the alkali catalyzed reaction [36].

Acid catalyzed transesterification starts by mixing the oil directly with the acidified alcohol, so that separation and transesterification occur in single step, with the alcohol acting both as a solvent and as esterification reagent [23].

The acid catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters [22]. Park et al. [37] did an investigation of the effect of water on transesterification of oleic acid with methanol in the presence of sulfuric acid as a catalyst. In their work, the yield of fatty acid methyl ester (FAME) was studied at oil to methanol molar ratios of 1:3 and 1:6 and reaction temperatures of 60 °C and 80 °C. According to the result of their study, the rate of esterification of oleic acid significantly decreased as the initial water content increased to 20% of the oil [37].

Since transesterification is an equilibrium reaction, there should always be more alcohol than the oil to favor the forward reaction for complete conversion of the oil to alkyl ester. It is also known that the temperature and the amount of acid catalyst affect the transesterification rate and the yield of alkyl ester. However, more alcohol beyond the optimum will also cause some extra cost on separation of more produced glycerol from the alkyl ester and that is why there should always be an optimization of the ratio for efficient production. Different studies have been conducted to investigate how the molar ratio of oil to alcohol to acid as well as how temperature ranges affect the transesterification and thus the alkyl ester yield.

Zheng et al. [38] showed that, with convenient molar ratios and temperature ranges, methyl ester conversion of waste cooking oil in acid catalyzed transesterification can reach up to 99%. By their study, they concluded that, the oil: methanol: acid molar ratios and the temperature were the most significant factors affecting the yield of fatty acid methyl ester (FAME). According to their study result, at 70 °C with oil: methanol: acid molar ratios of 1:245:3.8, and at 80 °C with oil: methanol: acid molar ratios in the range 1:74:1.9–1:245:3.8, the transesterification was essentially a pseudo-first-order reaction as a result of the large excess of methanol which drove the reaction to completion (99 ± 1%) at 4 hours. In the presence of the large excess of methanol, free fatty acids present in the waste oil were very rapidly converted to methyl esters in the first few minutes under the above conditions [38].

Sulphuric acid, sulfonic acid, and hydrochloric acid are the usual acid catalysts but the most commonly used is sulphuric acid. There are also various studies done to see the yield effect of using alternative acids.

Soriano et al. [39] demonstrated that $AlCl_3$ could be used to catalyze the esterification of stearic acid suggesting that it is a potential alternative catalyst for biodiesel preparation using cheaper vegetable oil containing high amount of FFA. In their study, optimum conditions to afford 98% conversion of canola oil to FAME is with the use of methanol to oil molar ratio of 24:1 and reaction time of 18 h at 100 °C in the presence of 5% $AlCl_3$ as catalyst [39].

Marchetti et al. [40] mentioned that one of the drawbacks of producing biodiesel using acid catalyzed transesterification is having more amount of free glycerol in the biodiesel higher than the maximum value allowed to satisfy the international standard ASTM. However, they also mentioned in their study that this could be improved either by adding equipment for purification of the product stream or by modifying some of the process variable such as residence time in the reactor [40].

The use of co-solvents to overcome the mass transfer resistance due to immiscibility of alcohol with oil as well as the use of different acids usually help to get different alternatives for efficient production of biodiesel from low value feedstock. In this regard, Miao et al. [41] studied the effectiveness of trifluoroacetic acid catalyzed transesterification of soybean oil to produce biodiesel. The results from their study showed that the oil could be converted to biodiesel directly by one-step trifluoroacetic acid catalyzed process without extreme temperature and pressure conditions. The optimum process combination was 2.0 M (M is for Molarity, which is defined as the number of moles of solute dissolved per liter of solution) catalyst concentration with 20:1 molar ratio of methanol to oil at temperature of 120 °C [41]. According to the authors this procedure represents a simple and mild method for biodiesel production with short reaction time and with high conversion rate, which would offer potential for an industrial process[41].

**Table 2.** Summary of the effect of process variables on acid catalyzed transesterification of different feedstocks.

| Feedstock | Alcohol | Process variables | | | | | | Yield % achieved | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| | | Alcohol to oil ratio | Temperature (°C) | Reaction time | Stirring speed | Acid Catalyst | Catalyst concentration | | |
| Mixed oil [b] | Methanol | 6:1 | 60 | - | 300 rpm | $H_2SO_4$ | 2.5% | 96.6% | [43] |
| Soybean oil | Methanol | 20:1 | 120 | 5 h | - | trifluoroacetic acid | 2.0 M | 98.4% | [41] |
| Canola oil | Methanol with terahydrofuran as Co-solvent | 24:1 | 110 | 18 h | | $AlCl_3$ | 5% | 98% | [39] |
| Corn oil | Methanol with dimethyl ether as Co-solvent | 6:1 | 80 | 2 h | - | p-toluenesulfonic acid | 4 wt.% | 100% | [44] |
| Canola oil up to 20% FFA | Methanol | 9:1 | 200 | - | - | 12-Tungstophosphoric acid | 3 wt.% | 90 wt.% | [45] |

[b] mixed oil- 50% sunflower and 50% soybean oil

Despite its relatively slow reaction rate, the acid-catalyzed process offers benefits with respect to its independence from free fatty acid content and the consequent absence of a pretreatment step. These advantages favor the use of the acid-catalyzed process when using feedstock types like waste cooking oil as well as most non-edible plant oil, which are usually associated with higher content of fatty acid [42]. Table 2 indicates some selected research results about the effect of process variables on acid catalyzed transesterification of different feedstock types.

### 2.4.2. Homogeneous alkaline catalyzed transesterification

The alkaline catalyzed transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol in the presence of alkaline catalysts such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates to form esters (biodiesel) and glycerol. Alkali catalyzed transesterification is much faster than acid catalyzed transesterification and is less corrosive to industrial equipment and therefore is the most often used commercially [26,46]. However, presence of water and high amount of free fatty acid in a feedstock gives rise to saponification of oil and therefore, incomplete reaction during alkaline transesterification process with subsequent formation of emulsion and difficulty in separation of glycerol [32]. The saponification reaction is represented by the equation shown below:

$$\underset{FA}{R_1 - COOH} \quad + \quad \underset{Sodium\ hydroxide}{NaOH} \quad \rightarrow \quad \underset{Soap}{R_1COONa} \quad + \quad \underset{Water}{H_2O}$$

The main disadvantage resulted due to saponification reaction is the consumption of catalyst and increased difficulty in separation process, which leads to high production cost. In addition to that, formation of water in the product will also inhibit the reaction. In this case, water generated either from vegetable oil (due to its high water content) or formed during saponification reaction will hydrolyze triglyceride to form more free fatty acid as shown in the equation below.

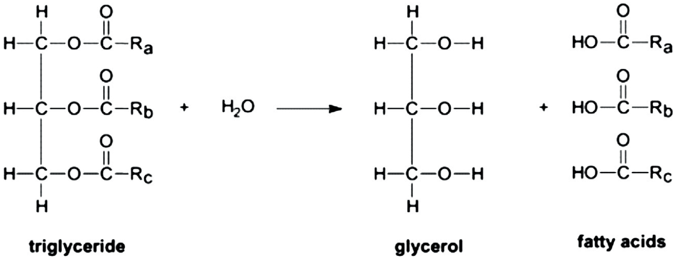

**Figure 5.** The chemical reaction depicting hydrolysis of triglycerides [47].

Generally, base catalyst manifest much higher catalytic activity than acid catalysts in the transesterification reaction, but are selectively suitable for deriving biodiesel only from refined oils having low content of free fatty acids (FFA) usually less than 0.5% [48]. This makes base catalyzed transesterification confined to use only best quality refined oil like vegetable cooking oil for input, which in turn makes it expensive way to produce biodiesel while creating food versus energy controversy. Here we can consider esterification as additional step to decrease the free fatty acid content of feedstock with greater than 0.5% FFA. This will enable us to choose among different feedstock types with higher FFA content. However, this additional process usually makes it more complex in the instrumentation (because of the addition of esterification unit) than the sole alkaline-catalyzed process, thereby resulting in an increase in equipment and operating costs.

The efficient production of biodiesel using base catalyzed transesterification is not only dependent on the quality of the feedstock, it is also dependent on the crucial reaction operation variables such as alcohol to oil molar ratio, reaction temperature, rate of mixing, reaction time, type and concertation of catalyst and also on the type of alcohol used [19,25,49].

Even though in theory, the stoichiometric ratio of alcohol (usually methanol) to oil is 3:1, in order to assist the forward reaction so that to get more conversion, the concentration of the methanol has to be increased. This is because; lower amount of methanol means slower forward reaction and less percentage of yield. In contrary, high methanol amount beyond the optimum, interfere with the separation of glycerin because of an increase in solubility; the glycerin remaining in the solution drives the equilibrium back to the left side of reaction, resulting in the lower yield of esters. This is due to the fact that methanol, with one polar hydroxyl group, can act as an emulsifier that enhances emulsions [19].

Sodium hydroxide, potassium hydroxide and sodium methoxide are catalysts usually used in base catalyzed transesterification. Sodium hydroxide is mostly preferable owing to its intermediate catalytic activity and a much lower cost [50]. Lueng et al. [51] evaluated the effect of catalyst on transesterification by comparing the maximum ester content and yield percentage attained using three base catalysts while other determinant variables were kept the same for all conditions during the base catalyzed transesterification processes. The result of their study is shown in Table 3.

**Table 3.** Comparison of different types of catalysts used in the transesterification of used frying oil (temperature at 70 °C, reaction time 30 min, and methanol/oil molar ratio of 7.5:1) [51].

| Catalyst | Concentration of the catalyst (wt.%, by weight of crude oil) | Ester content (wt.%) | Product yield (wt.%) |
|---|---|---|---|
| NaOH | 1.1 | 94.0 | 85.3 |
| KOH | 1.5 | 92.5 | 86.0 |
| $CH_3ONa$ | 1.3 | 92.8 | 89.0 |

This study revealed that sodium hydroxide is better in attaining purity percentage (ester content) than the others whereas sodium methoxide is good in providing higher yield percentage.

The relative concentration of catalysts required for maximum production is dependent on the type of feedstock used. Dias et al. [52] compared the performance of three alkali catalysts for transesterification of virgin and waste soybean and sunflower oil and they reported that, the optimum conditions which ensured that the attainment of the final product being in agreement with the European biodiesel standard were: 0.6 (wt.%) $CH_3ONa$ for both virgin oils; 0.6 (wt.%) NaOH for sunflower oil and 0.8 (wt.%) for soybean oil and; 0.8 (wt.%) using both sodium based catalysts for waste frying oils. They also reported that under these optimum conditions, a purity of 99.4 (wt.%) could be obtained.

In the study carried out by Hossain and Boyce [53] in spite of higher yield, using NaOH as catalyst during biodiesel synthesis from waste sunflower cooking oil, causes more emulsion than KOH and makes separation of biodiesel from glycerin complicated, as they reported. The solution of alkaline catalyst in methanol is recommended to be prepared freshly in order to avoid the moisture absorbance and to maintain the catalytic activity [54].

Leung et al. [51] reported that the conversion of waste cooking oil using sodium hydroxide catalysts was approximately 86%. As presented in Table 4, Ojolo et al. [55], explained that the increase of the catalyst concentration influences the ester yield in a positive manner up to 0.80% NaOH for Jatropha oil and then after that it decreases.

**Table 4.** The influence of catalyst content on ester yield [55].

| Catalyst (gm) | Oil (gm) | Methanol (gm) | Reaction Time (hr) | Reaction Temp. (°C) | Biodiesel (%) | Glycerin (%) |
|---|---|---|---|---|---|---|
| 1.2 | 100 | 20 | 1 | 65 | 87.20 | 30.80 |
| 1.0 | 100 | 20 | 1 | 65 | 92.40 | 27.35 |
| 0.8 | 100 | 20 | 1 | 65 | 95.33 | 24.22 |
| 0.6 | 100 | 20 | 1 | 65 | 74.45 | 45.37 |

Parawira [32] reported that, the alkaline catalyst concentration in the range of 0.5–1% by weight yield 94–99% conversion of most vegetable oils into esters. There are several disadvantages in using an alkaline catalysis process although it gives high conversion levels of triglycerides to their corresponding methyl esters in short reaction times. According to Parawira [32], the process is energy intensive, recovery of glycerol is difficult, the alkaline catalyst has to be removed from the product, alkaline wastewater generated requires treatment and the level of free fatty acids and water greatly interfere with the reaction. The risk of free fatty acid or water contamination results in soap formation that makes the separation process difficult [56].

**Table 5.** Summary on effect of process variables on base catalyzed transesterification of different feedstock types.

| Feedstock | Alcohol | Process variables | | | | | | Yield % achieved | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| | | Alcohol to oil ratio | Temperature (°C) | Reaction time | Stirring speed | Catalyst type | Cat. Concentration | | |
| Rice bran oil | methanol | 1:09 | 55 | 60 minute | - | NaOH | 0.75% (w/w) | Optimum | [57] |
| Sunflower cooking oil | methanol | 6:01 | 40 | - | 320 rpm | KOH | 1% | 99.50% | [53] |
| refined cooking vegetable oils | methanol | 6:01 | 65 | 60 minute | - | KOH | 1.2 wt.% | 97.50% | [58] |
| Waste cooking vegetable oils | methanol | 6:01 | 65 | 60 minute | - | KOH | 1.2 wt.% | 93.20% | [58] |
| Jatropha oil | methanol | 5:01 | 65 | 60 minute | - | NaOH | 0.80% | 95.5%. | [59] |
| Soybean oil | methanol | 6:01 | 60 ± 1 | 60 minute | - | NaOH | 1% | 90% | [60] |
| Cottonseed oils | methanol | 6:01 | 60 ± 1 | 60 minute | - | NaOH | 1% | 98.50% | [60] |
| Waste frying oils | methanol | 7.5:1 | 50 | 30 minute | - | NaOH | 0.50% | 96% | [61] |
| Karanja oil | methanol | 6:01 | 65 | 15 minute | 360 rpm | KOH | 1% | > 85% | [54] |
| Karanja oil | methanol | 12:01 | 65 | 60 minute | 360 rpm | KOH | 1% | 98% | [54] |
| Duck tallow | methanol | 6:01 | 65 | 180 minute | - | KOH | 1 wt.% | 97% | [62] |
| Silurus triostegus Heckel fish oil (STFO) | methanol | 6:01 | 32 | 60 minute | - | KOH | 0.50% w/w | 96% | [49] |
| Waste cooking oil | methanol | 6:01 | microwave power of 750 W | 3 minute | - | $CH_3ONa$ | 0.75 wt.% | 97.90% | [63] |
| soybean oil -assisted by low-frequency ultrasound (20 kHz) | Ethanol | 6:01 | 60 | 6 minute | 600 rpm | KOH | 1% (m/m) | 98% | [64] |
| Waste frying oils | methanol | 12:01 | 65 | 150 minute | - | Tetramethylguanidine | 3 wt.% | > 90% | [65] |

Table 5 summarizes the results of some researches done to study the effect of different process variables on base catalyzed transesterification of different feedstock types.

### 2.4.3. Heterogeneous catalyzed transesterification

The use of homogeneous catalysts, especially base catalysts, are associated with some amount of difficulty in purification of by-product glycerol as well as in the requirement of wastewater treatment. To alleviate these problems, the use of heterogeneous catalysts usually solid base catalyst is recommended. Solid base catalysts have many advantages, such as having mild reaction condition, easy separation, and high activity and less contaminant [66].

Many researchers argued that the use of heterogeneous catalysts both in acid and base form brought about the advantage of having easy and less costly separation as well as possibility of reusing the catalyst. Parawira [32] mentioned that, the heterogeneous catalyst eliminates the additional cost associated with the homogeneous sodium hydroxide to remove the catalyst after transesterification. In addition, the heterogeneous catalyst offers a wide option for the catalytic selection because of its high selectivity and reusability characteristics [67]. Dell'Anna et al. [68] investigated transesterification of polyunsaturated compounds catalyzed by a recyclable polymer supported palladium catalyst. They found out that the heterogeneous solid catalyst, palladium exhibited a remarkable activity and was reusable for eight consecutive cycles.

Heterogeneous solid catalysts are usually categorized as acid solids capable to catalyze free fatty acids esterification reaction; base solids, which are able to catalyze triglycerides transesterification reaction; and bifunctional solids (acid-base character) which show ability to simultaneously catalyze esterification and transesterification reaction [69].

There are various efforts made to find effective solid catalysts in both acid and basic form for heterogeneous catalyzed process. Bournay and Casanave [70] investigated the use of new solid catalyst for continuous transesterification process. They mentioned that this new solid catalyst consists of a mixed oxide of zinc and aluminum, which promotes the transesterification reaction without catalyst loss. Actually using this new catalyst, the reaction has to be performed at higher temperature and pressure than homogeneous catalysis processes, with an excess of methanol, which can finally be removed by vaporization and recycled to the process [70]. In contrary, however, there are some solid metal oxides, such as oxides of tin, magnesium, and zinc, which are well known as catalysts, and perform like homogeneous catalysis and end up as metal soaps or metal glycerates [70].

Bournay and Casanave [70] claimed also that, while using this new solid catalyst, neither catalyst recovery nor aqueous treatment steps are required. The purification steps of products could then be much more simplified so that very high yields of methyl esters, close to the theoretical value, could be obtained. In addition, the glycerin can directly be produced with high purity levels (at least 98%) without any salt contaminants.

Heterogeneous catalysts such as amorphous zirconia, titanium and potassium zirconias have also been used for catalyzing the transesterification of vegetable oils. Furuta et al. [71] evaluated amorphous zirconia catalysts, titanium-, aluminum-, and potassium-doped zirconias, in the transesterification of soybean oil with methanol at 250 °C, and the esterification of n-octanoic acid with methanol at 175–200 °C. They reported that, titanium- and aluminum-doped zirconias are promising solid catalysts for the production of biodiesel fuels from soybean oil because of their high performance, with over 95% conversion in both of the reactions.

In another study, Huaping et al. [72] demonstrated the potential of preparing biodiesel from Jatropha curcas oil catalyzed by solid super base of calcium oxide. When treated with ammonium carbonate solution and calcinated at high temperature, calcium oxide becomes a solid super base, which shows high catalytic activity in transesterification. They reported that, under the optimum conditions, the conversion of Jatropha curcas oil can reach 93%.

Sánchez et al. [73] studied the influence of the reaction temperature, the alcohol:oil ratio and the catalyst percent on the methanolysis of Jojoba oil using CaO as a catalyst, which was particularly derived from mussel shells. According to their study, the variables which had the higher positive effect on the methanolysis of Jojoba oil, in a pressurized environment (with approximate 10 bars in Parr reactor), are the methanol:oil ratio and the temperature, whereas the catalyst percent had a slight negative impact on the process. They reported that, using this catalyst, the reaction time could be reduced by half, from 10 to 5 hours and the Jojoba oil conversion reached a maximum of 96.3% with a pressurized environment in the reactor.

Avhad et al. [74] investigated the catalytic activity of glycerol-enriched calcium oxide for ethanolysis of avocado oil. The calcium oxide catalyst was derived from *Mytilus Galloprovincialis* shells through thermal and glycerol (with glycerol dosage of 10% with respect to catalyst weight) treatment before using for the ethanolysis reaction. This shell is simply a waste generated from the fish industry. In this study, they examined the influence of temperature, ethanol-to-oil molar ratio, and the catalyst amount on the variation in the concentration of triacylglycerols and biodiesel with reaction time. They also determined the interaction between the reaction variables (ethanol-to-oil molar ratio and catalyst amount), their influence on the ethanolysis process, and the optimum variables affecting the process through the response surface methodology. According to their conclusion, both catalyst amount and ethanol-to-oil molar ratio significantly affected the described ethanolysis process. They also reported that, temperature of 75 °C, ethanol-to-oil molar ratio of 9:1, and 7 wt.% catalyst amount was taken to be suitable for the studied glycerol-enriched CaO assisted avocado oil ethanolysis process.

The sensitivity of the base catalyzed transesterification to the FFA and water content of the feedstock still persist as the main problem in case of heterogeneous base catalyzed transesterification reaction too. Again, to solve such feedstock quality problem, solid acid catalyst for simultaneous esterification of FFAs and transesterification of triglycerides can be good alternative for biodiesel production from feedstock with higher FFA and water content. Moreover, Melero et al. [75] mentioned that a heterogeneous acid catalyst if incorporated into a packed bed continuous flow reactor, can simplify product separation and purification and reducing waste generation. Solid acid catalyst can be recycled, easily removed and can simultaneously catalyze esterification and transesterification [76].

Peng et al. [76] characterized and studied the activity of a solid acid catalyst comprising $SO_4^{2-}/TiO_2–SiO_2$ for the production of biodiesel from several low cost feedstocks with high FFAs. They studied the influence of reaction parameters and found out that optimum yield could be attained at reaction temperature of 200 °C, molar ratio of methanol to oil 9:1 and catalyst concentration of 3wt.%. They finally concluded that, the solid acid catalyst $SO_4^{2-}/TiO_2–SiO_2$ is inexpensive and environment friendly, has high catalytic activity, and is stable for biodiesel production from cheap raw feedstocks with high FFAs.

In another study, Juan et al. [77] carried out transesterification of refined and crude vegetable oils with a sulfonic acid-modified mesostructured catalyst. According to them the catalyst could enable to yield fatty acid methyl ester (FAME) with purity over 95 wt.% and oil conversion close to 100% under best reaction conditions of temperature 180 °C, methanol/oil molar ratio 10, and catalyst loading 6 wt. %. They reported that, regardless of the presence of free fatty acids, the sulfonic acid-modified mesostructured catalyst showed high activity towards simultaneous esterification and transesterification.

### 2.4.4. Lipase catalyzed transesterification

The other way of transesterification of oils and fats for biodiesel production is using enzymes in which there is no problem of saponification, purification, washing and neutralization so that it is always a preferred method from these perspectives. Enzymatic catalysts can also be applied on a feedstock with high FFA and can convert more of the oil into biodiesel. However, the problems associated with enzyme catalysts are their higher cost and longer reaction time [19]. Usually because of these two drawbacks, enzyme catalyzed transesterification method is not very frequently used.

In another view, it is more frequently pointed out that enzymatic transesterification has currently attracted much attention for biodiesel production as it produces high purity product (esters) and enables easy separation from the by-product, glycerol [26,78]. The enzymes that are usually found to be capable of catalyzing transesterification are the lipases.

The lipase catalyzed transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol in the presence of lipase enzyme as a catalyst to form esters (biodiesel) and glycerol. Mahanta et al. [22] mentioned that, in a lipase catalyzed process no complex operations are needed not only for the recovery of glycerol but also in the elimination of catalyst and soap. This is an environmentally more attractive option to the conventional process. However, Mahanta et al. [22] again argued that the reaction yields as well as the reaction times are still unfavorable compared to the alkaline catalyzed reaction systems.

Lipases for their transesterification activity on different oils can be found from different sources. Ability to utilize all mono, di, and triglycerides as well as the free fatty acids, low product inhibition, high activity and yield in non-aqueous media, low reaction time, reusability of immobilized enzyme, temperature and alcohol resistance are the most desirable characteristics of lipases for transesterification of oils for biodiesel production [79].

Some also argue that, biocompatibility, biodegradability and environmental acceptability of the biotechnological procedure when using lipase as a catalyst are the desired properties in this alternative biodiesel production method [46,78]. However, the use of extracellular lipase as a catalyst requires complicated recovery, purification and immobilization processes for industrial application [80]. Consequently, the direct use of whole cell biocatalyst of intracellular lipases has received considerable research efforts [78]. For the industrial transesterification of fats and oils, *Pseudomonas* species immobilized with sodium alginate gel can be used directly as a whole cell bio-catalyst [78].

Devanesan et al. [78] reported maximum yield (72%) of biodiesel from transesterification of Jatropha oil and short chain alcohol (methanol on hexane) using *Pseudomonas fluorescens* immobilized with sodium alginate gel at the optimum conditions of 40 °C, pH 7.0, molar ratio of 1:4, amount of beads of 3 g and reaction time of 48 h.

According to Parawira [32], in all the work in literature on lipases, the enzymes or whole cells are immobilized when used for catalysis. It is usually mentioned that, the advantage of immobilization is that the enzyme can be reused without separation. In addition, the operating temperature of the process is low (50 °C) compared to other techniques which operate at harsh conditions. However, the cost of enzymes remains a barrier for its industrial implementation [81].

Most of the time, in order to tackle this cost barrier of the process, the enzyme (both intracellular and extracellular) should be reused by immobilizing in a suitable support particle, which is usually associated with considerable increase in efficiency.

Enzymes are usually immobilized for better enzyme loading, activity and stability. Selecting and designing the support matrix are important in enzyme immobilization [82]. With this respect, there are a number ways to immobilize enzymes. These include cross-linked enzyme aggregates, microwave-assisted immobilization, click chemistry technology, mesoporous supports and most recently nanoparticle-based immobilization of enzymes [83]. Recently, the use of nanoparticles has emerged as a versatile tool for generating excellent supports for enzyme stabilization due to their small size and large surface area [82], which results in better stability and activity of enzymes immobilized on such materials. In addition, Nanoparticles strongly influence the mechanical properties of the material like stiffness and elasticity and provide biocompatible environments for enzyme immobilization [82].

However, during transesterification, the activity of immobilized enzyme is inhibited by methanol and glycerol which are always present in the reacting mixture. The use of tert-butanol as solvent, continuous removal of glycerol, stepwise addition of methanol are some of the ways to reduce the inhibitory effects thereby increasing the cost effectiveness of the process [26].

Guang Jin et al. [81] examined the use of whole-cell biocatalysts to produce biodiesel at room temperature (25 °C). They used *Rhizopus oryzae* (ATCC® 10260™) to catalyze the conversion of virgin and waste oils (triglycerides) into biodiesel fuel in the presence of 15% water. Their research results indicated that the whole-cell biocatalyst could produce about a 90% yield of fatty acid methyl ester from virgin oil, and nearly complete conversion of the remaining oil into free fatty acid, using a 96-hour reaction at room temperature (25 °C). They also reported that, in a 72 hour reaction, fatty acid methyl ester yields were about 75% for virgin oil, 80% for waste vegetable oil, and 55% for brown (trap) grease [81], which implies, whole-cell biocatalysts may be an effective way to trans esterify waste oils or greases that are high in FFA and difficult to dewater [81].

Du et al. [84] developed methyl acetate, a novel acyl acceptor, for biodiesel production and carried out a comparative study on *Novozym 435* catalyzed transesterification of soybean oil for biodiesel production with different acyl acceptors. They reported that methanol has a serious negative effect on enzymatic activity as for example a molar ratio of methanol to oil of above 1:1 leads to serious inactivation of the enzyme. In their study, they used methyl acetate as the acyl acceptor, and reported that, a yield of 92% of methyl ester could be obtained with a molar ratio of methyl acetate to oil of 12:1, and methyl acetate showed no negative effect on enzymatic activity. They also mentioned that, with crude soybean oil as the oil source and methanol as acyl acceptor, a much lower methyl ester yield was obtained than that with refined soybean oil, while with methyl acetate as acyl acceptor, an equally high yield of methyl ester (92%) was achieved for both soybean oils. Lipase loses its activity very rapidly during repeated experiments with methanol as the acyl acceptor, however, according to their report, there was almost no detected loss in lipase activity, even after being continuously used for 100 batches, when methyl acetate was used for biodiesel production [84].

During enzymatic transesterification for biodiesel production, it has been demonstrated that excessive methanol present in the reaction medium would cause significant deactivation of the lipase. However, effective methanolysis using extracellular lipase has been reported to improve by stepwise addition of methanol (usually, a three-step addition of methanol in solvent-free medium) through which, according to Watanabea, 90–95% conversion can be achieved even after 50 and 100 cycles of repeated operation [85].

In another study, Li et al. [86] used tert-Butanol, as a novel reaction medium, for lipase-catalyzed transesterification of rapeseed oil for biodiesel production, with which, they claimed, both the negative effects caused by excessive methanol and by-product glycerol could be eliminated. They reported the highest biodiesel yield of 95% achieved under the optimum conditions of tert-butanol/oil volume ratio 1:1; methanol/oil molar ratio 4:1; 3% *Lipozyme TL IM* and 1% *Novozym 435* based on the oil weight; temperature 35 °C; 130 rpm, and 12 hours. According to them, there was no obvious loss in lipase activity even after being repeatedly used for 200 cycles with tert-butanol as the reaction medium [86].

Shah et al. [87] also worked on three different lipases (*Chromobacterium viscosum*, *Candida rugosa*, and *Porcine pancreas*) for a transesterification reaction of Jatropha oil in a solvent-free system to produce biodiesel. They reported that, only lipase from *Chromobacterium viscosum* was found to give appreciable yield. Immobilization of lipase (*Chromobacterium viscosum*) on Celite-545 enhanced the biodiesel yield to 71% from 62% yield obtained by using free tuned enzyme preparation with a process time of 8h at 40 °C. Further addition of water to the free (1%, w/v) and immobilized (0.5%, w/v) enzyme preparations enhanced the yields to 73% and 92%, respectively. They mentioned also that, immobilized *Chromobacterium viscosum* lipase can be used for ethanolysis of oil. According to their conclusion immobilization of lipases and optimization of transesterification conditions resulted in adequate yield of biodiesel in the case of the enzyme-based process.

**Table 6.** Summary of some optimized productions of biodiesel from different feedstock types using lipase-catalyzed transesterification.

| Feedstock | Alcohol | Alcohol to oil Ratios | Enzymes | wt.% of Enzyme | Temp. (°C) | Stirring | Reaction time | Yield % | Remarks | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| Rapeseed oil | methanol with tert-butanol as a solvent | methanol/oil molar ratio 4:1 | *Lipozyme TL IM* | 3 wt.% | 35 | 130 rpm | 12 h | 95% | No loss in lipase activity after being repeatedly used for 200 cycles with tert-butanol as the reaction medium | [86] |
| | | Tert butanol/oil volume ratio 1:1 | *Novozym 435* | | | | | | | |
| Soybean oil | methanol | 1:1 | *lipozyme TL* | 0.04 | 40 | 150 rpm | - | 66% | - | [89] |
| Soybean oil | methanol | 1:1 | silica gel *lipozyme TL* | 0.06 | 40 | 150 rpm | - | 90% | Silica gel combined with lipozyme TL and three-step addition of methanol | [89] |
| Soyabean oil in ionic fluid - EmimTfO | methanol | 4:1 | *Novozym 435*<br>*Pseudomonas cepacia* immobilized on celite | 2 wt.%<br>0.1 | 50 | 250 rpm | 12 h | 80% | High production yield in ionic liquids show that ionic liquids are potential reaction media for biodiesel production | [88] |
| Jatropha oil | ethanol | 4:1 | | | 50 | 200 rpm | 8 h | 98% | With presence of 4–5% (w/w) water | [90] |

Some authors also argued that using convenient reaction medium would help increase conversion of oil to biodiesel in lipase-catalyzed transesterification reactions. In this respect, Ha et al. [88] demonstrated production of biodiesel through immobilized Candida antarctica lipase-catalyzed methanolysis of soybean oil in 23 different ionic liquids. They reported that, the highest fatty acid methyl esters (FAMEs) production after 12 h at 50 °C was achieved in EmimTfO (1-Ethyl-3-methylimidazolium trifluoromethanesulfonate). They also pointed out that around 15% higher free fatty acid production could be achieved using this ionic fluid as a reaction medium than the production system using tert-butanol as an additive. Table 6 summarizes results of some selected researches done to optimize production of biodiesel through lipase-catalyzed transesterification of different feedstock types.

According to Marchetti et al. [46], the use of lipase is a great viable method for production of ester from different sources of oil or grease even though, research on this topic is still in progress due to the enzyme flexibility and adaptability to new process.

However, when we compare enzymatic production of biodiesel with conventional chemical processes, the major obstacles repeatedly mentioned are the cost of lipases, the relatively slower reaction rate and lipases inactivation caused by methanol and glycerol. Some main advantages and disadvantages of using lipases as catalyst are summarized in Table 7.

**Table 7.** The advantages and disadvantages of using lipases [32].

| The advantages of using lipases |
|---|
| ✓ Biocompatible, biodegradable and environmental acceptability |
| ✓ Possibility of regeneration and reuse of the immobilized residue, because it can be left in the reactor if one keep the reactive flow |
| ✓ Use of enzymes in reactors allows use of high concentration of them and that makes for a longer activation of the lipases |
| ✓ Immobilization of lipase could protect it from the solvent that could be used in the reaction and that will prevent all enzyme particles getting together |
| ✓ Separation of product will be easier using this catalyst, producing product of very high purity with less or no downstream operations |
| Some disadvantages |
| ✓ Loss of some initial activity due to volume of the oil molecule |
| ✓ Number of support enzyme is not uniform |
| ✓ More expensive |

In general, process optimization in lipase-catalyzed transesterification, can be done at least in the following: screening of various commercial lipase preparations; pH tuning; immobilization; adjusting water content in the reaction media; adjusting amount of enzyme used; and adjusting temperature of the reaction [90].

### 2.4.5. Nano catalyzed transesterification

There a number of recent developments in catalytic conversion of oils and fats to biodiesel. Among them biodiesel production using Nano catalyst and Ionic liquid catalysts are more promising in terms of few advantages over the conventional acid/base catalysts.

Nano catalysis involves the use of nanomaterials as catalysts for a variety of homogeneous and heterogeneous catalysis applications. Nanoscale catalysts have high specific surface area and surface energy resulting in high catalytic activity. Generally, Nano catalysts improve the selectivity of the reactions by allowing reaction at a lower temperature, reducing the occurrence of side reactions, higher recycling rates and recovery of energy consumption [91]. With this respect, Nano catalysts are promising alternatives for efficient production of biodiesel from oils and fats as they have high specific surface area and high catalysis activities eliminating the specific problem of mass transfer resistance associated with conventional catalysts.

Wen et al. [92] studied that the solid base Nano catalyst KF/CaO can be used for biodiesel production with yield of more than 96%. This catalyst can efficiently be used to convert the oil with higher acid value into biodiesel [92,93]. It is porous with particle sizes of 30–100 nm. Wen et al. [92] could show, using X-ray powder diffraction analysis, that the Nano catalyst KF/CaO has new crystal $KCaF_3$, which increases catalytic activity and stability. The high specific surface area and large pore size are favorable for contact between catalyst and substrates, which effectively improve efficiency of transesterification [93].

Few have studied on the possible optimum conditions for production of biodiesel from different oil inputs using different Nano catalysts. Sidra et al. [94] investigated the production of biodiesel from Jatropha oil through transesterification process by using $CaO\text{-}Al_2O_3$ Nano catalyst. According to them, the optimization results for production of biodiesel from the transesterification of Jatropha *curcas* oil catalyzed by $CaO\text{-}Al_2O_3$ nanoparticles showed maximum yield of 82.3% at 5:1 methanol to oil molar ratio [94]. Similarly, Sivakumar et al. [95] did comprehensive study of smoke deposited Nano sized MgO as a catalyst for biodiesel production. They studied the transesterification reaction to determine the optimum conditions for different parameters like catalyst quantity, methanol oil molar ratio, reaction temperature and reaction time. A maximum conversion of 98.7% was obtained at 1.5 wt.% catalyst; 5:1 methanol oil molar ratio at 55 °C, achieved after 45 min. The conversion was three to five times higher than those reported for laboratory MgO in literature [95]. According to this study, the higher conversion was mainly due to the enhancement of surface area of the catalyst. The other advantage is that the catalyst can be easily recovered and reused up to eight times with easy regeneration steps [95]. Table 8 shows some of optimization studies on biodiesel production using Nano catalysts.

In another two separate studies Mookan et al. [96,97] conducted an investigation on the fuel quality of biodiesel produced from castor oil as well as Pongamia pinnata oil with methanol using iron nanoparticles as catalyst. The fuels properties that they investigated are specific gravity, kinematic viscosity, flash point, cloud point, water content, carbon residue, refractive index, copper corrosion and calorific value. They pointed out that, these properties of resulting biodiesel both from castor oil and Pongamia pinnata oil agree well with the specifications of biodiesel standards ASTM D6751 except for specific gravity and kinematic viscosity. According to them, most of the physico-chemical properties of castor oil biodiesel match well with the normal diesel. They also concluded that the use of iron nanoparticles as catalyst showed more advantages than the conventional acid/base catalyst for the production of biodiesel in terms of shorter reaction time as well as less amount and reusability of the catalyst.

More recently, Gupta et al. [98] did a research on the preparation and characterization of CaO nanoparticle for biodiesel production from Soybean oil. They synthesized Nanoparticle of CaO from calcium Nitrate (CaO/CaN) and Snail shell (CaO/SS) so as to investigate the performance of the catalysts in terms of biodiesel yield. According to their conclusion, the Nano catalyst from snail shell exhibits excellent catalytic activity and stability for the transesterification reaction, which suggested that this catalyst would be potentially used as a solid base Nano catalyst for biodiesel production [98].

**Table 8.** Summary of some optimized productions of biodiesel from different feedstock types through transesterification using Nano catalysts.

| Feedstock | Alcohol | Alcohol to oil Ratios | Nano catalyst | wt.% of catalyst | Temp. (°C) | Reaction time | Yield % | Remarks | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| Waste mixed vegetable oil | Methanol | 5:1 | smoke deposited nano sized MgO | 1.5 | 55 | 45 min | 98.7 | The transesterification reaction was studied under constant ultrasonic mixing for different parameters | [95] |
| Stillingia oil | Methanol | 12:1 | KF/CaO–$Fe_3O_4$ (Calcinated at 600 °C) | 4 | 65 | 3 h | 95 | The catalyst is able to be reused up to 14 times without much deterioration in its activity | [99] |
| Chinese tallow seed oil | Methanol | 12:1 | KF/CaO | 4 | 65 | 2.5 h | 96.8 | - | [92] |
| Waste cooking oil |  | 7:1 | Nano CaO | 1.5 | 75 | 6 h | 94.37 | - | [100] |
| Waste cooking oil |  | 7:1 | Mixture of Nano CaO and Nano MgO | 3 | 75 | 6 h | 98.95 | The optimum mass proportion for CaO to MgO is 0.7:0.5 | [100] |
| Soybean oil |  | 12:1 | Nanoparticle of CaO from calcium Nitrate (CaO/CaN) | 8 | 65 | 6 h | 93 | - | [98] |
| Soybean oil |  | 12:1 | Nanoparticle of CaO from Snail shell (CaO/SS) | 8 | 65 | 6 h | 96 | - | [98] |

The catalytic activity of such Nano catalysts are usually affected by calcination temperature during catalyst preparation with calcination. This is because in the preparation process of the catalyst, calcination treatment of catalyst at high temperature is favorable for the interaction between support and active ingredient, which generates new active sites for the catalyst [99]. With this respect Hu et al. [99], did an investigation on the optimum calcination temperature for the preparation of three Nano catalysts, KF/CaO–$Fe_3O_4$, KF/SrO–$Fe_3O_4$ and KF/MgO–$Fe_3O_4$. And they found out that the fatty acid methayl ester yield reaches the maximum value at calcination temperature of 600 °C, 600 °C, and 500 °C for KF/CaO–$Fe_3O_4$, KF/SrO–$Fe_3O_4$ and KF/MgO–$Fe_3O_4$, respectively [99]. Thus, calcination temperature can be taken as additional parameter to optimize biodiesel production using Nano catalysts prepared through calcination.

### 2.4.6. Transesterification using ionic liquids as catalysts

Ionic liquids are organic salts comprising of anions and cations that are liquid at room temperature. The cations are responsible for the physical properties of ionic liquids (such as melting point, viscosity and density), while the anion controls its chemical properties and reactivity [101]. Their unique advantage is that while synthesized, they can be moderated to suit required reaction conditions.

Another great advantage of using Ionic Liquids specifically to catalyze transesterification for biodiesel production is the formation of a biphasic system at the end of the reaction. This biphasic system occurs because the ionic liquid, insoluble in the organic phase, remains in the aqueous phase along with alcohol, the catalyst used and glycerol produced during the reaction [102]. This makes it very easy to separate the final products, because most of the top phase is biodiesel with very little amount of methanol. Pure biodiesel can then be isolated by simple vacuum evacuating of this very little amount of methanol [103]. The bottom phase contains methanol, glycerol and Ionic Liquids.

This bottom phase can then be rinsed with water for 3 to 4 cycles to separate glycerol with high purity [104], or pure glycerol can be obtained simply by distillation [103], which leaves the pure Ionic Liquid behind for further direct use for another reaction.

Among the different possible types of ionic liquids for catalysis of transesterification reaction for biodiesel production, Ionic liquids composed of the 1-n-butyl-3-methylimidazolium cation are the most widely studied and discussed compounds [105].

Very few researches are done to investigate the optimum reaction conditions for ionic liquid catalyzed transesterification with respect to temperature, molar ratio, catalyst amount, etc. Guo et al. [106] did a research to find out such optimum conditions for ionic liquid catalyzed transesterification of soybean oil with methanol by using ultrasound (24 kHz, 80 W). They found out that, at 60 °C under ultrasonic irradiation and a molar ratio of 14:1 methanol to oil, a biodiesel yield in excess of 96% can be achieved in a remarkably short time duration of 20 minutes or less in comparison to 5h or more using conventional method. They concluded that ionic liquid catalyzed transesterification is proved to be efficient and time saving for the preparation of biodiesel from soybean oil. They also mentioned the ionic liquid had a good reusability and can be easily separated from the biodiesel by simple decantation [106].

**Table 9.** Summary of few researches on optimized productions of biodiesel from different feedstock types through transesterification using different Ionic Liquids as catalysts.

| Feedstock | Alcohol | Alcohol to oil Ratios | Ionic liquid catalyst | Wt.% of catalyst | Temp. (°C) | Reaction time | Yield % | Remarks | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| Soybean oil | Methanol | 8:1 | Basic Ionic Liquids [Hnmm]OH | 4 | 70 | 1.5 h | 97 | The catalytic activity was affected by its alkalinity | [103] |
| Cottonseed Oil | Methanol | 12:1 | 1-(4-Sulfonic acid) butylpyridinium hydrogen sulfate | 0.057$^a$ | 170 | 5 h | 92 | The catalytic activity of the ionic liquid is dependent on its Brønsted acidic strength. | [107] |
| Rapeseed oil | Methanol | 10:1 | 1-propyl-3-methyl imidazolium hydrogen sulfate ([PrMIM][HSO4]) | 10 | 140 | 5 h | 19.74 | - | [108] |
| Rapeseed oil | Methanol | 10:1 | 1-propylsulfonate-3methyl imidazolium hydrogen sulfate ([PrSO3HMIM][HSO4]) | 10 | 130 | 5 h | 94.91 | - | [108] |
| Rapeseed oil | Methanol | 10:1 | 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO4]) | 10 | 110 | 5 h | 8.89 | - | [108] |
| Rapeseed oil | Methanol | 10:1 | 1-butylsulfonate-3-methyl imidazolium hydrogen sulfate ([BSO3HMIM][HSO4]) | 10 | 130 | 5 h | 100 | - | [108] |

[a] molar ratio of ionic liquid to oil

In another study, Ren et al. [103] investigated the influence of some reaction conditions, such as the amount of morpholine alkaline basic ionic liquid 1-butyl-3-methyl morpholine hydroxide ([Hnmm]OH) as a catalyst, the molar ratio of methanol to soybean oil, reaction temperature and time. The optimum reaction conditions to get the maximum biodiesel yield (97.0%) were found as 4% (mass fraction) of [Hnmm]OH, the methanol to soybean oil molar ratio of 8, temperature of 70 °C and reaction time of 1.5 hours. They pointed out that, the reaction exhibited high stability upon recycling, and the biodiesel yield remained more than 90% even after being reused for five times [103]. Table 9 shows the results of some few researches done on optimized reaction conditions for ionic liquid catalyzed transesterification.

### 2.4.7. Supercritical transesterification

One of the approaches to overcome problems associated with poor immiscibility between the reactants and at the same time, technical problems caused by catalysts is to use supercritical method. Supercritical alcohol transesterification reaction takes place under extremely high temperature and pressure. When a gas or liquid is under high pressure and temperature beyond its critical point, unusual phenomena are exhibited on its properties. In this case, liquid and vapor phase are no longer confined under these conditions and single supercritical fluid phase is generated [19]. In the supercritical transesterification method, methanol and oil, which are immiscible liquids at room temperature, will form a homogenous fluid. This is due to the sharp drop in the solubility of methanol and reduction in dielectric constant, which makes methanol a non-polar substance [19]. In this case, the reaction will be accelerated, as there is no mass transfer limitation under such conditions.

When we consider specific application of the mothed for biodiesel production, super critical methanol is usually used to speed up the transesterification reaction. Using this technique, the conversion of vegetable oils into biodiesel is done in about 4 min but extremely high pressure and temperature is required for this method, which makes it highly sensitive and costly [9]. A lot of energy is required to build such a high pressure and temperature. Some authors recommend use of co-solvent to improve the conversion efficiency.

The simple chemical catalyzed transesterification processes mentioned above (Acid catalyzed and Base catalyzed) are confronted with two problems, i.e. the processes are relatively time consuming and need separation of the catalyst and saponified impurities from the biodiesel. The first problem is due to the phase separation of the oil/alcohol mixture, which can be alleviated by vigorous stirring. These problems are totally mislaid in the supercritical method of transesterification. This is perhaps due to the fact that the tendency of two phase formation of vegetable oil/alcohol mixture is not encountered and a single phase is found due to decrease in the dielectric constant of alcohol in the supercritical state [9]. In general, the supercritical methanol process, which is non-catalytic, is simpler in purification, takes lower reaction time and lower energy use than the common commercial process[16,51].

It is argued that supercritical transesterification, as an alternative technology, satisfies all the requirements to produce biodiesel suitable to be used on normal engines. In addition, it produces more than a kilo of fuel per kilo of oils used [40]. According to a study done by Marchetti et al. [109], the techno-economic analysis of the supercritical process shows that, although the supercritical alternative appears as a good technical possibility to produce biodiesel, today, it is not an economic alternative due to its high operating cost. However, there is still a possibility in reducing the operating cost and making the method more economically advantageous too. Kasteren and Nisworo [110] have proved this by using one reaction step in the process as well as propane as a co-solvent in supercritical biodiesel production plant so as to decrease operating cost.

In another view, Atabania et al. [111] pointed out that, supercritical methanol method uses lower energy and completes in a very short time (2–4 minutes) compared to catalytic transesterification. According to them, since no catalyst is used, the purification of biodiesel and the recovery of glycerol are much easier, trouble free and environment friendly. However, the method has a high cost in reactor and operation (due to high pressures and high temperatures), and high methanol consumption (e.g., high methanol/crude-oil molar ratio of 40/1) [9].

Similarly, Marulanda [13] carried out a lab scale experiment on biodiesel production process by supercritical transesterification in a continuous reactor working at a 9:1 methanol to triglycerides molar ratio and 400 °C. The results of this study showed that for a specified biodiesel production plant capacity set at 10,000 tons/year the total energy consumption of this specific process (573 kW) was considerably lower than another supercritical process working at a 42:1 molar ratio and 300 °C (2407 kW), and the conventional base catalyzed process (2326 kW).

Different studies done on investigation of optimum condition for supercritical transesterification process agree that among the determinant variables temperature has the highest impact on yields, followed by reaction time and pressure. Kiss et al. [112] have done a series of experiments with ethyl alcohol to the effect of temperature, time and pressure. They found that, by increasing the reaction time at 350 °C and 12 MPa, yield increases during the whole range (from 63.36% to 93.22%). After reduction of pressure at 350 °C temperature, the maximum yield (80.1%) was reached within 30 min. They concluded that, in general, lowering the pressure would result in yield decrease. By reducing the reaction temperature (350–250 °C), the yield decreases which can in general be compensated with prolonging the duration of reaction. They attained lowest yield at a minimum temperature, minimum pressure and short reaction time (250 °C, 8 MPa, 7 min; the yield is 14.8%) [112]. Table 8 summarizes the results of some selected researches done on optimization of reaction conditions for supercritical transesterification of different feedstock types.

**Table 10.** Summary of the optimum reaction conditions for supercritical transesterification of different feedstock types for biodiesel production.

| Feedstock | Alcohol | Process variables | | | | | Methyl ester % | Ref |
|---|---|---|---|---|---|---|---|---|
| | | Alcohol to oil ratio | Temperature (°C) | Reaction time (min) | Stirring speed (rpm) | Pressure (MPa) | | |
| Refined lard | Methanol | 45:1 | 335 | 15 | 500 | 20 | 89.91% | [14] |
| Rapeseed oil | Methanol | 45:1 | 350 | 4 | - | 14 | 95% | [113] |
| Coconut oil | Methanol | 42:1 | 350 | 7 | - | 19 | 95% | [114] |
| Palm kernel oil | Methanol | 42:1 | 350 | 7 | - | 19 | 96% | [114] |
| Rapeseed oil | Methanol | 42:1 | 350 | 15 | - | 12 | 93% | [115] |
| Rapeseed oil | Ethanol | 42:1 | 350 | 20 | - | 12 | 91.9% | [115] |
| Rapeseed oil | 1-propanol | 42:1 | 350 | 25 | - | 12 | 91.1% | [115] |
| Jatropha oil | Methanol | 43:1 | 320 | 4 | - | 8.4 | 100% | [116] |
| Sunflower seed oil | Methanol | 41:1 | 252 | 20 | - | 24 | 95% | [117] |
| Sunflower seed oil | Methanol with 0.3% CaO | 41:1 | 252 | 17 | - | 24 | 95% | [117] |
| Sunflower seed oil | Methanol with 5% CaO | 41:1 | 252 | 13 | - | 24 | 100% | [117] |
| RBD[a] Palm oil | Methanol | 45:1 | 350 | 5 | - | 40 | 95% | [118] |
| Vegetable oil | Ethanol with $C_2O$ Co-solvent | 25:1 | 200 | 6 | - | 20 | 80% | [119] |

[a] Refined, Bleached and Deodorized

### 2.4.8. Comparison between transesterification techniques

As it has been tried to clearly put in the different research works reviewed in this paper, the different transesterification techniques do have their own advantages and disadvantages. These advantages and disadvantages can be seen with respect to cost of input material, degree of waste generation, cost of production, product purity, yield percentage, environmental and health hazard and the like. Table 9 shows a summary on advantages and disadvantages of these major transesterification techniques as well as required character of suitable feedstock for each method.

**Table 11.** Summary of the advantages and disadvantages of the different techniques for transesterification of oil and/or fat for biodiesel production.

| Transesterification method | Suitable feedstock character | Advantages | Disadvantages | Ref |
|---|---|---|---|---|
| Homogeneous Acid catalyzed | Any type of oil/fat feedstock including those with high free fatty acid. | ✓ Gives relatively high yield<br>✓ Insensitive to FFA content in feedstock, thus preferred-method if low-grade feedstock is used<br>✓ Esterification and transesterification occur simultaneously<br>✓ Less energy intensive | × Corrosiveness of acids damage equipment<br>× More amount of free glycerol in the biodiesel<br>× Requires higher temperature operation but less than supercritical<br>× Relatively difficult to separation of catalyst from product.<br>× Has slower rate of production (relatively takes longer time) | [22,40,43,44,120] |
| Homogeneous Base catalyzed | Oil/fat feedstock with FFA content less than 0.5% by weight of the oil | ✓ Faster reaction rate than acid catalyzed transesterification<br>✓ Reaction can occur at mild reaction condition and less energy intensive<br>✓ Common catalysts such as NaOH and KOH are relatively cheap and widely available<br>✓ less corrosive | × Sensitive to FFA content in the oil<br>× Saponification of oil is the main problem due to quality of feedstock<br>× Recovery of glycerol is difficult,<br>× Alkaline wastewater<br>× generated requires treatment | [19,32,46,48,52,120] |
| Heterogeneous Base Catalysis | Oil/fat feedstock with FFA content less than 0.5% by weight of the oil | ✓ Improved selectivity<br>✓ Easy to separate catalyst from reaction mixture<br>✓ Reduced process stages and wastes<br>✓ Enable to regenerate and reuse the catalyst<br>✓ Reaction can occur at mild reaction condition and less energy intensive | × Catalyst might be poisoned when exposed to ambient air<br>× Sensitive to FFA content in the oil so selective to feedstock type<br>× Soap will be formed if there is high FFA content<br>× Soap formation associated with reduced biodiesel yield and problem in product purification<br>× Leaching of catalyst active sites may result to product contamination | [32,66,69,71,120] |
| Heterogeneous Acid Catalysis | Any type of oil/fat feedstock including those with high free fatty acid. | ✓ Catalyst separation from reaction mixture is easy<br>✓ Has reduced process stages and wastes<br>✓ Insensitive to feedstocks' FFA content.<br>✓ Preferred-method if low-grade oil is used<br>✓ Esterification and transesterification occur simultaneously<br>✓ Solid acid catalyst can be easily removed recycled | × Complicated catalyst synthesis procedures lead to higher cost<br>× Requires high reaction temperature, high alcohol to oil molar ratio and long reaction time.<br>× Relatively energy intensive | [69,75,76,120] |

| | | | | |
|---|---|---|---|---|
| Lipase catalyzed transesterification | Any type of oil/fat feedstock including those with high free fatty acid and water content. | ✓ Insensitive to FFA and water content in the oil, thus preferred when low grade feedstock is used<br>✓ It is carried out at low reaction temperature<br>✓ Purification requires simple step, by enabling easy separation from the by-product, glycerol<br>✓ Gives high purity product (esters)<br>✓ Enables to reuse immobilized enzyme | × The cost of enzyme is usually very high<br>× Gives relatively low yield<br>× It takes high reaction time<br>× The problem of lipases inactivation caused by methanol and glycerol | [19,22,26,46,78,79,120] |
| Nano catalyzed transesterification | Any type of oil/fat feedstock including those with high free fatty acid and water content | ✓ Relatively with shorter reaction time<br>✓ Less amount of catalyst can be enough since has high specific surface area<br>✓ Catalyst can be reused many times<br>✓ Wide range of catalyst choice | × Requires relatively more alcohol for effective yield<br>× In some cases preparation of appropriate catalysts costs more | [91–97] |
| Ionic liquid catalyzed transesterification | Any type of oil/fat feedstock including those with high free fatty acid and water content but dependent on which type of ionic liquid is used (Acidic/basic) | ✓ Easy to separate final products due to formation of biphasic.<br>✓ Efficient and time saving<br>✓ While preparing catalysts their properties can be designed to suit a particular need<br>✓ Catalyst can be easily separated and reused many times<br>✓ High catalytic activity, excellent stability | × High cost of ionic liquid production<br>× Requires relatively more alcohol for effective yield | [101–106] |
| Supercritical transesterification | Any oil and fat with greater range and water content and high FFA content (in particular, used cooking oil) | ✓ It takes very less time to complete<br>✓ Insensitive to greater water content of the feedstocks<br>✓ Produces more than a kilo of fuel per kilo of feedstock<br>✓ No need of washing the product as there is no catalyst used<br>✓ It is more easier to design as a continuous process | × Requires higher temperature and pressure<br>× It is not an economic alternative due to its high operating cost, due to high pressures and high<br>× temperatures<br>× Relatively there is high methanol consumption (e.g.,high methanol/crude-oil molar ratio of 40/1) | [9,40,111,112,115,118,119] |

## 3. Conclusion

Even though biodiesel is a good alternative over petroleum diesel in various aspects, it is always jeopardized by the high cost of feedstock and absence of economically and technically viable technology for its efficient production from any feedstock type.

Different researchers recommend different methods of biodiesel production, which are usually dependent on properties of the feedstock. Among the methods to change fat and oil to biodiesel, the most convenient one is the transesterification or also called alcoholysis reaction. There are a number of techniques used to carry out transesterification of fat/oil for biodiesel production, each of which requiring specific feedstock property and optimum operating condition for efficient production of biodiesel.

From the review of different works, it can be concluded that:

(1) Homogenous acid catalyzed transesterification is relatively insensitive to FFA content of the feedstock, is relatively less energy intensive but requires higher temperature operation and the biodiesel produced usually has more amount of free glycerol (low purity percentage).

(2) Homogeneous base catalyzed transesterification is very sensitive to FFA and water content and thus is very selective in feedstock type. The reaction is fast, the catalysts are relatively cheap, and thus it is usually applied at industrial scale for biodiesel production.

(3) Heterogeneous acid catalyzed transesterification avoids the problem of product separation and purification and enable reuse of the catalyst. However, it relatively requires high alcohol to oil molar ratio and long reaction time.

(4) Heterogeneous base catalyzed transesterification reduces process stages and wastes, and enables easy catalyst separation and reuse. However, catalyst might possibly be poisoned when exposed to ambient air so that not environmentally friendly.

(5) Lipase catalyzed transesterification is insensitive to FFA and water content, carried out at low temperature, and convert more amount of the feedstock to biodiesel. Nevertheless, it is costly due to expensiveness of the enzymes and takes longer time to have good yield.

(6) Nano catalyzed transesterification is insensitive to FFA and water content, carried out relatively at low temperature and takes short time. The catalyst can be reused many times providing cost benefits. However, it requires more alcohol for effective yield and in some cases preparation of appropriate catalysts is expensive.

(7) Ionic Liquids catalyzed transesterification enables easy separation of final products due to formation of biphasic thus reducing process cost and be efficient and time saving. In addition, it enables modulating desired properties of catalysts while preparing them. Catalysts have high catalytic activity, excellent stability and can also be easily separated and reused many times. However it requires relatively more alcohol for effective yield and usually expensive to have ionic liquids.

(8) Supercritical transesterification is insensitive to FFA and water content of feedstock and thus enable to use wider feedstock types, usually takes shorter time and produces more fuel amount per feedstock mass. However, it requires higher temperature and pressure and consumes more methanol so that it is not economically profitable due to its high operating cost.

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## Conflict of Interest

All authors declare no conflicts of interest in this paper.

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Review

# Economics of biodiesel production: Review

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ABSTRACT

Biodiesel is an alternative fuel similar to conventional diesel. It is usually produced from straight vegetable oil, animal fat, tallow, non-edible plant oil and waste cooking oil. Its biodegradability, non-toxicity and being free of sulfur and aromatics makes it advantageous over the conventional petrol diesel. It emits less air pollutants and greenhouse gases other than nitrogen oxides. In addition, it is safer to handle and has lubricity benefits than fossil diesel. However, with all these environmental benefits, biodiesel could not be extensively applied as a complete substitute fuel for conventional diesel. The main reason, repeatedly mentioned by many researchers, is its higher cost of production. Reduction of the cost of biodiesel production (unit cost of production) can be attained through improving productivity of the technologies to increase yield, reducing capital investment cost and reducing the cost of raw materials. These demand a thorough execution of economic analysis among the available possible technology alternatives, catalyst alternatives, as well as feedstock alternatives so that the best option, in economic terms, can be selected. With this respect, there are a number of researches done to investigate economically better way of producing biodiesel as a substitute fuel. Accordingly, this paper is meant to review the researches done on economics of biodiesel production, emphasizing on the methods of assessment and determination of total investment cost and operation cost, as well as on assessment of economically better technology, catalyst and feedstock alternatives. It also gives emphasis on profitability of biodiesel production and the major system variables affecting economic viability of biodiesel production.

## 1. Introduction

The world total energy consumption has been significantly increasing [1]. According to the International Energy Outlook 2016 (IEO2016) projection, the total world consumption of marketed energy expands by 48% from 2012 to 2040. The larger share of such growth in world energy use goes to countries outside of the Organization for Economic Cooperation and Development (OECD) [1]. In these countries, economic growth and population expansion are driving forces for energy consumption. In an economy experiencing considerable economic growth, living standards improve resulting in demand for more energy per capita. This together with population growth inevitably boost up the total energy consumption.

Currently the most dominant resources for world energy supply are crude oil, coal and gas [2]. However, the limited reserve of such fossil fuels prompts the consideration of alternative fuels from renewables. Most renewables do have environmental advantages over the conventional fuels, such as net greenhouse gas and pollution reduction [3]. These environmental advantages are additional points to strengthen the concept of replacing the fossil fuels with renewable energy sources. In line with this, the IEA Renewable Energy Medium Term Market Report 2016 indicated that the renewable energy share in the total world energy consumption is expected to have at least 39% increment by 2021 [4].

According to the Organization of the Petroleum Exporting Countries, OPEC [5], by 2040 world fuel oil demand will reach up to 109.4 million barrel per day from which, diesel fuel demand is expected to dominate by 5.7 million barrel per day as shown in Fig. 1.

However, this higher oil fuel demand is facing two major challenges, scarcity of the resource and negative environmental impact due to its use. These two challenges alone can impose an urge towards looking for better and long lasting substitute fuel. Accordingly, many researchers are becoming interested in investigating alternative energy resources. Among such alternatives, biodiesel is getting more emphasis for some reasons. It can be produced from a wide variety of resources including wastes like waste cooking oil, oily sludge from factories and waste animal fat [6,7]. In addition, there are a number of technological choices to produce biodiesel based on the quality of the feedstock, giving possible alternatives to minimize overall production expenses [8].

When it is compared to conventional petrol diesel fuel, biodiesel has no sulfur. It also produces less carbon monoxide, particulate matters,

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*Acronyms*

| | |
|---|---|
| AEC | Annualized Total Investment Cost |
| AOC | Annual Operational Cost |
| ARR | After-tax Rate of Return |
| ASTM | American Society for Testing and Materials |
| BBP | Biodiesel Break-even Price |
| BPC | Biodiesel Production Cost |
| CIC | Capital Investment Cost |
| CD | Catalytic Distillation |
| DCFR | Discounted Cash Flow Rate of return |
| FAME | Fatty Acid Methyl Ester |
| FCC | Fixed Capital Cost |
| FCI | Fixed Capital Investment |
| FOB | Fixed on Board |
| HCl | Hydrogen Chloride |
| IEA | International Energy Agency |
| IRR | Internal Rate of Return |
| ISBL | Inside Battery Limits |
| NNP | Net Annual Profit after Taxes |
| NPV | Net Present Value |
| NPW | Net Present Worth |
| OECD | Organization for Economic Cooperation and Development |
| OPEC | Organization of the Petroleum Exporting Countries |
| OSBL | Outside Battery Limits |
| PBP | Pay Back Period |
| PFR | Plug Flow Reactor |
| R&D | Research and Development |
| ROI | Return on Investment |
| SIC | Specific Investment Cost |
| TCC | Total Capital investment Cost |
| TEC | Total Equipment Cost |
| TMC | Total Manufacturing Cost |
| UPC | Unit Production Cost |

smoke and hydrocarbons and has more free oxygen than the conventional petrol diesel [3,9]. Having such more free oxygen results in complete combustion and reduced emission [10,11]. Biodegradability, higher flashpoint and inherent lubricity are other worth mentioning advantages of biodiesel over the conventional petro diesel [12].

The major challenges associated with biodiesel as a fuel are, having higher cost of production, having relatively less energy content compared to fossil diesel and releasing nitrogen oxide emissions when it is burnt [13]. However, it is usually the higher cost of production that makes the fuel not to be extensively used [14–16]. Succinctly, there are three possible paths to attain unit cost reduction concerning biodiesel production processes such as improving the production technologies for better productivity/yield, reducing capital cost and reducing raw material cost for which feedstock cost is the most dominant [17,18].

All of these possible paths demand economic analysis to be done among various alternative production technologies, catalysts, feedstock types as well as various biodiesel and glycerol purification technologies to pinpoint economically better ones. There are a number of worth mentioning investigations performed to test economics of biodiesel production processes.

Accordingly, in this paper more emphasis is given on reviewing the various studies done to investigate the economics of biodiesel production related to determination and comparison of total cost of investment, direct production costs as well as various system variables affecting profitability among different production technology types and production scales.

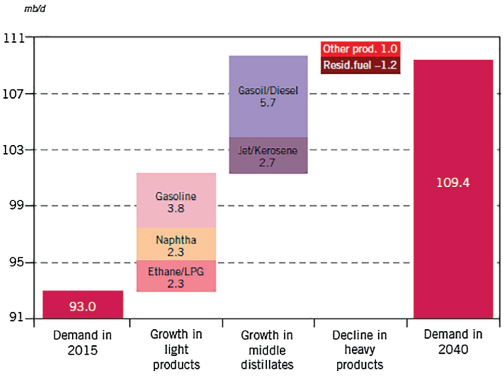

**Fig. 1.** Oil demand growth by type from 2015 to 2040 [5]

## 2. Methods to assess total investment cost for biodiesel production

The total investment cost to produce biodiesel vary depending on a number of factors like the type of production technology chosen, the production scale (plant size), type and market price of raw materials used, among others. The total investment cost can be categorized into fixed capital investment cost and operating (working capital investment) cost [19]. Fixed capital investment cost represents the capital necessary for the installed process equipment with all auxiliaries, which are desirable for comprehensive process operation whereas operating cost considers raw materials cost, utility cost, labor dependent costs, facility dependent costs and other similar variable expenses required for manufacturing of the biodiesel at a given rate.

A number of studies have been done on estimation of the total investment cost of biodiesel production, one different from the other in terms of cost considerations and the approach to calculate the required cost categories for a given production scale.

### 2.1. Capital investment cost

There are five known classifications of capital investment cost estimation ways in chemical processing industries[20]. These are order-of-magnitude estimates (class 5), study estimates (class 4), preliminary estimates (class 3), definitive estimates (class 2) and detailed estimates (class 1)

The capital cost estimates done using order-of-magnitude and study estimates are usually for preliminary feasibility analysis to compare process alternatives. The other two classes (preliminary estimates and definitive estimates) are employed to further carry out accurate estimation of the capital cost on the profitable process alternative screened using class 5 and/or class 4. Eventually, detailed estimates is usually applied as the final detail estimation of all the costs associated with the construction of the new plant so that a construction decision could be done based on the estimate[20].

Various researches that are done to estimate the capital investment cost for biodiesel production, make use of the study estimate approach, which is usually performed to give an overview on the economic feasibility of potential technological alternatives [18,21,22].

The major cost categories under capital investment cost are equipment purchasing cost and direct plant costs. Direct plant costs include those required for equipment installation, instrumentation, piping, electrical facilities, yard improvement, auxiliary facilities, among others. There are different techniques to calculate the fixed capital investment cost for biodiesel production processes. In all of these techniques, the primary activity demands estimation of total equipment cost for that the calculation of all other components of capital cost are based on total equipment cost, installed or purchased costs.

Furthermore, the accuracy of the estimation of total capital investment cost is mainly dependent on how the total equipment purchasing cost is precisely determined. Concerning calculation of capital investment cost for a given biodiesel production process, there are very crucial activities to be performed prior to doing the cost estimation. These include designing the complete process flow, selecting the equipment type, determining required equipment size, selecting type of construction material for the equipment in question and performing material and energy balances [19]. It is obvious that the most updated and accurate value of equipment purchased cost can be found from relevant vendors or from data of previously purchased similar equipment. If such cost data are for different plant capacity and at different purchasing time, it is necessary to adjust the equipment purchasing cost based on the capacity of the equipment and purchasing time differences [20]. While scaling up or scaling down the equipment purchasing cost based on unit capacity of the equipment, one can use cost relation like the six-tenth rule or the thirds power law described by Remer et al. [23]. Similarly, cost indexes, such as Chemical Engineering Plant Cost Index (CEPCI) and Marshall & Swift Process Industry Index (MSPII) are the two commonly used indexes to update the purchasing cost of equipment in time [20]. Such indexes are used to account for price changes due to inflation. For study estimates of equipment purchasing cost, however, cost summary graphs for various equipment can be used [20].

Different scholars follow different techniques for estimation of total equipment cost for specified production capacity. Apostolakou et al. [18] used a formula for each type of equipment considered in the design to calculate the Fixed on Board (FoB) cost of the equipment. For instance, the formula they used to estimate the purchasing cost of a reactor constructed from a stainless steel and having volume from 0.1 up to 20 $m^3$, was $C_R^o = 15{,}000V^{.55}$; where V stands for volume of the reactor. Accordingly, using its own formula for each equipment considered in the process, the total purchasing cost could easily be determined.

Another simple way to get estimates of equipment cost can be using a software such as Peters and Timmrhaus method [24] developed to calculate the estimated purchasing cost of equipment. This method requires specific design parameters for each equipment. Depending on the type of equipment, the parameters to be considered include the equipment size, material of construction, process method, power consumption, output capacity and process condition such as pressure. The approximate purchasing cost would then be determined when we enter the latest Chemical Engineering Plant Cost Index and its date to the software [24].

Haas et al. [21] used Richardson Construction Estimating Standards (now known as Cost Data Online) and Chemcost Capital Cost and Profitability Analysis Software for estimation of purchasing cost of all equipment included in the design. These softwares enable to calculate total installed costs using Installation Factors, to convert the supply cost of equipment into total installed costs. Total installed cost considers equipment purchasing cost plus costs for transport and associated insurance, cost of purchase tax, installation cost as well as electricity and pipping costs in some cases. For such calculation, the initial cost of equipment can be found from similar projects, suppliers, or from designer's own files.

The total capital investment cost considers many cost categories in addition to the equipment purchasing cost. These include direct expenses such as cost of labor and materials for installation as well as indirect expenses such as transportation & associated insurance, purchase taxes, contingencies, contractor's fee, construction overhead, auxiliary facilities among others.

For preliminary economic feasibility analysis of biodiesel production processes, the calculation of these additional cost categories is usually done based on the percentage allocation of the total equipment purchasing cost [25]. A number of available methods can be used for the estimation of capital investment cost through estimating the additional cost categories from the equipment cost. Among the methods are Peters and Timmrhaus method, Chilton method, and Holland method [26]. Peters and Timmrhaus method considers the purchasing cost of equipment including delivery costs from which the other cost categories can be calculated using the percentage allocation of the equipment purchasing cost as shown in Table 1, which indicates different values of percentages of equipment purchasing cost for calculation of other investment cost categories.

**Table 1**
Direct plant cost categories and their percentage allocation with respect to equipment purchasing cost for biodiesel production processes.

| Direct Plant cost categories | Percentage allocation with respect to equipment purchasing cost | | | |
|---|---|---|---|---|
| | Peters & Timmerhaus Method[a] [24] | Karmee et al. [27] | Marchetti [16] | Chilton Method [26] |
| Equipment cost | 100 | 100 | 100 | 100[b] |
| Equipment delivery cost | – | 10 | – | – |
| Piping | 66 | 20 | 35 | 60 |
| Installation | 47 | 20 | – | 47 |
| Instrumentation | 18 | 10 | 40 | 20 |
| Insulation | – | – | 3 | – |
| Electrical facilities | 11 | 15 | 10 | – |
| Building | 18 | 15 | 45 | 20 |
| Yard improvement | 10 | 10 | 15 | – |
| Auxiliary/Service facilities | 70 | 25 | 40 | 2 |
| Land acquisition | 6 | 10 | – | – |
| Unlisted equipment installation | – | – | 50 | – |

[a] The Peter and Timmerhaus method is for any fluid processing technology.
[b] equipment cost includes delivery cost (it is delivered cost).

Santana et al. [28] followed a different approach in the estimation of the capital investment cost required for construction of a give plant size. This method is usually applied for initial projects since it considers all possible physical structures required for construction of process plant. In this approach, fixed investment cost is divided into direct and indirect costs. The direct fixed investment cost considers financial resources allocated in development of installations. These are again subdivided into ISBL (Inside Battery Limits) and OSBL (Outside Battery Limits). ISBL include the financial resources required for equipment purchase, transportation, structural supports, insulation, paint, instruments, pipes, valves, electrical supplies and installation. All these expenses are directly related to the process. Whereas, the OSBL includes financial resources required for development of the facilities outside the main processing area. These include investment for housing and auxiliary buildings, water treatment, land acquisition for building the process plant, among others. In this study done by Santana et al. [28], the authors took the value of OSBL to be equal to 45% of the value of the ISBL. But in another study, Van kasteren et al. [29] took OSBL to be 20% of ISBL.

For preliminary design and study cost estimates, the value of ISBL can be determined from the total equipment cost using Lang factor especially for major expansion of existing project [20]. Similarly, Van kasteren et al. [29], took a factor of 5 to get the ISBL from total equipment cost. The authors pointed out that the factor 5 was in agreement with the Lang factor 4.74 for predominantly fluid processing plant [29]

### 2.2. Operating cost

Operating cost of biodiesel production process include the expenses associated with raw materials, utilities, labor, repairs, maintenance, and depreciation among others. Raw materials mainly comprising of oil feedstock, catalyst, alcohol, washing water, and the like. In all of the biodiesel production technologies, the cost of raw materials took the upper share of the operating cost [15,27,30]. This is more magnified when pure vegetable oil is considered as the feedstock in the process at any production scale. Skarlis et al. [31] shown that the most crucial parameter affecting the operating cost in a small scale biodiesel production process plant is the cost of the vegetable oil feedstock constituting a 77% of the total operating cost. The cost analysis for biodiesel production done in this particular study, indicated that raw materials and utilities together took 86% of operating cost whereas labor and maintenance cost, depreciation cost and other costs took 5%, 5%, 4% respectively [31].

The amount of raw materials required are dependent on the biodiesel production capacity of the process plant. Moreover, the material balance of the biodiesel production process is used as a reference to calculate the amount of raw materials needed to achieve the desired production capacity. Similarly, the utilities consumption are dependent on the type of process routes and type and size of equipment employed and it is usually estimated based on the energy balance of the process [27]. Table 2 shows typical methods to calculate operating cost categories for a biodiesel plant. During calculation of the total operating cost, the values for the cost of raw materials and utilities are typically based on latest market prices. The labor cost estimation is entirely dependent on the type and number of labor required as well as the payment rate allocated for each labor type. The labor required can be estimated based on the number of workers required for the given plant capacity. The other cost categories included in operating cost such as repair and maintenance costs are usually taken as percentages of the operating cost [32]. Whereas, depreciation cost is usually expressed in terms of percentage of equipment purchasing cost.

Many researchers argue that the expensiveness of the biodiesel production processes is largely attributed to the cost of the feedstock [17,18,21,28]. In some cases, this cost contribution of the feedstock even increases as the production scale gets higher, making it less probable to scale up the production of biodiesel. According to the study done by Apostolakou et al. [18], the feedstock cost share of the total production cost can get as high as 75% for low production capacities and could get higher and higher up to 90% when the production capacities increase. In another study, Haas et al. [21] reaffirmed that, the higher contribution to cost of biodiesel production comes from cost of oil feedstock, scoring about 88% of the total production cost. In this study, it was indicated that the total production cost of biodiesel is linearly dependent on the cost of soy oil feedstock [21].

The total cost of investment for biodiesel production is expected to be different for different technological routes. This is usually due to the difference in the amount and type of raw materials and equipment used in the processes. Thus, it seems logical to determine and compare the total cost of such technologies to find out the most cost effective technological option.

## 3. Alternatives to economize biodiesel production

Higher cost of production is the major barrier for extensive use of biodiesel as a substitute fuel for petroleum diesel [33,34]. In this regard, a number of possibilities have been studied and being under investigation to lower the cost of biodiesel production at least to the point to make it better competitive fuel. Among these possible ways are using cheaper catalyst alternatives [33,35], as well as using technologies with minimum overall energy input and faster transesterification reaction [27,36]. The other best viable option is using cheaper alternative feedstock material as it has the major share in cost of production [6,37].

### *3.1. Alternative feedstock for economic advantages*

As it has been repeatedly mentioned in this review, the higher percentage share of biodiesel production cost is from the feedstock. Thus, logically, using cheaper feedstock reduces the unit production cost [38,39]. However, most of the cheaper feedstocks are waste oils or fats or non-edible oil crops, which are usually associated with higher FFA and water content [40,41]. Obviously, as far as biodiesel production for fuel use is concerned, higher FFA and water content of the feedstock jeopardize the yield and quality of biodiesel as there are side reactions producing unwanted products and reducing the yield from the transesterification reaction [42,43]. This, otherwise, demands the use of multiple chemical process steps or alternative approaches to produce biodiesel with better quality and yield, which in turn incur additional costs [44–46]. In addition, in economic terms, there is a wide variability on being profitable using these different low cost feedstock alternatives. With this respect, Olkiewicz et al. [6] studied the economic feasibility of producing biodiesel from liquid primary sludge. The study was done using scale up process model simulated using Aspen Hysys based on the data found from the laboratory scale experiment [6]. Due to using liquid primary sludge as feedstock, different lipid extraction steps were included in the process model incurring cost to the whole production process. However, the economic analysis of the different configuration of the lipid extraction steps indicated that the optimized extraction process could provide better breakeven price of biodiesel and make the biodiesel as cheap as fossil diesel. [6].

The alkali-catalyzed transesterification is the most economically viable process used at industrial scale to produce biodiesel from high quality oil [47–49]. However, when least cost feedstock types are considered, their high free fatty acid and water content make the alkali-catalyzed transesterification process unprofitable. This is because there should be additional cost incurring steps for feedstock pretreatment and product separation and purification [47]. Acid catalyzed transesterification can esterify the FFA into biodiesel. However, acid catalyzed transesterification reaction is very slow, requires more alcohol, requires larger reactor and the corrosiveness of the acid impose equipment deterioration [50]. All of these do have cost implications. The other alternative is supercritical transesterification reaction as it has some technical advantages. It does not use catalyst so there is no additional step for pretreatment of the feedstock to minimize the FFA, and removal of soap [51,52]. In addition, it takes shorter time to complete. However, it requires high amount of alcohol and high reaction pressure and temperature [53–55], which incur considerable cost. Therefore, when we choose a certain configuration of feedstock and production technology for its low cost option, there should be a compromise between the cost reduction due to using the cheaper configuration option and the cost incurred due to additional steps and/or techniques for pretreatment of the low value feedstock, product separation and

**Table 2**
Methods to calculate operating cost/annual production cost for a biodiesel plant [18].

| No | Cost item | Calculation methods used |
|---|---|---|
| 1 | Raw material cost | From material balance |
| 2 | Miscellaneous materials | 1% of FCI |
| 3 | Utility cost | From material balance |
|  | Variable cost | (1) + (2) + (3) |
| 4 | Maintenance | 10% FCI |
| 5 | Operating labor | Manning estimates |
| 6 | Labor cost | 20% of operating labor |
| 7 | Supervision | 20% of operating labor |
| 8 | Overheads | 50% of operating labor |
| 9 | Capital charges | 15% FCI |
| 10 | Insurance, local tax and royalties | 4% FCI |
|  | Fixed costs | (4) + (5) + (6) + (7)+ (8) + (9) + (10) |
|  | Direct production cost | (Variable cost) + (Fixed cost) |
| 11 | General overheads + R&D | 5% of the direct production costs |
|  | Annual production costs | Direct production cost + (11) |
|  | Unit production cost | Annual production cost/Plant capacity |

product quality improvement.

When large-scale production of biodiesel is considered, sustainable feedstock supply is the main issue [56]. Currently, edible oil crops produced through large-scale agricultural systems are considered as the main supply to produce more than 95% of the world biodiesel product [40]. However, enduring large-scale production of biodiesel from edible oil is not sustainable as there is clear controversy with crops for food, which also makes biodiesel an expensive fuel [57]. In this regard, potential substitutes are non-edible oil crops, which can be produced at large scale at relatively cheaper price.

The assessment done by Gui et al. [40] compared economic performances of production of edible and non-edible oil crops so that to indicate the cheapest feedstock. The comparison was done in terms of cost of plantation. The plantation cost considers costs for fertilizer, herbicides and insecticides among others. According to their assessment result, the cost per kg oil required for plantation of non-edible oil crops is lower than that for edible oil crops. However, among the non-edible oil crops, the plantation cost for palm oil was found to be higher, which could actually be balanced by high oil yield [40]. The higher plantation cost associated with most of the edible oil crops is clearly due to requirements of better soil nutrient and good irrigation system. The high yield from palm oil plantation can make the feedstock economically more attractive for profitable biodiesel production business. As main non-edible and relatively draught resistant oil crops, castor and Pongamia pinnata indicate low plantation cost as they require very minimum fertilizer and irrigation [40].

However, as far as alternative feedstock for a standard quality of biodiesel fuel are concerned, the price of the feedstock cannot be taken as the sole criterion to reduce the cost of biodiesel production. Rather, there should be a compromise between the price of the feedstock alternatives and the quality of the biodiesel produced from the alternatives in question. This is because the saturated free fatty acid content in such alternative feedstock may risk quality of the biodiesel produced [58]. One of the techniques to improve the quality of biodiesel produced from feedstock with high content of saturated fatty acid is using additives to improve the cold properties of the fuel [43]. However, such quality improvement measures do have cost implications. Thus, the economic advantages of the alternative feedstock can be seen from perspectives of its low price as well as the impurities of the feedstock that may jeopardize the quality of the biodiesel, requiring expensive feedstock pretreatment and/or product quality improvement processes.

Another possible feedstock alternative for reduced cost of biodiesel production is waste cooking oil [7,29,38,39,43]. Waste cooking oil practically contain more free fatty acids, water content and particulates as impurities. The higher contents of free fatty acid and water are the main reason why such feedstock types are not convenient for commercially known production process, which is alkali-catalyzed transesterification [59]. However, there are other possible technical alternatives such as acid catalyzed [59], enzyme catalyzed [60] and supercritical [61] transesterification reactions enabling production of fuel grade biodiesel from such low quality oil feedstock.

### 3.2. Alternatives technologies for economic efficiency

The economics of biodiesel production can also be seen among different technologies using the same feedstock. Some of the technologies do have economic advantages over the others usually due to having less number of unit operations, which in turn reduce the overall energy input and number of equipment and thus minimize the required investment [62]. In another perspective, such economic advantages may also be due to the relative minimum cost of input materials usually catalysts [36,63].

Using neat vegetable oil as feedstock, generally, the alkali catalyst technologies are most cost effective as there are less number of unit operations and less number of equipment and thus relatively less total investment compared to other potential alternatives [15,64]. However, among the alkali catalyst technologies, heterogeneous ones are more cost effective due to reusability of the catalysts for a number of process cycles [65–67]. The cheapest of all possible heterogeneous alkali catalysts is calcium oxide, which can be prepared from waste materials at very low cost [68,69].

In cases, where low value feedstock, those with higher FFA content, are to be used for biodiesel production, the cost effective alternatives are the acid catalyst technologies [70,71]. This is because the acid catalysts can esterify the excess free fatty acids into additional biodiesel, which otherwise could be changed into soap in alkali catalyst technology by consuming considerable amount of the catalyst, which also incur extra investment for product separation and purification [72,73]. Heterogeneous acid catalysts do have better economic performances among the acid catalyst technologies for that they can be easily separated and reused in the process cycle, are less corrosive, as well as have no washing steps required to purify the product [72]. In addition, the coproduct glycerol can be produced in better quality for higher market value [16,70].

The other possible technologies tolerating high free fatty acid and water content of the feedstock for biodiesel production are, the enzyme catalyzed and supercritical transesterification methods. Both of them could not compute with acid catalyst options in economic terms [27,74].

The study done by Jegannathan et al. [22] revealed that it is very cheaper to produce biodiesel from palm oil feedstock using alkali catalyst than biocatalysts. The authors compared economics of biodiesel production from palm oil feedstock among three catalyst alternatives; alkali catalyst, immobilized enzyme catalyst and soluble enzyme catalyst. The expensive way among the three alternatives was the soluble enzyme catalyst option. This is because, generally, the enzyme catalyzed transesterification reaction takes longer time [22,75] and the expensive soluble enzyme cannot be reused. However, in the case of immobilized enzyme catalyst option, the catalyst can be reused a number of times reducing the additional cost required at least to some extent [22].

In this particular study by Jegannathan et al. [22], the authors also compared the total plant cost among the technological alternatives in producing 1000 tons of biodiesel from palm oil feedstock. According to their result, to produce the required product amount, with in equal batch process time, the immobilized enzyme catalyst process took higher plant cost than the two other options. The plant cost for the immobilized enzyme catalyst method was 57.18% higher than the alkali catalyst process and the plant cost difference between the two enzyme catalyst methods was about 0.40% [22]. This higher plant cost for the immobilized and soluble enzyme process alternatives was mainly due to additional reactor units required to achieve the same product amount with in the same batch process time. The plant cost variation between the soluble and immobilized enzyme options was also due to the additional operation unit for enzyme immobilization [22].

In another study, Marchetti et al. [16] did techno-economic investigation of three possible alternative technologies to produce 36,036 metric ton biodiesel per year from spent oil with 5% FFA. The processes were homogeneous alkaline catalyst with acid pre-esterification, homogeneous acid catalyst and heterogeneous solid catalyst. According to their conclusion, the cheapest option was the homogeneous alkaline with acid pre-esterification process. Even though the total investment cost for this option was the higher among the three, its operating cost was estimated to be the lowest making the unitary production cost of biodiesel to be the minimum. However, the total investment cost was higher for both homogeneous scenarios. This was due to additional equipment required for product separation and purification in both homogeneous catalyst options as similarly indicated in [27]. The authors also argued that the heterogeneous alternative could also be the possible future technology for having lower amount of waste and high purity of the coproduct glycerol for its potential market value

[16].

The study done by Zhang et al. [38] provide more insight into how technology and feedstock pairing could make the process profitable or not. They analyzed the economic feasibilities of biodiesel production through alkali and acid catalyzed processes using waste cooking oil and virgin vegetable oil as feedstock. The processes studied were; alkali catalyzed process using virgin vegetable oil, alkali catalyzed process using waste cooking oil with acid catalyzed pre-esterification, acid catalyzed process using waste cooking oil and acid-catalyzed process using waste cooking oil with hexane as an extraction solvent. The results of this study indicated that the alkali catalyzed option to produce biodiesel exhibited lowest fixed capital cost. However, the more economically feasible option was the acid catalyzed process using waste cooking oil as feedstock, indicating lower total production cost, better after tax return rate and lower biodiesel break-even price [38]. The smaller sizes of the equipment used and low cost of their construction material, which is carbon steel, could make the total capital cost of the alkali catalyzed process option the minimum of the others [38].

An economic comparison among the three possible homogeneous catalyst options was done by Karmee et al. [27]. The homogeneous catalysts studied were; acid, base and enzyme catalysts for transesterification of waste cooking oil for biodiesel production. For such feedstock character, the acid catalyst option was found to be the most cost effective due to absence of feedstock pre-treatment as well as less steps for product purification compared to the alkali catalyzed option [27]. Comparatively, the enzyme catalyst option was very expensive mainly due to higher cost of enzyme catalyst [27].

The economics of a production technology can be improved by making the byproducts and recovered materials valuable for market and/or recycling them in the process. With this respect, having recyclable catalyst, recovering excess alcohol and producing high quality glycerol are the most crucial entry points in biodiesel production processes. Accordingly, concerning the new feedstock type, which is algal biomass, being studied by various researchers, there is a possibility of recycling the coproduct glycerol for algal consumption so that to have more and cheap feedstock for biodiesel production.

Brunet et al. [76] studied how recycling the coproduct glycerol affect the economics of biodiesel production from microalgae through sulfuric acid catalyzed transesterification. The two technological alternatives studied were similar in all aspects except the second alternative considered glycerol produced in the transesterification process as a carbon source to grow the microalgae. In the second scenario, the glycerol produced was supposed to be absorbed by algae in photo bioreactor and then converted into triglycerides through metabolic processes. Then the produced triglyceride could be used as feedstock to continue the biodiesel production process. Summary of the economic performances of these two technological alternatives is shown in Table 3.

The authors found out that the alternative scenario was better in its economic performance indicating less unit biodiesel production cost and higher net present value [76]. In terms of the total investment cost, the alternative scenario had 71% increment than the conventional. This was mainly due to additional bioreactor operating units for microalgae production. In another view, since there were no any feedstock purchase, the alternative scenario could have 10% less in its operating cost minimizing the unit production cost compared to the first scenario [76].

Most recently, Gaurav et al. [59] compared the economic performances of two different processes for biodiesel production from waste cooking oil; conventional reactor with separation process and Catalytic Distillation (CD) process. Both processes were heterogeneous acid catalyzed. The catalytic distillation process could reduce the number of required equipment by avoiding the plug flow reactor and flash separation unit, which are required in the conventional reactor plus separation arrangement. This actually led to significant reduction of capital and production costs making this technological option economically efficient [59]. Table 4 summarizes some studies done on cost of producing biodiesel using different technologies.

### 3.3. Alternative catalysts for economic advantages

There are a number of alternative catalysts, with economic advantages, to catalyze transesterification reaction for biodiesel production. The economic advantages of such alternative catalysts can be seen at least from three perspectives: having lower price, reusability and acquiring higher catalytic activity. The lower price of the catalyst would bring a direct reduction in the overall production cost. The reusability of some alternative catalysts, like immobilized lipase catalysts [75,78,79] and heterogeneous solid catalysts [8,73], could avoid considerable amount of money for repeated purchase of catalysts. Whereas the higher catalytic activity accelerates transesterification reaction and minimize the overall process cycle, which, in turn, would improve the process throughput per unit time [33].

However the main criteria to choose a catalyst for the transesterification is not primarily governed by economic terms like its price; rather the feedstock character, such as free fatty acid and water content, are the dominant factors determining the type of catalyst to be used [73,80]. Low cost feedstocks for biodiesel production are usually associated with higher free fatty acid and water content, for which acid catalysts are found to be more convenient [64,71,81], especially; heterogeneous acid catalysts do have economic advantage of being easily and cheaply recovered for reuse [70]. Thus, this implies that heterogeneous acid catalysts are more efficient than other conventional catalyst technologies in terms of reducing unit cost of biodiesel production.

In general heterogeneous catalysts options do have more advantages than homogeneous ones in terms of reusability, having less process steps required for product separation and purification, producing high purity glycerol and enabling easy catalyst recoverability [8,72,82–84]. All of these advantages do have economic implications making heterogeneous catalysts better candidates to reduce unit cost of biodiesel production.

Even though there are considerable studies done on alternative catalysts for biodiesel production, only few investigate and analyze such catalysts for their direct economic advantages. Wei et al. [65] studied the application of waste eggshell as low-cost solid catalyst for biodiesel production. The preparation of solid catalyst from waste eggshells can simply be done by calcination of the eggshell at higher temperature [65]. In this study, the effect of calcination temperature on the structure and activity of the eggshell catalyst was investigated and the reusability of eggshell catalyst was examined. It is very understandable that utilizing eggshell as a catalyst could brought about economic and environmental benefits through recycling the waste to produce least cost catalyst. Accordingly, the authors concluded that the whole process could enable to reduce the price of biodiesel in a manner to make it competitive with petro diesel [65]. This economic advantage is mainly due to catalyst reusability as well as cheap cost of source material and catalyst preparation process.

**Table 3**
Executive economic summary of the conventional and alternative biodiesel processes [76]

| Economic parameters | Conventional biodiesel process | Alternative biodiesel process |
|---|---|---|
| Net Present Value [M$] | 70.575 | 75.442 |
| Total Capital Investment [M$] | 7.456 | 12.756 |
| Operating Cost [M$/year] | 20.910 | 18.882 |
| Production Rate [tones/year] | 23.700 | 33.700 |
| Unit Production Cost [$/kg] | 0.620 | 0.580 |
| Unit Selling Price [$/kg] | 0.820 | 0.820 |
| Total revenues [M$] | 28.919 | 28.919 |

**Table 4**
Summary of studies on cost of biodiesel production using different technologies and feedstock types.

| Production technology type | Capacity | Feedstock | Production cost $/ton | Ref |
|---|---|---|---|---|
| KOH Catalyzed transesterification with methanol | 8000 ton per year | Waste cooking oil | 868,60 | [27] |
| $H_2SO_4$ Catalyzed transesterification with methanol | | Waste cooking oil | 750,38 | |
| Lipase (Novozym-435) Catalyzed transesterification | | Waste cooking oil | 1047,97 | |
| Alkali catalyst process | Batch mode with a production capacity of 1000 tons | Palm oil | 1166,67 | [22] |
| Soluble lipase catalyst process | | Palm oil | 7821,37 | |
| Immobilized lipase catalyst process | | Palm oil | 2414,63 | |
| Homogeneous $H_2SO_4$ catalyzed and using purchased feedstock | Continuous reactor operating at 30 °C | Microalgae oil | 620 | [76] |
| Homogeneous $H_2SO_4$ catalyzed and using self-produced feedstock from recycled glycerol | | Microalgae oil | 580 | |
| Homogeneous KOH catalyst and hot water purification process | Batch mode with a production capacity of 1452 tons per year biodiesel | Waste cooking oil | 921 | [77] |
| Homogeneous KOH catalyst and vacuum FAME distillation process | | Waste cooking oil | 984 | |
| Heterogeneous CaO catalyst and hot water purification process | | Waste Cooking Oil | 911 | |
| Heterogeneous CaO catalyst and vacuum FAME distillation process | | Waste cooking oil | 969 | |
| Homogeneous KOH catalyst and hot water purification process | Batch mode with a production capacity of 7260 tons per year biodiesel. | Waste cooking oil | 598 | [77] |
| Homogeneous KOH catalyst and vacuum FAME distillation process | | Waste cooking oil | 641 | |
| Heterogeneous CaO catalyst and hot water purification process | | Waste cooking oil | 584 | |
| Heterogeneous CaO catalyst and vacuum FAME distillation process | | Waste cooking oil | 622 | |

In another study, Hidayat et al. [85] studied the possibility of catalyzing the esterification of palm fatty acid distillate with a cheap catalyst prepared from coconut shell bio-char. Sulfonating with concentrated $H_2SO_4$ was the method used to prepare the solid catalyst from coconut shell bio-char [85]. They argued that sulfonating coconut shell bio-char using $H_2SO_4$ could create sulfonic acid groups as well as additional week acid groups favoring the catalytic activity of the solid catalyst prepared. This in turn enable to esterify low value and very cheap feedstock for efficient production of fuel grade biodiesel. Table 5 shows some low cost catalyst alternatives from cheap sources.

## 4. Profitability of biodiesel production

Profitability is the capacity to make a profit, which is a mathematical difference between income earned and all costs and expenses used to earn the income. Profitability is usually measured using a profitability ratio. One such important profitability ratio is Return on Assets (Return on Investment). It measures the efficiency of a firm in managing its investment in assets and using them to generate profit. Profitability of a production process can be improved through managing costs and boosting productivity. Cost management demands minimizing the expense as much as possible without compromising the quality and quantity of the product. In addition, increasing productivity requires production technologies, which are better in technical and economic efficiencies.

A number of other economic parameters can also be used to measure the profitability of a given biodiesel production process as well as to compare among a number of available technologies for their economic feasibility. Among them are Net Present value, Break-even Price of Biodiesel, after tax Internal Rate of Return, Gross Margin, and Payback time.

The profitability of biodiesel production process depends on various variables like the type of the technology in question, which determines the productivity, as well as the market values of inputs and outputs. The type of the technology determines the quantity and quality of the biodiesel product affecting the economic feasibility of the whole process. In another view, the economic feasibility of a given biodiesel production technology can also be affected by the production scale.

### 4.1. The effect of market variables over profitability of biodiesel production

Obviously, the effect of a given market variable might not be the same among two or more technological alternatives, because the amount and quality of the market variables, i.e. input materials and products, could not necessarily be the same for different technological options. Accordingly, a number of studies have been carried out to investigate which market variables affect profitability of biodiesel production using different technologies at different market scenarios with respective production capacities [38,92–94].

A study done by Mulugetta [17] indicated that the major market variables, which could have strong effect on the profitability of biodiesel production business, include biodiesel selling price, raw feedstock purchasing cost, cost of oil extraction and selling price of the glycerol. The cost of oil feedstock, as considered by many authors, is the main dominant market variable affecting the economic feasibility of the business while using most of the possible technological alternatives [16,18,27,30,93]. This is mainly because this cost category took the larger share of the operating cost directly affecting the unit cost of production.

In another study done by Van Kasteren et al. [29], it was indicated that, when supercritical methanol method is used for producing biodiesel, the major market variables that could directly affect the economic feasibility include raw material price, plant capacity, glycerol price and capital cost. In this case, cost of raw materials comprise cost of oil feedstock (waste cooking oil) and cost of methanol. Most studies did not include more market variables other than the raw materials and the products to investigate their effect over economic feasibility of biodiesel production. Marchetti et al. [93] considered additional market variables such as advertisement and selling expenses, tax incentives, investment in research and development and product failure over profitability of biodiesel production using supercritical methanol method. The author indicated that, still the major effect on the economic feasibility of the biodiesel production process was due to the income (biodiesel and glycerol) and outcome (raw materials) variables.

As can be clearly understood, the effect of these market variables on the profitability of biodiesel production is not expected to be uniform and equal in any case. In this respect, Marchetti [92] studied how the possible market variables affect the profitability of biodiesel production using homogeneous alkali catalyzed process. It was concluded in this study that, the entire income variables (selling price of glycerol as well as biodiesel) have positive effect on the internal return rate and payback time, which was also showed by Haas et al. [21]. However, the outcome variables did the opposite by reducing the internal return rate and increasing the payback time and made the process less profitable [93]. Among the outcome variables considered, usually oil feedstock and alcohol have more effect on the profitability of the process as their required amounts are high. But the other outcome variables like catalyst and washing water, are required relatively in small fractions,

**Table 5**
Catalyst alternatives from cheap sources.

| Source Material | Method of catalyst preparation | Catalyst | Reusability | Remarks | Ref. |
|---|---|---|---|---|---|
| Waste eggshell | Through Calcination under air | Solid catalyst with CaO the active phase | Reusable up to 13 times with no apparent loss of activity | Eggshell sample calcined above 800 °C was the most active catalyst | [65] |
| Coconut shell biochar | Sulfonating the coconut shell biochar using concentrated $H_2SO_4$ | Coconut shell char based catalyst | – | Sulfonation using $H_2SO_4$ significantly increased surface area and pore structure formed in the biochar. | [85] |
| Carbonaceous ash-like waste, a common residue from biomass gasification processes | Through Calcination at 800 °C under air | A metal oxide (particularly CaO) rich catalyst | Reusable up to 4 times with little loss in activity | The activity of this waste material was lower as compared to similar pure metal oxides (Ca and MgO) in the Literature | [86] |
| Mussel shells (*Mytilus galloprovincialis* species) | Through calcination at 800 °C during 6 h | CaO | – | The catalyst should be used immediately after calcination process to avoid poisoning of catalyst by $H_2O$ and $CO_2$ | [87] |
| Scallop waste shell | Through Calcination at 1000 °C for 4 h | Solid catalyst mainly composed of CaO (97.53 wt%) | – | The catalyst performed equally well as the laboratory-grade CaO | [88] |
| Crustacean shells | Through Calcination at 900 °C for 1 h | Calcined calcium/chitosan spheres | – | Chitosan particles without calcium are not active for biodiesel production. | [89] |
| Incompletely carbonized sugar produced through pyrolysis | Sulfonating the incompletely carbonized sugar with $H_2SO_4$ | Solid sulfonated carbon catalyst | – | Solid Catalyst with a high density of active sites | [90] |
| Kraft lignin | Chemical activation with phosphoric acid, pyrolysis and $H_2SO_4$ | High acid density Catalyst | Reusable 3 times with little deactivation | Simplify biodiesel production procedure and reduce costs | [91] |

resulting in a relative smaller effect [93]. Summary of some studies done on the effect of system variables over economic viability of different biodiesel production technologies is shown in Table 6.

### 4.2. Production scale as a factor affecting economic viability of biodiesel production

Profitability of biodiesel production may also be dependent on the production scale because producing biodiesel using the same technology and the same feedstock at different scales could show variability in oil productivity, in terms of the rate of output per unit of input, thus either reducing or increasing unit cost of biodiesel production [18]. Very few have been studied to investigate how production scale affects the feasibility of biodiesel production processes. Van Kasteren et al. [29] did a comparative study among three scales of biodiesel production through supercritical method. The result of this study indicated that as the production scale gets higher the unitary cost of biodiesel production gets cheaper making the business more profitable. The same result was reported by Apostolakou et al. [18], which was done on a biodiesel production process from vegetable oil using homogeneous alkali catalyst. The result of this research indicated that, until about plant capacity of 60,000 tons per year, an increase in the plant capacity would improve the feasibility of the process since the unit production cost could be significantly reduced. However, the higher the production scale it gets beyond about 60,000 tons per year, the less would be its effect on reducing the unit production cost [18]. This effect of biodiesel production scale on the unit production cost is shown in Fig. 2.

In another study, You et al. [94] analyzed the effect of production scale on the feasibility of biodiesel production process using NaOH catalyzed transesterification of food grade soybean oil. The comparison was done among three production scales with 8000, 30000, and 100,000 tons per year. It was concluded that the larger production scale was better in economic performances by providing a higher NNP and more attractive ARR with a lower BBP [94]. The authors also argued that increasing the plant capacity using a feedstock of soybean oil has the same economic effects as using waste cooking oil as feedstock.

Navarro-Pineda et al. [96] made an economic model for estimating the viability of biodiesel production from Jatropha curcas, starting from plantation to biodiesel production and pellet production from waste cakes found from oil extraction. The biodiesel production process considered was alkali-based transesterification reaction. The authors concluded that at production capacities over 10,000 $m^3$ per year the production cost could remain constant and expenses always be greater than income. They also mentioned that this could only be reversed by higher Jatropha seed yields.

Most recently, Glisic et al. [97] did a study on process and techno-economic analysis of green diesel and ester type biodiesel production from waste vegetable oil. In this study, the authors investigated the influence of plant capacity (production scale) on the NPV of three biodiesel production processes. The processes investigated were catalytic hydrogenation, homogeneous alkali catalyzed transesterification and supercritical non-catalytic transesterification. They found out that, compared to feedstock cost, plant capacity showed less effect on NPV. However, there was considerable effect of the plant capacity on NPV, especially in catalytic hydrogenation process, for which an increase in plant capacity from 100,000 to 200,000 tons per year could increase NPV from 7.0 to 53.1 million US$. According to their conclusion, unit capacities of the investigated processes, which are below 100,000 tons per year, are likely to result in negative net present values after 10 years of project lifetime [97].

The study done by Kookos et al. [98] indicated that a biodiesel production plant producing fuel grade biodiesel from spent coffee grounds could be economically competitive (i.e. to have biodiesel selling price lower than the current market price) if the annual production capacity can be greater than 42,000 tons per year. This capacity is lower than the normal medium level production capacities [99,100].

**Table 6**
Summary of studies done on system variables affecting economic viability of different biodiesel production technologies.

| Production technology | Production capacity | Variables affecting economic viability | Economic parameters | Explanations | Ref |
|---|---|---|---|---|---|
| Alkali-catalyzed process using sodium hydroxide catalyst<br>Acid-catalyzed process using sulfuric acid catalyst | 8000 tons per year | Plant Capacity, Prices of Feedstock Oils and Price of Biodiesel | Internal Return Rate (IRR) and Break-even Price of Biodiesel | These were the major factors affecting the economic feasibility of the biodiesel production in both cases.<br>Moreover, acid-catalyzed process was economically competitive alternative to the alkali process for biodiesel production. | [38] |
| Base, Acid and Lipase Catalyzed transesterification of WCO | 8000 tons per year | Waste Cooking Oil Price<br>Biodiesel Price | Internal Return Rate (IRR) | Production of biodiesel using acid and base as catalysts can withstand variations from the WCO and biodiesel price | [27] |
| Alkali Catalyzed transesterification of vegetable oil | 10,000 tons per year | Vegetable oil price for different CIC | Internal Return Rate (IRR) | For lower CIC values, the project's viability may be able to resist to higher oil feedstock price forcing. | [31] |
| Homogeneous base catalyzed transesterification of triglyceride with methanol | 150,480 tons per year | Biodiesel price<br>Glycerol price<br>Alcohol price Catalyst price<br>Shipping distance<br>Washing water price<br>R&D<br>Oil price | Internal Return Rate (IRR)<br>Payback Time | Selling prices of glycerol & biodiesel have positive effect over the IRR & in reducing the payback time<br>The outcome variables have the negative effect making the process less profitable. Even though their effect is dependent on their relative required amount | [92] |
| Supercritical technology with no catalyst and no co-solvent | 39910.5 tons per year | Oil price<br>Biodiesel price<br>Glycerol price Alcohol price<br>Advertisement and selling expenses<br>Tax incentives Investment in research and development | Internal Return Rate (IRR)<br>Payback Time | Selling prices of glycerol & biodiesel have positive effect over the IRR & in reducing the payback time<br>The outcome variables have the negative effect making the process less profitable. Even though their effect is not the same as it is dependent on their relative required amounts. | [93] |
| NaOH catalyzed transesterification of soybean oil | Three plant capacities with 8000, 30000, and 100,000 tons per year | Plant capacity, Price of feedstock oil and diesel, Yields of glycerin and biodiesel | Net annual profit after taxes (NNP), Internal Return Rate (IRR), and Biodiesel break-even price (BBP) | These system variables were found to be the most significant variables affecting the economic viability of biodiesel production | [94] |
| Homogeneous acid-catalyzed esterification | 1000 tons per year | Price of Salmon oil | Net Present Value (NPV) | Feasibility of proposed plant was limited by the price of salmon oil | [95] |

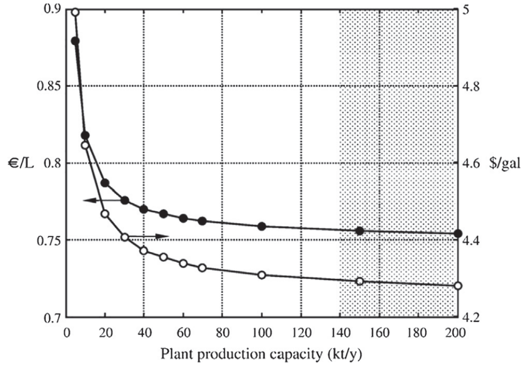

**Fig. 2.** Unit production cost as a function of plant capacity [18]

However, the availability of the raw material (spent coffee grounds) limits the capacity that can be achieved, making the capacity of 42,000 tons per year difficult to be attained in an economically feasible way due to higher logistics and collection costs of the spent coffee [98].

## 5. Summary/Conclusion

Cost of raw materials, especially cost of feedstock, accounts for most of the cost of biodiesel production, irrespective of the technology type. Thus, the economic feasibility of biodiesel production processes is mainly affected by the cost of feedstock. This demands looking for cheaper feedstock types such as non-edible oil plants, waste cooking oil and animal fats. The problem with these low cost feedstock types is their higher amount of impurities. The higher FFA and water content in such feedstock demands the use of additional pretreatment and product separation and purification units and process steps in order to produce quality biodiesel fuel, which complies with ASTM standards. This in turn incurs considerable amount of money to the total manufacturing cost. Therefore, to be profitable in biodiesel production, there should be a compromise between the cost reduction due to using cheaper feedstock and the cost incurred due to additional steps and/or techniques for pretreatment of the low value feedstock, product separation and product quality improvement.

Among the conventional technologies, the acid catalyzed transesterification reaction is the most cost effective to produce fuel grade biodiesel from cheaper feedstock with higher FFA content. Acid catalysts can catalyze both esterification and transesterification reactions without feedstock pretreatment steps. This economic feasibility is manifested by having lower total manufacturing cost, and lower biodiesel breakeven price.

Heterogeneous catalysts do have more advantages than homogeneous ones in terms of reusability, having less process steps required for product separation and purification, producing high purity glycerol and enabling easy catalyst recoverability. These advantages do have economic implications making heterogeneous catalysts good choice to reduce unit cost of biodiesel production. Again, among the heterogeneous catalysts, heterogeneous acid catalysts do have added economic advantage of catalyzing cheap feedstock types, those with higher FFA content.

There are a number of catalyst alternatives prepared from wastes and cheap materials. Such cheap materials include eggshell, scallop waste shell, crustacean shells, bio-char from coconut shell, Kraft lignin and pyrolyzed sugar. These type of catalysts are cheap and most of them are reusable. Least cost and reusable catalysts would bring considerable economic advantages through reducing manufacturing cost and improving throughput per unit time.

Among the different possible system variables that might have effect on the economic feasibility of biodiesel production plant; purchasing cost of feedstock, selling price of biodiesel, selling price of glycerol and plant capacity are the most significant.

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## Conflict of interest

All authors declare no conflicts of interest in this paper.

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# Paper III

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# Techno-economic feasibility of producing biodiesel from acidic oil using sulfuric acid and calcium oxide as catalysts

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A R T I C L E I N F O

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A B S T R A C T

Biodiesel is becoming one of the best alternative fuels to substitute conventional diesel fuel for its environmental and fuel benefits. However, its full-fledged substitution to conventional diesel is hindered mainly due to its high cost of production. More than 85% of the production cost is attributed to feedstock cost. This forces to look for alternative feedstock at lower cost, which usually do have higher free fatty acid content. A number of investigations have been done to evaluate the technical and economic efficiency of biodiesel production from such acidic oil. Accordingly, in this study, three alternative production processes using two catalysts have been designed for techno-economic analysis. Sulfuric acid ($H_2SO_4$) catalyzed Transesterification and Esterification of Acidic oil; Calcium oxide (CaO) Catalyzed Transesterification of Acidic oil; and CaO catalyzed Transesterification with Pre-Esterification of Acidic oil with $H_2SO_4$.

Super Pro design and Aspen Plus softwares were used to perform the conceptual design and simulation of the different alternatives. The techno-economic competitiveness of three different scenarios were evaluated. The technical parameters were amount and quality of biodiesel and glycerol as well as the amount of biodiesel produced per feedstock used. The economic parameters considered were Total Investment Cost, Operating Cost, Unit Cost of Production, NPV, ROI and Payback time. The CaO catalyzed process could show better economic performances.

## 1. Introduction

Biodiesel is a mono alkyl ester of long chain fatty acids. It is a renewable fuel produced from oils and/or fats feedstock such as vegetable oil, animal fat, non-edible plant oil, and waste cooking oil, among others. As a fuel, biodiesel possesses a higher number of benefits than conventional petrol diesel. The most referred benefits are environmental ones such as its biodegradability, non-toxicity, emitting insignificant amount of sulfur, emitting less air pollutants and greenhouse gases other than nitrogen oxides. It also has worth mentioning use benefits as a fuel. These include better lubricity (reduce engine wear) and having higher oxygen content (encourage complete combustion).

The commercial practice to produce biodiesel involves homogeneous alkali catalysis of oil feedstock with free fatty acid content of less than 0.5% [1–3]. The higher the purity of the feedstock (lesser amount of FFA) the more expensive it would be, increasing the production cost to the point of making it a non-competitive alternative. Different investigations have been carried out to find alternative technologies for efficient and affordable production of biodiesel. Among such alternatives, the use of cheaper feedstock, cheaper catalyst and efficient production technologies have been considered. The most widely studied alternatives include heterogeneous and homogeneous acid catalyzed [4–9], heterogeneous alkali catalyzed [10–14], Enzyme catalyzed [15–18] and supercritical [19–22] transesterification reactions. There are also few promising but less studied alternative technologies. These include Nano Catalysts [23–25], Nano Immobilized Enzymes [26–28], Ionic Liquid Catalysts [29–31], and membrane reactors among others [32–34].

The studies so far done on the up supra mentioned biodiesel production technologies include those focusing on finding the optimum reaction conditions [2,35–38], determining the reaction kinetics [39–44], assessing technical efficiencies and evaluating economic performances [45–49] of selected technological alternatives. The technical and economic studies are usually done together as techno-economic analysis. Such studies are typically based on the stated reaction kinetics and optimum reaction conditions determined for max possible biodiesel yield.

Techno-economic study of biodiesel production technologies enable us to compare both technical and economic efficiencies of alternative technologies so that to choose the better performing option(s). The

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**Nomenclature**

| | |
|---|---|
| ASTM | American Society for Testing and Materials |
| DG | Di-glyceride |
| DFC | Direct Fixed Cost |
| E | Ethanol |
| FAEE | Fatty Acid Ethyl Ester |
| FFA | Free Fatty Acid |
| G | Glycerol |
| IRR | Internal Rate of Return |
| MG | Mono-glyceride |
| NPV | Net Present Value |
| ROI | Return on Investment |
| TG | Triglyceride |

technical performances are usually determined through energy and material balances of the whole production process. Karmee et al. [47] did a techno-economic study on three alternative technologies; base, acid and enzyme catalyzed transesterification for biodiesel production from waste cooking oil. The technical performances of these alternatives were made to be equal in terms of 100% biodiesel yield based on the optimum reaction conditions. This was then used to compare the cost effectiveness of the technologies. A more distinctive technical comparison was made by Marchetti et al. [50] on three biodiesel production alternatives, where the authors evaluated the technical performances based on material balances. The parameters used to compare the technical performances among the technologies were, biodiesel yield, total glycerol in biodiesel (referring the quality), amount of biodiesel produced per amount of raw materials used (referring performance), and yield of co-product glycerol.

In another way, the technological assessment can also be done through evaluating the technical benefits and limitations of the alternatives while attaining a given quantity and/or quality of biodiesel. These can include the number of process steps and the number of equipment required to achieve a given quantity and/or quality. This depicts how complex or how simple the whole production process of the alternative technology might be. Zhang et al. [51] assessed the technological performances of four alternative technologies for biodiesel production from waste cooking oil and vegetable oil. The authors used the size and number of equipment used in each process scenario to evaluate their technical performances and found out that the homogeneous alkali catalyzed process using virgin oil was the least sophisticated option requiring less number of process steps and equipment. They also found out that the acid-catalyzed process using waste cooking oil was less complex (requiring less process steps and less number of equipment) than the alkali-catalyzed process using the same oil character [51].

The economic performance evaluations should be done based on the results of the technological assessments. There are a number of economic parameters to test if technically efficient production alternative is cost effective or not, given a specified market scenario. Different researchers used different economic indicators. Zhang et al. [52] used total manufacturing cost, fixed capital cost, after tax rate of return and biodiesel break-even price to evaluate the economic performances of four process alternatives. Total investment cost and manufacturing cost are the most widely used economic parameters to have a clue on which technology option is cost effective. West et al. [53] used after tax rate of return as a parameter in addition to total capital investment and total manufacturing cost. However, it is realistic to consider more economic indicators to get deep insight into the profitability and sustainability of the technological options. Marchetti et al. [50] took a number of economic indicators to compare the economic feasibility of three proposed technological options to produce biodiesel from spent oil with 5% free fatty acid. The main parameters were total capital investment cost, total operating cost, NPV, unit cost of biodiesel, IRR, Gross Margin, and ROI.

It is obvious that the uncertain parameters (market variables) associated with biodiesel production could have considerably different effect on the techno-economic feasibility of the production process. Zhang-Chun et al. [54] investigated the effects of some parameters in the techno-economic assessments of biodiesel production. These include capital cost, interest rate, feedstock price, maintenance rate, biodiesel conversion efficiency, glycerol price and operating cost. The global sensitivity analysis done to quantify the contribution of each parameter to Life Cycle Cost and Unit Cost revealed that the feedstock price and the interest rate indicated considerable effects on the techno-economic assessment. In another study, Zhang-Chun et al. [55] also indicated that price of biodiesel, price of feedstock, and cost of operating can considerably affect techno-economic assessment of biodiesel production

The studies so far done on techno-economic assessment could cover only a limited type of technological alternatives. This triggers a need to investigate the techno-economic performances of more potential technologies for biodiesel production. Therefore, this study was aimed at assessing and comparing the techno-economic performances of biodiesel production from acidic oil using three process alternatives; $H_2SO_4$ catalyzed transesterification, CaO catalyzed transesterification, as well as CaO catalyzed transesterification with $H_2SO_4$ catalyzed pre-esterification.

A conceptual simulation of the processes were designed using Super Pro design software from Intelligen, Inc. [56] and Aspen Plus software from Aspentech [57]. Using the process flow sheets, a material balance for the total capacity of 41 thousand tons feedstock per year was done. Accordingly, the technical performances were evaluated in terms of the quantity and quality of biodiesel produced, amount and quality of glycerol produced, and the amount of biodiesel produced per raw material consumed. The economic competitiveness of three different scenarios were compared based on the economic parameters such as Total Investment Cost, Capital Investment Cost, Operating Cost, Unit Production Cost, NPV, ROI, and Gross Margin. The economic effects of change of oil cost and biodiesel selling price were also analyzed using NPV as the main economic indicator.

## 2. Reaction model

The dominant process in the production of biodiesel is the transesterification of the triglycerides. This reaction takes place in three steps sequentially as shown in Fig. 1. There are also some side reactions that could take place, depending on the quality of the feedstock considered and the technology employed. The dominant side reactions that can take place, due to the presence of acidic feedstock, are saponification in the presence of base catalyst and esterification in the presence of an acid catalyst. However, the hydrolysis of triglycerides can also take place depending on the water content of the feedstock as well as the amount of water produced during the esterification reaction.

In this study, two main catalysts were investigated separately and in combination to find out the most efficient and affordable option(s). Sulfuric acid as homogeneous and calcium oxide as the heterogeneous catalyst. Sulfuric acid was considered because it is the most

$$TG + E \xleftrightarrow{Catalyst} FAEE + DG$$

$$DG + E \xleftrightarrow{Catalyst} FAEE + MG$$

$$MG + E \xleftrightarrow{Catalyst} FAEE + G$$

**Fig. 1.** The three major reaction steps in catalyzed transesterification of triglycerides with ethanol.

recommended efficient catalyst for production of biodiesel from feedstock with higher FFA content [58,59]. Similarly, the CaO catalyst was considered for comparison, because it is the most studied in its catalyzing performance and cheap basic catalyst for biodiesel production, which can be prepared from wastes like eggshell [60,61]. Ethanol was the alcohol considered in the reactions because it could be produced from renewable resources and it is safe to handle. In all of the study cases, excess ethanol, in terms of molar ratio, was considered in order to favor the forward reaction [3,35].

## 3. Study models

Three biodiesel production process models based on catalyst options were investigated. Model I: Homogeneous sulfuric acid catalysis; Model II: Heterogeneous calcium oxide catalysis; and Model III: Heterogeneous calcium oxide catalysis with sulfuric acid pre-esterification. The optimum reaction conditions, for all of the process models in this study, were considered from literature [41,62,63]. All these technological scenarios were considered to be continuous process to fulfill their requirement for industrial scale application. The investigation was made to see the efficient and affordable technological option (s) for production of biodiesel from acidic oil. The oil considered in all of the cases had FFA content of 10% in molar basis. Such feedstock with higher FFA content are cheaper and have potential to reduce the overall production cost. The models presented in this study were based on the simulations done by Super Pro software. However, each technological alternative was redesigned using Aspen Plus software, to substantiate the accuracy of the designs. Aspen Plus provides more choice of physical parameters and methods to select for each specific process considered in the design. And Super Pro design software is also very flexible in executing the economic analysis as it provides easy but detail data entry opportunity. Using the two softwares together would improve the accuracy of the results.

### 3.1. Model I

This model was designed to investigate the production of biodiesel from acidic oil using $H_2SO_4$ catalyzed transesterification reaction. The process flow diagram is shown in Fig. 2.

The optimum reaction conditions for the sulfuric acid catalyzed ethanolysis of such acidic oil was taken to be 55 °C reaction temperature, 2.1% wt. of catalyst, and 6.1 as molar ratio of alcohol to oil [62]. At these optimum reaction conditions, 97.57% conversion could be achieved in 21 h [62]. Using these optimum reaction conditions and the rate of oil supply of 5177.23 kg/h, the required amounts of sulfuric acid catalyst and ethanol were calculated.

Streams of concentrated sulfuric acid (108.72 kg/h) and pure ethyl alcohol (1645.7 kg/h) were fed into a mixer and then heated up to 55 °C. At the same time, acidic oil stream (5177.23 kg/h) was also pumped through another heater and heated up to 55 °C. Both streams were let into the continuous stirred tank reactor (RI-101), where transesterification of the triglyceride and esterification of the FFA were taken place. In this scenario, hydrolysis of the triglyceride was not considered because the water content of the biomass as well as the water formed from esterification was negligible. The product from the reactor was then passed through a short cut distillation column (CI-101) for recovery of the excess ethanol so that it can be reused in the process and considered as credit in the economic calculation. The distillation column was designed to have nine actual stages and 1.6 reflux ratio, beyond which there were no change in the purity of the recovered ethanol. The bottom output from the distillation column, which is mainly composed of ethyl ester, sulfuric acid, water, glycerol and unreacted oil was then cooled down to 25 °C and taken to the neutralization reactor (RI-102) so as to neutralize the sulfuric acid with calcium oxide. The required amount of CaO was determined based on the amount of sulfuric acid to be neutralized.

After the neutralization, a centrifuge (DCI-101) was employed to separate the biodiesel from the rest of the products. The separated biodiesel was further purified in another distillation column (CI-102). This distillation column was designed to work in vacuum (0.25 bar pressure) so that to lower the temperature below 275 °C, because above this temperature biodiesel would be thermally degraded through isomerism, polymerization and pyrolysis [64]. The actual stage of the column was taken to be 6 and its reflux ratio was 1 because increasing the values beyond these could not show significant change in purity of the biodiesel. The bottom output from this distillation column was nontoxic waste, which can be further treated or safely disposed. The bottom product from the centrifuge (DCI-101) was poor quality glycerol byproduct with purity of 76%. The glycerol with such low purity does not have considerable market value. Thus in order to get better quality glycerol (about 96% pure glycerol) for higher market value, further purification might have been considered using another centrifugal decanter. However, this would result in higher equipment purchasing cost and facility dependent costs, making the whole process more expensive.

### 3.2. Model II

Using this model a simple CaO catalyzed transesterification of acidic oil was studied. The process flow diagram is shown in Fig. 3. The designed reactor was a continuous stirred tank reactor packed with CaO catalyst. The optimum reaction conditions considered for best result in CaO catalyzed ethanolysis of acidic oil was taken to be 75 °C reaction temperature, 7% wt. CaO catalyst and 9 as molar ratio of ethanol to oil [41]. Accordingly, with these optimum reaction conditions, a maximum conversion of 97.58% could be achieved in 2 h [41]. The flow rate of the alcohol and the amount of the catalyst required were calculated using the supply rate of the oil and the optimum reaction conditions.

Acidic oil and ethyl alcohol were separately preheated to 75 °C and pumped into the continuous stirred tank reactor (RII-101) at a constant flow rate. In this scenario, due to the presence of considerable amount of FFA in the oil feedstock, saponification of the FFA was considered as the main side reaction. Accordingly, the reaction between some of the CaO catalyst and oleic acid could produce calcium soap (Calcium oleate, $C_{36}H_{66}CaO_4$). The product from the reactor was then let into the short cut distillation column (CII-101) for recovery of the excess ethanol for possible reuse. This distillation column was designed to work at 0.25 bar pressure to avoid thermal degradation of the biodiesel [64] and designed to have 6 actual stages and 1.6 reflux ratio as the maximum values to get the higher purity of the recovered ethanol in the upper output. The bottom output from the distillation column was cooled down to 25 °C and taken into a centrifugal decanter (DCII-101) for separation of the biodiesel. Another distillation column (CII-102)

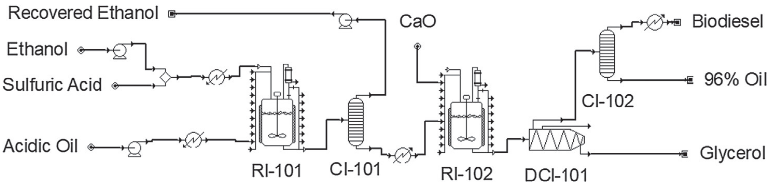

**Fig. 2.** Model I – Sulfuric acid catalyzed transesterification of acidic oil.

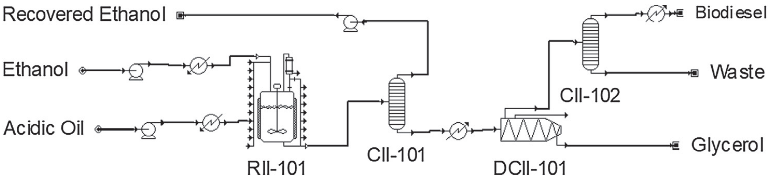

**Fig. 3.** Model II – Calcium oxide catalyzed transesterification of acidic oil.

was engaged to further purify the biodiesel component from the top output of the centrifugal decanter. The maximum biodiesel purity was attained when the actual stage was 4 and reflux ratio was 1.5. The bottom output from the centrifugal decanter (DCII-101) was mainly composed of glycerol with relatively higher percentage of purity (99.8%) than produced from the two other scenarios. Similar results from literature are discussed later in result section. The waste stream from this scenario was non-toxic and mainly composed of calcium soap and unreacted oil, which can be further treated or safely disposed.

### 3.3. Model III

In this model, the effect of the combination of the two catalysts was investigated. The homogeneous sulfuric acid catalyst for esterification of FFA and the heterogeneous CaO catalyst for transesterification reaction were studied simultaneously in a process following the flowsheet as presented in Fig. 4. Two stoichiometric reactors were separately designed. The first reactor (RIII-101) was for pre-esterification of the FFA in the presence of the triglycerides using sulfuric acid catalyst and the other reactor (RIII-102) was for transesterification of the triglycerides using CaO catalyst.

The significant reactions considered in the first reactor were esterification reaction between the alcohol and the FFA to produce water and ethyl ester as well as the transesterification reaction, as a side reaction, between the triglyceride and the alcohol to produce ethyl ester and glycerol. The optimum reaction conditions in the first reactor were taken to be 55 °C temperature, 2.26% wt. sulfuric acid, and 6.1 ethanol to oil molar ratio [63]. With these optimum reaction conditions, a 96% FFA conversion and around 30% conversion of the triglyceride could be achieved in 4 h [63]. Similarly, the optimum reaction conditions required to achieve best result in CaO catalyzed ethanolysis process in the second reactor were taken to be 75 °C temperature, 9 ethanol to oil molar ratio and 7% wt. CaO catalyst [41]. At these optimum reaction conditions, a maximum conversion of 97.58% could be achieved within 2 h [41]. Accordingly, the amount of sulfuric acid catalyst and ethanol were calculated based on these stated optimum reaction conditions and the oil supply rate of 5177.23 Kg/h.

The proportion of the alcohol for pre-esterification reaction (1646 kg/h) was mixed with sulfuric acid (117 kg/h) in a simple mixer. The mixture was then heated up to 55 °C and let into the first stirred tank reactor (RIII-101). Simultaneously, the alcohol proportion for transesterification reaction (1639 kg/h) was also heated up to 75 °C and let into the second continuous stirred tank reactor (RIII-102). The second reactor was a fixed bed reactor packed with CaO catalyst in which transesterification of the triglyceride was taken place to produce more biodiesel. In this scenario, hydrolysis of the triglyceride, in the first reactor, was not considered for that the water content of the biomass as well as the water formed from esterification was negligible. In addition, the occurrence of saponification reaction in the second reactor was also neglected because almost all FFA were supposed to be consumed in the first reactor during esterification reaction.

The product from the esterification process, mainly composed of unreacted triglyceride, ethanol, sulfuric acid, FAEE and water, was directly taken into the neutralization reactor (RIII-103) to neutralize the sulfuric acid so that to avoid calcium salt formation and consumption of the catalyst in the second reactor. CaO was used to neutralize the sulfuric acid, as it can easily be prepared from wastes like eggshell with less expense. The outlet from the neutralization process was directly let into the second reactor (RIII-102) where CaO catalyzed transesterification reaction dominantly took place to produce more FAEE. The product from the transesterification reactor was let into a short cut distillation column (CIII-101) for recovery of excess ethanol for possible reuse. This distillation column had 1.5 reflux ratio and 3 actual stages for maximum possible purity of recovered ethanol. The bottom product from the distillation column then fed into centrifugal decanter (DCIII-101) for separation of the biodiesel component from the rest of the product. The separated biodiesel from the top output of the decanter was further purified in another distillation column (CIII-102). This distillation column was designed with 7 actual stages and 0.3 reflux ratio at which the maximum possible biodiesel purity could be achieved. The bottom product from this distillation column was mainly composed of 86% unreacted oil (123 kg/h), which could be reused with minor treatment. The bottom product from the centrifugal decanter (DCIII-101) was glycerol with 76% purity. Since glycerol with this purity could not get higher value in the market, further purification might have been considered like in the case of model I. Nevertheless, this would, otherwise incur additional cost into the process to make it more expensive.

In all of the three models, storage tanks for both raw materials and products were not included in the designs assuming that the raw materials would be consumed and the products would immediately be used without storage. The waste streams in all of the models were non-toxic and could safely and easily be treated or disposed, or otherwise be reused. For instance, if the glycerol byproducts from Models I and III were to be further purified, calcium sulfate (with more than 86% purity) would be another valuable byproduct. Calcium sulfate, in its direct application, as uncalcined gypsum, can be used as a soil conditioner. If it is further purified and calcined, it can also be used to make tiles and wallboard among others.

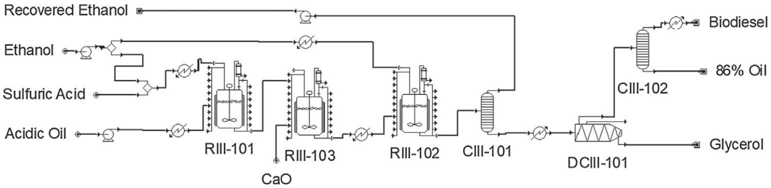

**Fig. 4.** Model III – Calcium oxide catalyzed transesterification with sulfuric acid catalyzed pre-esterification of acidic oil.

## 4. Results and discussion

The models designed were mainly for techno-economic study of production of biodiesel from acidic oil with 10% FFA content on molar basis. These could be used to identify the better option(s) in terms of technical efficiency and affordability. The technical efficiency was assessed based on the quality and quantity of products through material balance and the affordability was assessed based on the total investment, operating cost, ROI, Gross Margin, and NPV. The results of the study are more explained in the following sections.

### *4.1. Process descriptions and technical performances*

The process in the models were designed using commercial software called Super Pro design from Intelligen Inc. [56] as well as Aspen Plus from Aspentech [57]. Each model was designed to accommodate a capacity of 41 thousand tons of acidic oil per year. In all of the three models, the reaction condition was isothermal at required optimum reaction temperatures taken for each reaction type according to literature [41,62,63]. The allocation of the catalysts and alcohol amounts were based on their relative optimum amounts with respect to the proportion of the feedstock considered in each reaction type recommended to get the maximum conversion. More amount of CaO was considered in Model II, where both transesterification and saponification reactions were supposed to take place. Eventually, the least amount of CaO catalyst was allocated for Model III for that only transesterification reaction needed the catalyst. In terms of the overall catalyst amount, Model I required the least catalyst amount, because only sulfuric acid catalyst with 2.1% wt. was considered. In addition, the calculation of the amount of alcohol required were based on the type of reaction as to whether esterification, transesterification or both, since the optimum molar ratio required is dependent on the reaction type.

All the models guaranteed a potential to produce biodiesel with required quality. It was possible to get more than 99% pure biodiesel in all of the process models studied. These results were in agreement with similar studies in literature [65–67]. Table 1 indicated some significant technical aspects of the three process models for comparison.

Model III gave the higher amount of biodiesel whereas model II provided the least amount. This was because in Model II considerable amount of the FFA was consumed by saponification reaction, which could otherwise be converted into FAEE. In Model III, the pre-esterification reaction could provide additional FAEE, increasing the amount of biodiesel produced throughout the whole process. Model II showed the minimum performance by producing 0.99 metric ton of biodiesel for each metric ton of oil feedstock used, but it could still be taken as standard achievement. In all of the models, the use of distillation column for biodiesel purification could help to get high quality product to meet the ASTM standards. For instance, the higher percentage of glycerol was about 0.07 in the biodiesel from Model III, which was still far below the maximum allowable amount (0.24% wt.) according to the ASTM standard [68]. Higher amount (505 kg/h) and better quality (99%) of glycerol was attained in Model II. This was mainly because the catalyst was heterogeneous (with higher density difference) making the separation process very effective to get high amount and high quality glycerol [9,69]. This result was in agreement with some results from literature [13,70].

**Table 1**
Technical aspects of the process models studied.

| | Model I | Model II | Model III |
|---|---|---|---|
| Capacity (Thousands ton/year) | 41 | 41 | 41 |
| Process Temperature (°C) | 55 | 75 | 55&75[a] |
| Input stream (Kg/h) | | | |
| Oil feedstock | 5177.23 | 5177.23 | 5177.23 |
| Alcohol | 1646 | 2341 | 3285 |
| Sulfuric Acid | 109 | – | 117 |
| Output Streams | | | |
| Biodiesel (kg/h) | 5187 | 5132 | 5308 |
| Glycerol in biodiesel (wt. %) | 0.06 | 0.0014 | 0.07 |
| Performance[b] | 1 | 0.99 | 1.03 |
| Glycerol (kg/h) | 500 | 505 | 501 |
| Glycerol Purity (%) | 76 | 99.8 | 76 |
| Ethanol recovered (%) | 52 | 67.5 | 76 |

[a] 55 °C was in reactor number one and 75 °C was in reactor number two.
[b] Amount of biodiesel produced per amount of feedstock used.

### *4.2. Economic assessment*

The capital, operating, equipment, raw material, utilities and labor costs were estimated based on literature and market price from different suppliers in Ethiopia. The purchasing cost (delivered cost) of equipment were estimated based on Peters and Timmerhaus method [71] using the latest Chemical Engineering Plant Cost Index of 591.335 [72]. While calculating the equipment costs using this method, the cost of associated utilities, as well as installation and instrumentation costs were not included but the calculations of these cost categories are indicated under Section 4.2.1. The list and cost of equipment for each model are shown in Table 2.

#### *4.2.1. Capital costs*

In addition to the equipment purchasing cost, total capital investment cost includes working capital and startup & validation costs as well as direct and indirect expenses associated with instrumentation, insulation, piping, electrical facilities, auxiliary facilities and construction overheads, among others. The calculation of the direct and indirect expenses were based on percentage allocation on total purchasing cost of equipment as shown in Table 3.

Startup & validation cost for each scenario was taken to be 5% of the DFC. The two common indirect plant costs considered in the designs were engineering cost (25% of DFC) and construction cost (35% of DFC). Table 4 indicates capital cost categories and total capital investment cost for each Model for comparison.

As shown in Table 4, the most expensive alternative was Model I. In this alternative, the dominant reaction was the acid catalyzed transesterification reaction. Acid catalyzed transesterification is very slow reaction [73,74] and due to this it requires larger volume to attain equivalent production rate with its counterparts, such as alkali catalyzed transesterification. Therefore, in this scenario, Model I required a larger volume reactor in order to attain comparable production rate with the two other models. Such larger reactor volume resulted in higher equipment purchasing cost, higher facility dependent costs as well as very high amount of utilities required to run the process. Model II was the cheapest alternative. The dominant reaction in this model was the CaO catalyzed transesterification reaction. This reaction is relatively fast, it only takes 2 h to attain more than 97% conversion [41], favoring the alternative to have relatively smaller reactor volume. In addition, the use of CaO heterogeneous catalyst enabled to have less process steps required to attain a comparable production amount and quality with respect to the two other models. Model II, had total investment cost of 4.8 million US$, which was 31% less than that of Model III and 37% less than that of Model I. In all of the Models, the materials of construction for the reactors were stainless steel with 345kpa pressure.

#### *4.2.2. Operating costs*

The calculation of the operating costs included estimation of raw materials cost, facility dependent cost, labor dependent costs, costs associated with laboratory & quality control, utilities costs and some miscellaneous costs.

The raw materials, utilities and labor costs were taken based on current market prices from different sources in Ethiopia, since this

**Table 2**
List and cost of equipment involved in designing the three process models.

| Equipment | Equipment Cost for each Model (US$) | | |
|---|---|---|---|
| | Model I | Model II | Model III |
| Stirred tank reactor(s) | 628,562 | 165,000 | 477,000 |
| Distillation columns | 82,000 | 79,000 | 54,000 |
| Decanter Centrifuge(s) | 102,000 | 102,000 | 102,000 |
| Heat exchangers | 42,000 | 21,000 | 42,000 |
| Pumps | 6,000 | 6,000 | 6,000 |
| Unlisted equipment | 215,000 | 95,000 | 179,000 |
| Total Equipment cost | 1,077,000 | 476,000 | 897,000 |

**Table 3**
Direct plant cost categories and their percentage allocations with equipment cost [47].

| Cost category | % allocation with equipment cost |
|---|---|
| Piping | 20 |
| Instrumentation | 10 |
| Electrical | 15 |
| Insulation | 3 |
| Building | 15 |
| Yard improvement | 10 |
| Auxiliary facilities | 25 |
| Unlisted equipment | 20 |

**Table 4**
Total capital investment cost for each model for comparison (thousand US$).

| Capital cost category | Model I | Model II | Model III |
|---|---|---|---|
| Direct Fixed Capital Cost | 4437 | 1963 | 3715 |
| Working Capital | 3064 | 2765 | 3078 |
| Startup & Validation Cost | 222 | 98 | 186 |
| Total Capital Investment Cost | 7723 | 4827 | 6978 |

study envisioned possible development of biodiesel production plant in Ethiopia using Jatropha oil as feedstock. The cost of raw materials (delivered costs), utilities and labors considered in the process designs are indicated in Table 5. The oil feedstock used in all of the three models had FFA content of 10% of the oil on molar basis. According to some literatures, the cost of such feedstock can be put in a range of 478–684US$/ton [75,76]. For this study the average value, 580US$/ton or 0.58US$/Kg was taken as the cost of the acidic oil feedstock in all three designs.

Labor cost calculation was based on the basic rate estimated for each labor category. The estimation of the basic rate was done using the current wage indicator in Ethiopia [77] as minimum starting scale and by scaling up these payments to certain label to match international standards. The utilities considered in these processes models were steam, chilled water and electricity.

**Table 5**
Cost of raw materials, utilities and labor considered in the three process models.

| | |
|---|---|
| *Raw Material* | |
| Oil | 0.58 US$/Kg |
| Alcohol | 0.30 US$/Kg |
| Sulfuric Acid | 0.4 US$/Kg |
| CaO | 0.12 US$/Kg |
| *Utilities* | |
| Electricity | 0.09 US$/KW-h |
| Steam | 12 US$/MT |
| Chilled water | 0.4 US$/MT |
| *Labor (Basic rate)* | |
| Operator | 10 US$/h |
| Reactor Operator | 15 US$/h |
| Supervisor | 20 US$/h |

**Table 6**
Operating cost categories and their calculated values for each model.

| Operating Cost category | Operating cost amount in US$ | | |
|---|---|---|---|
| | Model I | Model II | Model III |
| Materials | 28,095,704 | 29,373,303 | 32,029,315 |
| Facility dependent | 2,371,419 | 981,693 | 1,858,907 |
| Labor dependent | 813,214 | 513,951 | 904,294 |
| Laboratory | 243,964 | 154,185 | 271,288 |
| Utilities | 4,792,603 | 531,308 | 921,461 |
| Miscellaneous | 110,000 | 110,000 | 110,000 |
| Total annual operating cost | 36,426,905 | 31,664,441 | 36,095,266 |
| *% of Raw Material Cost* | *77* | *93* | *89* |
| *% of Facility Dependent Cost* | *7* | *3* | *5* |
| *% of Utilities Cost* | *13* | *2* | *3* |

Table 6 displays the operating cost categories with their calculated amount for all models. Cost of materials include cost of oil, catalysts, and alcohol. Model III showed higher amount of material cost than the other two. This was due to a higher amount of alcohol and two catalysts, sulfuric acid and CaO, used in the two separate processes. The facility dependent and utility costs were very high in Model I mainly due to larger volume of the reactor. The facility dependent cost included cost for maintenance, depreciation, insurance, local tax and factory expenses.

The economic competitiveness of the models were evaluated based on the same assumptions for all the process. The process lifetime in all the models was considered to be 15 years with all the process plants operating in their full capacity. All the projects were supposed to be funded by own finance without any loan. It was also assumed that all the equipment depreciate throughout the lifetime of the project. Local tax was taken as 35% of the DFC and insurance was 2% of the DFC. The local tax amount was determined based on the possible tax allocations (such as corporate income tax and turnover tax) for such kind of investment in Ethiopia [78]. The calculation of the labor cost was using the detailed rate, where the basic rate was multiplied by the sum of the benefit, supervision, supplies and administration rates. The percent of work time devoted to process-related activities, which was used to estimate the labor time, was taken to be 70% in all of the models considering that they are continuous processes. Based on the same optimum market values of inputs for the three Models, their economic performance was evaluated and shown in Table 7 for comparison.

The unit production cost variation among the studied Models was considerable, with maximum variation of 0.11US$/kg. Moreover, these calculated unit production cost values were more or less in agreement with some similar studies done using different catalyst technologies and feedstock types [46,47,79]. For instance the unit production costs

**Table 7**
Economic performances of the models studied.

| | Model I | Model II | Model III |
|---|---|---|---|
| Feedstock Capacity (kg/year) | 41,003,662 | 41,003,662 | 41,003,662 |
| Annual Biodiesel Production (kg/year) | 41,115,414 | 40,644,750 | 42,115,566 |
| Total Investment cost (US$) | 7,723,101 | 4,827,041 | 6,978,211 |
| Annual operating cost (US$) | 36,426,905 | 31,664,441 | 36,095,266 |
| Total Annual Revenue (US$) | 34,342,293 | 33,305,116 | 33,187,279 |
| Unit Production Cost (US$/kg) | 0.8860 | 0.7791 | 0.8571 |
| Net Unit Production Cost (US$/kg) | 0.8034 | 0.6867 | 0.7240 |
| Unit Production Revenue (US$/kg) | 0.8353 | 0.8194 | 0.7880 |
| Gross Margin (%) | 3.81 | 16.19 | 8.12 |
| Return Over Investment, ROI (%) | 15.63 | 75.09 | 28.36 |
| Payback Time (year) | 6.4 | 1.33 | 3.53 |
| Net Present Value at 7% (US$) | −19,345,239 | 7,051,638 | −30,424,382 |

calculated by Karmee et al. [47] using three catalyst technologies (base, acid and lipase) to produce biodiesel from waste cooking oil were in a range of 0.75 US$/kg up to 1.048US$/kg. In our study, the maximum unit cost of production was 0.886US$/kg in Model I and the minimum was 0.779US$/kg in Model II.

As shown in Table 7, Model I took longer time to payback the investment and had the second minimum NPV at 7% interest rate. It was also more expensive to produce biodiesel using Model I and Model III than Model II. Model II found to be the better alternative in terms of economic performances. Even though the amount of biodiesel produced was the least, Model II showed positive NPV at 7% interest, higher ROI and minimum payback time. However, Model I and III had poor economic performances, which could be indicated by negative NPV for the same optimum market values of inputs and outputs applied for the three Models.

### 4.3. Sensitivity analysis

There was a wider gap in economic performances among the Models studied. This in turn invited to further investigate the sensitivity of the technologies towards the possible fluctuation of market values of the input and output variables. Because, the economic feasibility of such technologies are always compromised by the market prices of inputs and outputs, such as price of biodiesel, price of feedstock, as well as operation cost [55]. This demands a systematic investigation of how these market variables affect the feasibility of the business. With this respect, the effect of two main market variables (oil cost and biodiesel price) were tested to investigate how the economic feasibility of process alternatives could be affected by change of cost of these market variables. The economic parameter used to test the effect of the market variables was the NPV. It denotes the present value of net cash inflows generated by a project minus the initial investment on the project. It is one of the most meaningful measures of capital budgeting in a project because it considers time value of money.

#### 4.3.1. Effect of change of oil purchasing cost on NPV

The first sensitivity analysis was done on the purchasing cost of oil feedstock. Oil feedstock took the higher share of the material cost and thus the total operating cost. This implied that the fluctuation of the cost of oil feedstock could affect the biodiesel production business. To test how NPV changes with change in cost of feedstock, a feedstock price range of 0.45 up to 0.59US$/kg was taken. Fig. 5 shows the effect of change of oil feedstock purchasing cost on NPV among the models.

The percentage share of cost of oil feedstock from total raw material cost was 85% for Model I, 81% for Model II and 74% for Model III. As shown in Fig. 5, the tendency of change of NPV with oil feedstock purchasing cost was the same for Model I and II, with a little change for Model III in this regard. In addition, among the three models, Model III showed more sensitivity to the change in oil feedstock cost, particularly above 0.480US$/kg. For instance, a 0.02US$/kg change in oil feedstock cost would result a decrease in NPV of 7.5 Million US$ for Model III and 5.8 Million US$ for Model I. In Model III, oil feedstock price above 0.490US$/kg would make the business unprofitable. For Model I, the maximum oil cost that could still make the business profitable was 0.509US$/kg. Accordingly, Models I and III were the least dependable alternatives for sustainable production of biodiesel. However, Model II showed more tolerance to fluctuation of oil cost, enabling to accommodate relatively expensive feedstock, up to 0.590US$/kg, and make the business profitable with positive NPV.

#### 4.3.2. Effect of change of biodiesel selling price on NPV

The other market variable considered for sensitivity analysis was the biodiesel selling price. As biodiesel is the main product stream for all the processes, its selling price could have strong effect on the profitability of the businesses. For this study a selling price range of 0.75 up to 0.87 US$/kg of biodiesel was taken into consideration. Fig. 6 shows the effect of change of biodiesel selling price on NPV among the three models.

As shown in Fig. 6, Models I and II had the same tendency in change of NPV due to change in biodiesel selling price. Whereas, Model III had a little difference in tendency of change of NPV, indicating higher change, particularly below 0.870US$/kg of biodiesel price. Because of this, Model III was the most sensitive to a decrease in the selling price of biodiesel. The minimum price, below which the business would be unprofitable, was 0.865US$/kg for Model III and 0.853US$/kg for Model I. Model II had more tolerance to market fluctuation of the selling price of biodiesel up to the minimum value of 0.754US$/kg.

## 5. Conclusion

The techno-economic analysis of biodiesel production from acidic oil was carried out for three production technologies using two catalyst types. The technical performances of the three technologies were compared in terms of the amount and quality of biodiesel, amount and purity of glycerol produced as well as the amount of biodiesel produced per amount of raw materials consumed. Accordingly, it was possible to get higher amount of biodiesel produced using Model III. Model II produced the least amount of biodiesel. At optimum production conditions, the biodiesel yield variation among the models could get up to 176 kg/hr. Model III showed the maximum performance by producing

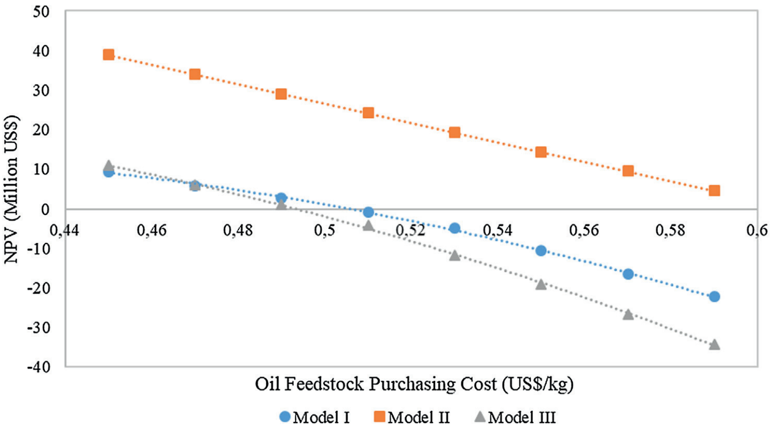

**Fig. 5.** Effect of change of oil cost on NPV for Model I (●), Model II (■) & Model III (▲).

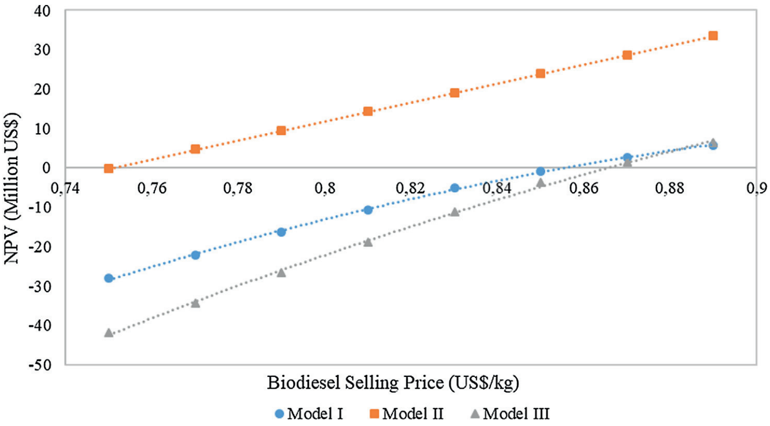

**Fig. 6.** Effect of change of biodiesel selling price on NPV for Model I (●), Model II (■) & Model III (▲).

1.03 metric ton of biodiesel for each metric ton of oil feedstock used. The purity of the biodiesel produced from all technological alternatives studied was in line with the quality requirement of ASTM in terms of percentage of total glycerol. Model II could produce high quality glycerol, as it used heterogeneous catalyst. Whereas, in Models I and III, the quality of glycerol produced was less due to the presence of $CaSO_4$ as a product of catalyst neutralization reactions in the two Models. The presence of $CaSO_4$ could make the separation inefficient resulting in poor quality of the glycerol. Model I produced less amount of glycerol compared to the other two models.

The economic performances of the three alternatives were assessed in terms of the total investment cost, total operating cost, unit production cost, ROI, Gross Margin, payback time and NPV. Accordingly, compared to the two other models, Model II was the superior alternative scoring better results in all of the parameters. It showed lower unit production cost, shorter payback time, and larger amount of NPV at 7% interest rate, to mention some.

The effect of change of oil feedstock cost and biodiesel selling price on NPV was analyzed for the three models and the results were compared. It was clearly indicated that Model II was more tolerant than the two models for market fluctuations of purchasing cost of oil feedstock and selling price of biodiesel.

## Disclaimer

The authors do not have responsibility for a decision made based on the results of these process designs. The process designs indicated in this work are solely for research purposes. For specific applications, please contact the authors to get information about the limitations and scope of the process designs.

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## Conflict of Interest

All authors declare no conflicts of interest in this paper.

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# Paper IV

Modeling and Analysis

Biofpr Biofuels Bioproducts & Biorefining

# The effect of economic variables on a bio-refinery for biodiesel production using calcium oxide catalyst

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Abstract: This study investigates the effect of market variables on biodiesel production and considers a calcium oxide catalyzed transesterification process. A conceptual process simulation of a plant using Super Pro software was used to vary the economic scenarios and to evaluate the effects of selected variables such as prices of biodiesel, glycerol, oil, alcohol, catalyst, equipment maintenance, labor, and tax variation. Changing the values of these variables led to large effects on the overall economics of the production process. Oil purchasing cost exerted a larger influence on the economic outcome, with an approximately 73% decrease in net present value (NPV) for a 22% increase in the oil purchasing cost. Under optimum conditions the process would be profitable for oil costs below 590US\$ ton$^{-1}$. Varying the equipment maintenance costs produced a smaller effect, which could allow the amount of cost allocated for routine maintenance activities to be increased to sustain the productivity of the process. The study could also provide cutoff values for each variable for economic feasibility of the process at the given market scenario. © 2019 The Authors. *Biofuels, Bioproducts, and Biorefining* published by Society of Chemical Industry and John Wiley & Sons, Ltd.

Keywords: biodiesel; calcium oxide; economic variables; sensitivity analysis

## Introduction

Biodiesel is mono alkyl ester of long-chain fatty acids, which is produced through the transesterification of renewable feedstock like vegetable oil, animal fat, tallow, non-edible plant oil, and waste cooking oil. As a fuel, it has significant benefits over fossil diesel. Biodegradability, non-toxicity, lower pollution, and lower greenhouse gas (GHG) emissions are the main advantages.[1, 2] Lower emission of pollutants and GHGs is attributed to the existence of more free oxygen than is the case with conventional diesel. More free oxygen leads to complete combustion and reduced emissions.[3, 4] Moreover, biodiesel has better lubricity than fossil diesel.

Homogeneous base catalyzed transesterification is the conventional commercial way of producing biodiesel. It results in much higher catalytic activity in the transesterification reaction and causes less corrosion of equipment than acid catalysts.[5] However, with this method it is a considerable challenge to make the overall biodiesel production economics competitive with fossil diesel. This is mainly because it requires high oil quality

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with free fatty acid (FFA) content of less than 0.5%.[6] Such high-quality feedstock is associated with high purchasing costs, thus making the final product expensive.[7] Several studies have been conducted to investigate possible alternatives, which can suggest technical possibilities for producing biodiesel in an economically competitive manner. These include using cheaper feedstock and catalyst or using least-cost technological options.[7–9] Particular interest has been directed towards heterogeneous alkaline catalyzed,[10–13] homogeneous and heterogeneous acid catalyzed,[14–18] enzyme catalyzed,[19–21] and supercritical[22–24] transesterification of oil / fat feedstock with different FFA content. Some advanced technologies are also receiving attention as alternative technological options. Among them are nanocatalysts,[25–27] nano-immobilized enzymes,[28,29] and ionic liquid catalysts.[30–32]

Heterogeneous base catalyzed transesterification has shown great advantages over the rest and therefore it has been a focus of attention with the aim of reducing the overall cost involved when producing biodiesel.[13,33] This particular method uses cheaper catalysts with relatively higher catalytic activity, and requires easy catalyst recovery, which enables repeated use of the catalysts.[34–36]

Calcium oxide is the most widely studied heterogeneous catalyst among the alkaline earth metal oxides, which could give a fatty acid methyl ester (FAME) yield up to 98%.[35, 37, 38] The effective character of this catalyst is attributed to its nano-crystallized particle size and smaller defects, which give a higher surface area. Moreover, CaO presents higher basicity, lower solubility, and a lower price, and it is easier to handle than the conventional homogeneous alkaline catalysts such as NaOH and KOH.[39] Ljupkovic *et al.* [4] investigated the significance of the structural properties of a CaO catalyst in the production of biodiesel and discovered that the catalyst has benefits such as short contact time (up to 2 h), standard operating temperature (64 °C) and atmospheric pressure, a relatively low molar ratio (6:1), and small catalyst loading (1 wt.%). This study revealed that all the above factors could result in attaining a very high biodiesel yield with a high level of purity (> 95%).[4] In another study, by Avhad *et al.*,[40] it was reported that the optimum reaction conditions to obtain the maximum conversion within 2 h, for ethanolysis of avocado oil using glycerol enriched CaO catalyst, is 75 °C reaction temperature, 9:1 molar ratio of ethanol to oil, and 7% catalyst amount with respect to weight of the oil. A similar study by Sánchez *et al.* [41] indicated that it took about 10 h to reach the maximum 93.3% conversion of Jojoba oil into biodiesel using a CaO catalyst prepared through calcination of mussel shells. The optimum reaction conditions for this process were taken to be 65 °C reaction temperature, the catalyst amount, respect to the oil mass is 8 wt%, and 9:1 methanol-to-oil ratio.[41] Table 1 shows a summary of studies of the optimization of biodiesel production from different feedstocks using heterogeneous CaO catalysts.

Although some studies mentioned that CaO can be reused many times as a catalyst for transesterification,[13,45,49] its reusability is usually compromised by a fast decrease in surface basicity, reducing its catalytic activity, because it adsorbs $CO_2$ and water from the atmosphere when exposed to air.[50] However, one can simply wet the catalyst with methanol, oil, or biodiesel to prevent poisoning of the CaO by $CO_2$, because these liquids could occupy the pores of the catalyst and significantly minimize the $CO_2$ and water adsorption.[51] For instance, if a biodiesel is added to activated CaO catalyst to form a catalyst paste, its catalytic activity could be maintained at least for 24 h because the formation of the paste prevents the diffusion of $CO_2$ and water.[51]

The immediate use of a recycled catalyst can be another option to avoid the poisoning of the catalyst due to the formation of a layer of $CaCO_3$ and $Ca(OH)_2$. Furthermore, the formation of calcium oxide glycerin complex, due to the presence of glycerin and the CaO catalyst, could make the catalyst tolerant to air exposure [52] and this complex could function as the main catalyst to accelerate the transesterification reaction.[53–55] This can be considered as the other advantage of using CaO as a catalyst for the transesterification reaction.

There are some works where the economics or the effect of market variables for a biodiesel production plant using CaO have been studied. Sakai *et al.* [56] conducted a feasibility study for producing biodiesel from waste cooking oil using four processes with four different catalysts. Among them, a heterogeneous CaO catalysis together with hot water purification process (CaO-W) and a heterogeneous CaO catalysis together with a vacuum FAME distillation process (CaO-D) were presented and analyzed. The authors studied the fixed and manufacturing costs for biodiesel production using each of the four processes at a different production capacity. They concluded that the manufacturing costs for CaO-W and CaO-D process were competitive in comparison to the two other homogeneous KOH catalyst alternatives. Moreover, the combined effect of the low cost of the CaO catalyst and the absence of the expensive distillation process gave the CaO-W process alternative the lowest manufacturing cost within the production range of 1452 ton year$^{-1}$ to 14 520 ton year$^{-1}$.[56]

The promising technical capability of the CaO catalyst for biodiesel production invites further investigation of the feasibility of using this catalyst in the production of fuel-quality biodiesel. Accordingly, this work has analyzed the effect of a number of economic variables over biodiesel production plant using CaO as a catalyst. The analysis could help to understand how sensitive the selected production process might become towards the change in market values of most economic variables, which are more influential in the process of biodiesel production. The market variables considered were biodiesel price, glycerol price, oil feedstock price, alcohol price, catalyst price, labor cost, equipment maintenance cost, and variations in local taxes. The objective was to test how these variables could affect the feasibility of the business.

To perform this study, a complete simulation of the process flow was designed using both Super Pro and Aspen Plus software. The Aspen Plus design was used to recheck the accuracy of the simulation done by Super Pro, as it considers a wider choice of property methods and physical parameters. Even though there are wider differences between process simulation results and the actual process operation, it is possible to obtain reliable information on process operations when we use Super Pro software. This is because the Super Pro design considers specific chemical component properties and the application of advanced calculation techniques.

**Table 1. Summary of optimum reaction conditions for CaO catalyzed biodiesel production processes.**

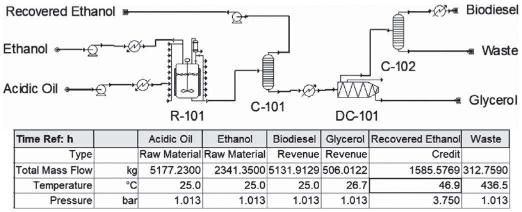
| Feedstock | Alcohol | Catalyst | Optimum reaction conditions | | | | Catalyst reusability | Yield (%) | Conversion (%) | References |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Temperature (°C) | Alcohol to oil molar ratio | Reaction time (h) | Catalyst amount (%) | | | | |
| Fried vegetable oil | Methanol | CaO | 65 | 6:1 | 1.5 | 5 | NA | 92 | 85 | 42 |
| *Jatropha curcas* oil | Methanol | CaO in $(NH_4)_2CO_3$ | 70 | 9:1 | 2.5 | 1.5 | NA | 95.45 | 93 | 43 |
| Sunflower oil | Methanol | CaO | 60 | 13:1 | 1.67 | 3 | NA | 94 | NA | 44 |
| Soybean oil | Methanol | CaO | 65 | 12:1 | 1.5 | 8 | 20 times | 95 | NA | 45 |
| Palm oil | Methanol | CaO in $Al_2O_3$ | 65 | 12:1 | 5 | 6 | NA | 98.64 | 95 | 46 |
| Waste cooking oil | Methanol | CaO | 65 | 13:1 | 3 | 5 | 11 times | 90.7 | 98 | 38 |
| Palm oil | Methanol | CaO from waste crab shell | 65 | 13:1 | 2.5 | 5 | 11 times | 98.8 | NA | 47 |
| Soybean oil | Methanol | CaO from egg shell | 65 | 9:1 | 3 | 3 | 17 times | >95 | NA | 48 |
| Avocado oil | Ethanol | CaO enriched with glycerol | 75 | 9:1 | 2 | 7 | NA | 91.82 | 97.58 | 40 |
| Jojoba oil | Methanol | CaO from mussel shell | 65 | 9:1 | 10 | 8 | NA | NA | 93.3 | 41 |

## Study case and process description

This study considered the production of biodiesel from acidic oil using CaO as a solid catalyst. The FFA content of the oil feedstock was taken to be 10% on a molar basis with respect to the oil. Acidic oil is considered to represent most of non-edible plant oil, which has higher FFA content and is usually cheaper. A conceptual process model with a biodiesel production capacity of 40 700 ton year$^{-1}$ was designed. The process flowsheet designed using Super Pro is as shown in Fig. 1. The entire process has four main unit procedures: transesterification, ethanol recovery, biodiesel, and glycerol separation and biodiesel purification.

### Transesterification

The transesterification reaction considered in the process design is the typical CaO catalyzed reaction between ethanol and acidic oil. Acidic oil at 5177.23 kg h$^{-1}$ and ethanol at 2341.35 kg h$^{-1}$ are heated to 75 °C and simultaneously supplied to the fixed bed reactor (R-101) packed with 362.41 kg CaO catalyst. In the reactor both transesterification and saponification reactions are considered to happen. Transesterification takes place when triglyceride reacts with ethanol in the presence of the solid



| Time Ref: h | | Acidic Oil | Ethanol | Biodiesel | Glycerol | Recovered Ethanol | Waste |
|---|---|---|---|---|---|---|---|
| Type | | Raw Material | Raw Material | Revenue | Revenue | Credit | |
| Total Mass Flow | kg | 5177.2300 | 2341.3500 | 5131.9129 | 506.0122 | 1585.5769 | 312.7590 |
| Temperature | °C | 25.0 | 25.0 | 25.0 | 26.7 | 46.9 | 436.5 |
| Pressure | bar | 1.013 | 1.013 | 1.013 | 1.013 | 3.750 | 1.013 |

Figure 1. Flow diagram for production of biodiesel using CaO catalyst: R-101 fixed bed reactor for biodiesel production, C-101 first short cut distillation for excess ethanol recovery, DC-101 centrifugal decanter for glycerol separation and C-102 distillation column for biodiesel purification.

catalyst CaO to produce biodiesel and glycerol, whereas saponification is between oleic acid and some amount of CaO catalyst to produce calcium oleate (calcium soap) and water. The reaction conditions in the reactor are set to 75 °C, 7% catalyst amount with respect to oil amount, and a 9:1 ethanol to oil molar ratio, based on the optimum reaction conditions indicated in the literature.[40, 49, 57] Under these reaction conditions, the maximum conversion of triglyceride of 97.58% can be achieved within 2 h.[40] Accordingly, 2 h of reaction time and 97.58% triglyceride conversion are taken during designing the reactor. The product is removed from the reactor at a rate equal to the rate of charging with reactants in such a manner as to give a residence time of 2 h in the reactor. The product from the reactor is then let into a distillation column to recover excess ethanol.

## Ethanol recovery

The transesterification reaction is an equilibrium reaction with a stoichiometric molar ratio of alcohol to oil of 3:1. It is advisable to use excess alcohol to encourage a forward reaction and thus obtain more product.[58] For this reason, in this particular process, the ethanol-to-oil molar ratio considered is 9:1 and thus excess ethanol after the reaction has to be recovered for reuse. To recover the excess ethanol, a distillation column (C-101) is designed with a 1.6 reflux ratio and working under vacuum at 0.25 bar to prevent thermal decomposition of biodiesel and glycerol during distillation.[59] The heating agent is steam. The stage efficiency of the column is taken to be 80% resulting in six actual stages. The upper output from the distillation column is 99.3% pure ethanol, which can be reused or taken as credit in the economic calculations. The bottom output, mainly composed of ethyl ester, glycerol, and the calcium soap is further made to flow into a centrifugal separator (DC-101) where crude biodiesel is separated from glycerol.

## Biodiesel and glycerol separation

The use of heterogeneous catalysts does have the advantage of making the biodiesel and glycerol separation and purification processes very easy. In this particular process model a simple centrifugal decanter (DC-101) is designed to separate the crude biodiesel from the glycerol. The decanting is based on oil removal – crude biodiesel with higher purity is separated. The crude biodiesel, from the upper outlet of the DC-101, is then let into the second distillation column (C-102) for further purification of the biodiesel product. The bottom outlet from the centrifugal decanter (DC-101) is mainly composed of glycerol byproduct with few impurities from the remaining biodiesel, water, and unreacted oil. The glycerol produced using heterogeneous catalysts like CaO is expected to be easily separated and have very high purity up to 98%.[11, 43, 46]

## Biodiesel purification

Biodiesel purification is mostly performed using wet and dry washing.[60–62] Washing has some disadvantages, such as higher process costs, longer washing time, production of a large amount of wastewater, and emulsification because of continuous stirring to facilitate the washing.[63, 64] Moreover, when basic heterogeneous catalysts like CaO are used, soaps form, which cannot be removed easily and effectively through washing.[61, 62, 64] In this study, a distillation column is designed to obtain the maximum possible pure biodiesel. The distillation column (C-102) is with three reflux ratio and seven number of stages, beyond which there would be no change in improving purity of the biodiesel. The upper output from this distillation column, the distillate, is the pure biodiesel at higher temperature. This has to be cooled to ambient temperature using a cooler. The bottom outlet from the distillation column, which mainly consists of unreacted oil and calcium soap, is considered to be waste, for safe disposal without further waste treatment. Table 2 shows a summary of operating conditions for each of the four main unit procedures required to complete the whole production process.

# Economic assessment

This study considered eight groups of market variables known to affect the economic feasibility of chemical production processes. The downstream equipment and the unit procedures involved are well known for providing fuel-quality biodiesel. The simulation of the process used Aspen Plus and Super Pro, which is commercially available

**Table 2. Summary of operating conditions in each main unit procedures.**

| | |
|---|---|
| *Transesterification reaction in R-101* | |
| Reactor type | CSTR (22.85 $m^3$) |
| Temperature | 75°C |
| Pressure | 1.013 Bar |
| Catalyst | CaO |
| Alcohol-to-oil ratio | 9:1 |
| Conversion | 97.58% of triglyceride |
| *Ethanol recovery in C-101* | |
| Stage efficiency | 80% |
| Number of actual stages | 6 |
| Reflux ratio | 1.6 |
| Column pressure | 0.25 bar |
| Distillate flow rate | 1579.5 $kg\,h^{-1}$ |
| Recovery | 67.46% |
| Distillate purity | 99.6% |
| *Biodiesel separation in DC-101* | |
| Sedimentation efficiency | 30% |
| Equipment rating | Based on oil/fat removal |
| Oil concentration in oil stream | 870 $g\,L^{-1}$ |
| Purity of the biodiesel | 92% |
| Glycerol flow rate | 505 $kg\,h^{-1}$ |
| Glycerol purity | 99 |
| *Biodiesel purification in C-102* | |
| Stage efficiency | 80% |
| Number of actual stages | 11 |
| Reflux ratio | 3 |
| Distillate flow rate | 5132 $kg\,h^{-1}$ |
| Distillate purity | 99.99% |

software. Aspen Plus was used for energy and material balance, as it has a wider choice of thermodynamic and property methods, depending on the type and properties of the chemicals and the chemical reactions involved. This could improve the accuracy of the design and the reliability of the results. The results from this process design could apply to most of the non-edible oil types, which have an FFA content of up to 10%.

A technical assessment indicated that this method is capable of producing biodiesel of the required quality and quantity. This is in agreement with similar studies.[40, 46, 48] For instance, the yield before purification is about 92% biodiesel. This is also in agreement with the results reported in the literature,[37, 40, 45] which investigated production under similar reaction conditions. This encourages further assessment of the economic feasibility of the whole production process. However, not many studies have investigated the economic aspects of producing biodiesel from acidic oil using CaO as catalyst. In this study, the current best values of materials, equipment, utilities, and labor costs are used in the calculation of capital investment costs and operating costs using the process model that was designed.

## Estimation of capital costs

Total capital investment includes direct plant costs (equipment purchasing cost, installation, instrumentation, insulation, etc.), indirect plant costs (such as engineering and construction costs), working capital, and startup and validation costs. The equipment costs were calculated based on the Peters and Timmerhaus method [65] and the latest Chemical Engineering Plant Cost Index used was 591.34. Based on the process flow diagram shown in Fig. 1 and the estimated cost of equipment, and the market price of input materials, labor and utilities, it was possible to calculate capital cost, production cost, and revenue. Table 3 summarizes the capital cost calculation.

A considerable amount of the plant's direct cost is for equipment purchase, and the reactor and the centrifuge have the largest cost of the process equipment considered in this design. Other components of the direct fixed capital cost are calculated based on the equipment purchasing cost following a percentage allocation from the literature,[8] as presented in Table 3. Engineering cost and construction cost are the two main indirect plant cost components. These costs are taken to be 25% and 35% of the direct cost respectively. The total plant cost, which is the sum of the plant direct costs and the plant indirect costs, is calculated to be US$1 526 000. The direct fixed capital cost includes the total plant cost, contractor's fee, and contingency, and comes to US$1 756 000. Finally, by adding the working capital, validation cost, and the direct fixed capital cost, the total capital investment cost for the construction of the designed plant capacity is estimated to be US$4 646 000.

## Estimation of operating costs

The literature and current market prices from different suppliers have been used as main sources of cost estimation for raw materials, labor, and utilities. The cost of raw materials, labor, and utilities considered in this process design are indicated in Table 4. Raw materials include oil feedstock, ethanol, and CaO catalyst. The oil feedstock considered has a FFA content of 10% of the oil on a weight basis. The potential cheaper feedstock types do have a higher FFA value.[7, 66, 67] According to some sources from the literature, the cost of such feedstocks can be placed in a range from US$478–684 $ton^{-1}$.[68, 69] For this study the

**Table 3. Capital costs for the construction of a biodiesel production plant with 40 700 ton year$^{-1}$ production capacity.**

| Cost categories | % allocation* | Amount (US$000) |
|---|---|---|
| *Direct plant cost (DC)* | | |
| Equipment purchasing cost (PC) | | 341 |
| Installation | 20 × PC | 68 |
| Process piping | 20 × PC | 68 |
| Instrumentation | 10 × PC | 34 |
| Insulation | 3 × PC | 10 |
| Electrical | 15 × PC | 51 |
| Building | 15 × PC | 51 |
| Yard improvement | 10 × PC | 34 |
| Auxillary facilities | 25 × PC | 85 |
| Purchasing cost of unlisted equipment (UEPC) | 20 × PC | 68 |
| Installation cost of unlisted equipment | 50 × UEPC | 34 |
| *Total plant direct cost (DC)* | | ***844*** |
| *Indirect plant cost (IC)* | | |
| Engineering | 25 × DC | 211 |
| Construction | 35 × DC | 296 |
| Other indirect costs | | 175 |
| *Total Plant indirect cost (IC)* | | ***682*** |
| Contractors' fee | 5 × (DC + IC) | 76 |
| Contingency | 10 × (DC + IC) | 153 |
| *Sum of Contactor's fee and contingency (CFC)* | | ***229*** |
| *Total direct fixed capital cost (DC + IC + CFC)* | | ***1756*** |
| *Working capital (WC)* | | ***2764*** |
| *Startup and validation cost (SVC)* | | ***87.8*** |
| *Total capital investment cost (DC + IC + CFC + WC + SVC)* | | 4608 |

*Percentage allocation is based on Karmee *et al.*[8]

**Table 4. Cost of raw materials, labor, and utilities for optimum production of biodiesel using the process models.**

| | |
|---|---|
| *Raw material* | |
| Oil | 0.58 US$ kg |
| Alcohol | 0.3 US$ kg$^{-1}$ |
| Catalyst | 0.12 US$ kg$^{-1}$ |
| Water | 0.02 US$ kg$^{-1}$ |
| *Utilities* | |
| Electricity | 0.09 US$ KW-h |
| Steam | 12 US$ MT$^{-1}$ |
| Chilled water | 0.4 US$ MT$^{-1}$ |
| *Labor (basic rate)* | |
| Operator | 20 US$ h$^{-1}$ |
| Reactor operator | 25 US$ h$^{-1}$ |
| Supervisor | 30 US$ h$^{-1}$ |

average value, 580US$ ton$^{-1}$ or 0.58US$ kg$^{-1}$, is taken as the cost of the acidic oil feedstock. The costs for alcohol, catalyst, and water are based on the current market price in Ethiopia. Table 4 summarizes operating / production cost categories considered in the design.

The labor cost calculation is carried out using the basic rate estimated according to the labor category. The current wage indicator in Ethiopia [70] is the basis for estimation of the basic rate. Such a calculated labor cost is used as a minimum payment and then it is scaled up to a certain payment level. The utilities considered in this process model are steam, chilled water, and electricity. The market values for each of these utilities are estimated based on the literature and on current market prices in Ethiopia. Table 5 summarizes the operating cost categories.

The dominant cost category in the production cost calculation is that of raw materials. It accounts for 93% of the total production cost, and 81% of this material cost is due to cost of oil feedstock for biodiesel production. This agrees well with most similar studies using different catalysts and feedstock.[8, 71] The unit production cost is around 0.78 US$ kg$^{-1}$ or 0.67 US$ L$^{-1}$ biodiesel. This value is relatively lower than the value reported by Apostolakou *et al.* [71] (1.15 US$ L$^{-1}$ or 1.318 US$ kg$^{-1}$) and higher than the values reported by Marchetti *et al.* [67] (0.5084 US$ kg$^{-1}$ up to 0.5223 US$ kg$^{-1}$) and Haas *et al.*[66] (0.53 US$ L$^{-1}$).

## Sensitivity analysis over some market variables

The cost of raw materials and prices of products in the chemical industry scheme are commonly dictated by the global economy. Similarly, in biodiesel production processes, the price of the biodiesel and the cost of raw materials in the market can sometimes make the business profitable. This kind of situation reduces the confidence of investors in such businesses. In line with this, it is always necessary to investigate how such market variables can affect the economic feasibility of the business, considering the possible ranges of prices.

In this study, price ranges have been set for biodiesel, glycerol, acidic oil feedstock, ethanol, CaO catalyst, labor

**Table 5. Summary of operating cost calculations for biodiesel production capacity of 40 700 ton per year.**

| Cost category | Calculation | Amount (US$000) | % |
|---|---|---|---|
| 1. Raw materials | From material balance | 29 373 | 93 |
| 2. Utilities cost | From material balance | 476 | 1.5 |
| *Variable costs (VC)* | *(1) + (2)* | ***29 849*** | |
| 3. Maintenance | 6% × PC | 26 | 0.8 |
| 4. Operating labor | Manning estimates | 560 | 1.8 |
| 5. Laboratory cost | 30% × (4) | 168 | 0.5 |
| 6. Depreciation | 11.6 × DC | 98 | 0.3 |
| 7. Insurance | 2% × DFC | 35 | 0.1 |
| 8. Local tax | 35% × DFC | 615 | 1.8 |
| 9. Factory expense | 5% × DFC | 89 | 0.3 |
| 10. Miscellaneous | Fixed | 70 | 0.2 |
| *Fixed costs (FC)* | *(3) + (4) + ……+ (9)* | ***1661*** | |
| *Annual operating cost* | *(VC) + (FC)* | ***31 510*** | |
| *Unit production cost* | *31.51 M$/40.7MKg biodiesel* | = 0.775 $\text{US\$ kg}^{-1}$ | |
| | | = 0.67 US$ L | |

cost, local tax, and maintenance cost as main market variables to see how the payback time and net present value (NPV) change in response to different values of these eight market variables. The market variables and their respective price ranges are shown in Table 6.

## Effect of changes in biodiesel selling price

The selling price of biodiesel has a distinctive influence on the profitability of the biodiesel production business. This price, in turn, is governed by market demand and government policy interventions, like taxes and subsidies associated with services using the fuel. Thus, analyzing profitability of the business by considering different price scenarios would help to maintain confidence when attempting to sustain the business in the market. For this study the range of biodiesel selling prices has been taken as 0.77–0.84 $\text{US\$ kg}^{-1}$, considering all the above factors. This price range is in agreement with the current market price of biodiesel.[72] Figure 2 shows the effect of the change in the price of biodiesel on payback time and NPV.

The NPV increases linearly as the biodiesel selling price increases. The payback time is decreasing in a non-straight manner as the selling price of the biodiesel is increasing. At the beginning, the increase in selling price causes a very large response in terms of the payback time, which tends to slow as the price becomes higher, above about 0.81 $\text{US\$ kg}^{-1}$. Figure 2 shows that a fraction increase in biodiesel selling price would bring about a considerable change in the NPV. With optimum production conditions, this analysis has indicated that selling the biodiesel with a price below 0.775 $\text{US\$ kg}^{-1}$ is not profitable.

**Table 6. Studied ranges for the market variables.**

| Market variables | Minimum value | Standard value | Maximum value |
|---|---|---|---|
| Biodiesel selling price ($\text{US\$ kg}^{-1}$) | 0.77 | 0.78 | 0.84 |
| Glycerol selling price ($\text{US\$ kg}^{-1}$) | 0.05 | 0.12 | 0.18 |
| Oil purchasing cost ($\text{US\$ kg}^{-1}$) | 0.45 | 0.58 | 0.68 |
| Ethanol purchasing cost ($\text{US\$ kg}^{-1}$) | 0.1 | 0.30 | 0.35 |
| CaO purchasing cost ($\text{US\$ kg}^{-1}$) | 0.08 | 0.12 | 0.22 |
| Equipment maintenance (% of PC) | 3 | 6 | 40 |
| Local tax (% of DFC) | 15 | 30 | 45 |
| Labor cost (basic rate in $\text{US\$ h}^{-1}$) | | | |
| Operator | 10 | 20 | 30 |
| Reactor operator | 15 | 25 | 35 |
| Supervisor | 20 | 30 | 40 |
| Total basic rate ($\text{US\$ h}^{-1}$) | 45 | 75 | 105 |

## Effect of changes in the glycerol selling price

As the main byproduct of the biodiesel production industry, glycerol can be a significant factor in the profitability of the

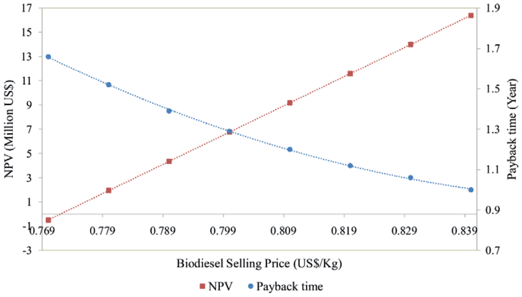


Figure 2. The effect of the variation of biodiesel price on payback time (●) and NPV (■).

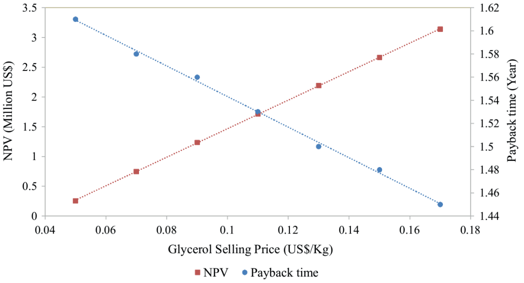


Figure 3. The effect of change of glycerol selling price on payback time (●) and NPV (■).

biodiesel production process by increasing the total revenues of the business. However, its market value is mostly determined by its quality. The required quality of glycerol in the market can be as high as pharmaceutical quality or, on the other hand, as low as the quality of unrefined industrial glycerol. Pharmaceutical-quality glycerol (refined glycerol) has a higher price and, in the current US market, it can be sold for up to 960US\$ ton$^{-1}$.[73] The industrial-quality glycerol (unrefined glycerol), mainly from the biodiesel production process, may vary in quality depending on the technology involved. Consequently, these industrial glycerol products can be sold for up to 0.15US\$ kg$^{-1}$.[74]

In this particular study, the amount of glycerol produced with 87.8% purity is about 9.8% of the total production of biodiesel. It is therefore worth considering the glycerol for market. A price range of 0.05 up to 0.18 US\$ kg$^{-1}$ has been assumed in order to investigate how payback time and NPV could change.

Figure 3 indicates that the payback time changed inversely with the glycerol selling price whereas the NPV increased with an increasing glycerol price. A 0.05US\$ kg$^{-1}$ increase in the glycerol price would make a US\$1.21 million change in the NPV. However, the effect of the glycerol price on the payback time is less significant in comparison with the effect when the biodiesel price varies. An increase in price of glycerol by US\$0.12 (three fold increment) could only decrease the payback time by 0.15 years but resulted in an increase in the NPV by about US\$2 881 000 (an 11-fold increment). If glycerol is considered to have a zero value, the production process could become unprofitable.

## Effect of change of oil purchasing cost

The cost of feedstock takes a larger percentage of cost of biodiesel production. The highest share is when an oil with less free fatty acid content, like vegetable oil, is used. Feedstock with high free fatty acid content does have a relatively lower cost and this would provide opportunities to reduce the cost of production. This implies that the feedstock chosen could largely affect the profitability of biodiesel production business. In this study a cost range of 0.45–0.68 US\$ kg$^{-1}$ has been used. This cost range has been set based on the literature on the cost of acidic oil feedstock.[68, 69]

The feedstock type considered here is the same feedstock with the same FFA content within the stated cost range. However, it is also possible to consider feedstock with a range of costs based on its FFA content, to investigate the effect of the cost (due to the FFA content) on the profitability of the production process.

As it is depicted in Fig. 4, the NPV shows a strong response to a change in the cost of oil feedstock. Moreover, an increase in oil feedstock purchasing cost by about 0.1US\$ kg$^{-1}$ (from 0.45 up to 0.55 US\$ kg$^{-1}$) could result in a decrease in NPV of about US\$24 502 000, whereas the payback time increment is only about 6 months. A feedstock cost of 0.59 US\$ kg$^{-1}$ and beyond made the business unprofitable, with a negative NPV. The effect of the change in price of oil shows very little effect on the payback time for low prices. However this tendency becomes more significant for oil prices above 0.5 US\$ kg$^{-1}$ . Above 0.5 US\$ kg$^{-1}$ of oil feedstock price an increase in the oil price by 0.09 US\$ kg$^{-1}$ could increase the payback time by 3.32 years. In this case, one can say that the oil price can have a more profound effect on the profitability of the business than the other two market variables.

## The effect of change of alcohol purchasing cost

As an input, ethanol has the second highest cost after oil feedstock. This implies that the cost of alcohol does have

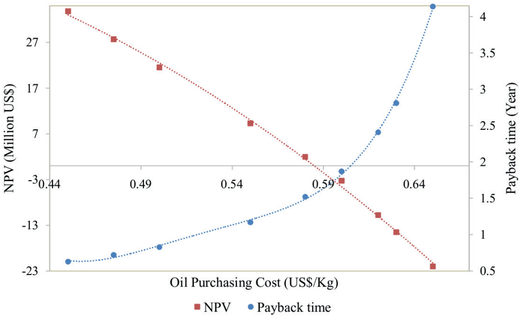


Figure 4. The effect of change of oil purchasing cost on payback time (●) and NPV (■).

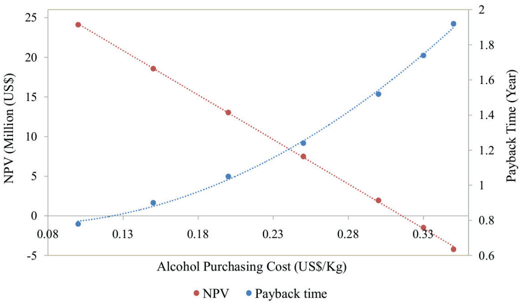


Figure 5. The effect of change of alcohol purchasing cost on payback time (●) and NPV (■).

a meaningful impact on the profitability of the biodiesel production business. To investigate the effect of the ethanol market price on the process's profitability, a price range of 0.1 to 0.335 has been assumed considering the possible market fluctuations.

As can be seen from Fig. 5, the change in the NPV due to the increase in the cost of ethanol is very high. An increase in the cost of ethanol by 0.05$ kg$^{-1}$ could bring about a decrease in the NPV by US$5.54 million. The effect of the ethanol cost on the payback time is also very interesting. A strong effect is observed when the cost of ethanol increases beyond about 0.25US$ kg$^{-1}$. The maximum cost of ethanol for profitable production process is about 0.31US$ kg$^{-1}$. However, as the alcohol used in this process is much greater than the stoichiometric amount, the excess ethanol that is recovered in the process could be reused. This could help to reduce the effect of the alcohol purchasing cost on the profitability of the business over time.

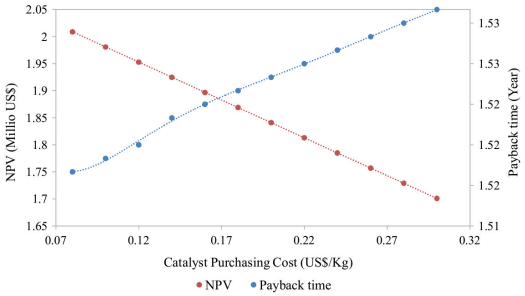


Figure 6. The effect of change of catalyst purchasing cost on payback time (●) and NPV (■).

## The effect of change of catalyst purchasing cost

The effect of the cost of the catalyst on the economic feasibility of biodiesel production is expected to be less than that of oil and alcohol purchasing costs. This is more pronounced when a cheaper catalyst like CaO is used in the production process. However, to be more practical in comparing the economic effect of available market variables, the same test has been carried out on the effect of change of catalyst purchasing cost. Accordingly, for this study, a catalyst purchasing cost range of 0.08 up to 0.22 US$ kg$^{-1}$ has been taken based on the average market price of 0.12US$ kg$^{-1}$.

Figure 6 shows that the whole process could be insensitive to a considerable change in the cost of the catalyst because, even with a higher cost of the catalyst, the NPV from the project is in the positive range. However, this small effect for the change in catalyst purchasing cost is more profound on NPV than payback time. An increase in the cost of the catalyst by 0.1US$ kg$^{-1}$ could result in a reduction of the NPV by about US$140 000. However, the effect of the change in cost of the catalyst on the payback time of the project is not very significant. A catalyst price change from 0.08 to 0.3S$ kg$^{-1}$ would not result in a considerable change in payback time.

## Effect of change of equipment maintenance cost

Equipment maintenance in any kind of production process is crucial to sustain the process as effectively as possible up to the lifetime of the whole project. It involves actions necessary for retaining or refurbishing the equipment to a specified operable condition to achieve its maximum useful life. Such actions fundamentally include corrective maintenance and preventive maintenance. Similarly, any equipment involved in the biodiesel production process should be subject to both corrective and preventive maintenance to sustain the production for a longer time and obtain the best possible economic advantage. In this study the maintenance cost has been estimated based on a percentage allocation of the purchasing cost of each item of equipment using recommended values from the literature.[75] It is recommended that between 1% and 12% of the equipment purchasing cost should be used. Accordingly, the optimum value is set to be 6% of the purchasing cost of each item of equipment. Usually, half of this cost is for materials and the other half is for labor. However, to investigate the effect of the possible increment in the amount of maintenance cost, a percentage range of 3% up to 40% has been considered.

As shown in Fig. 7, even at a higher percentage equipment purchasing cost, about 45%, the business could still be feasible with around 1 200 000 US$ NPV and 1.5 years' increment in payback time. So, the effect of equipment maintenance cost is insignificant. This indicates that enough money can be allocated for better equipment maintenance without compromising the profitability of the business to sustain the productivity of the project for a longer time.

## Effect of change in total required labor cost

An estimation of the manufacturing cost for biodiesel production considers the cost of various labor categories – mainly professional workers. The basic payment rate for a given professional title might have varied substantially based on experience or level of education. The level of the basic payment rate can also be affected by the availability of skilled labor in the market. The probability of market fluctuations in the labor cost should thus be given due emphasis so that the effect of the variability of labor cost on the profitability of the business can be investigated. Accordingly, labor cost ranges have been set based on the basic payment rates for each labor category considered in the design, as shown in Table 6. In this case, only the basic payment rate is considered to fluctuate in the given range with respect to the labor type. However, the percentage of benefits factor, the operating supplies factor, the supervision factor, and the administration factor are kept the same in each labor category, and in each of the basic payment rate ranges. Figure 8 indicates the effect of variations in labor costs on NPV and on the payback time of the process.

Compared to the cost of materials and the prices of products, the labor cost have a medium effect on the feasibility of the business, which could manifest itself more in terms of NPV than payback time. The total basic rate (the sum of basic rates for supervisor, operator, and reactor operator) above 100US$ $h^{-1}$ could make the business unprofitable. In other words, an increase of 15US$ $h^{-1}$ in the basic rate of payment for labor could reduce the NPV by about US$982 000, resulting in a very insignificant addition to payback time.

## Effect of change in local tax amount

As a production business, there might be a number of taxes applied to the biodiesel production process, which usually differ in type and amount from place to place. Due to the renewable nature of the biofuel, it is most common to have governmental subsidies for this type of process. However, we have considered the scenario where instead of having the tax deduction, the process will be considered as any other chemical industry process and therefore taxes could be higher. Such huge tax amounts involve an extra cost to the production process, jeopardizing the feasibility of the business. This requires an analysis of the sensitivity of the production process to variation in total local tax amounts set based on various possible tax considerations

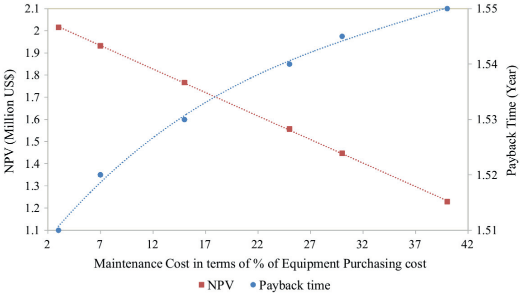


Figure 7. The effect of change of equipment maintenance cost on payback time (●) and NPV (■).

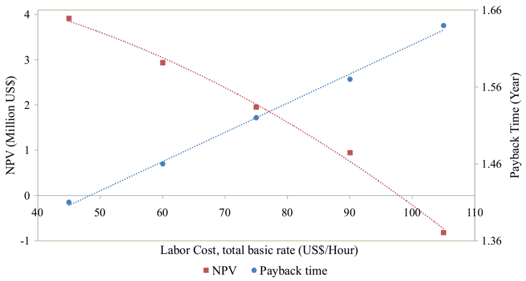


Figure 8. The effect of change of labor cost on payback time (●) and NPV (■).

like corporate income tax, turnover tax, and value added tax, among others. In Super Pro software, the possible amount of the total local tax is considered in terms of the percentage of the direct fixed cost (DFC). Thus, a range of percentage of DFC of 15% up to 45% has been taken as the representative of the tax variations to investigate how the NPV and payback time would response to this variation. Figure 9 indicates the effect of the variation in local taxes on the NPV and the payback time of the process.

The effect of tax variation on the NPV is straightforward. An increase in the local tax amount by US$175 612 (10%DFC) could reduce the NPV by US$1 073 000 (a 35% decrease in NPV). This effect is reflected less in terms of the payback time because a 200% increment in the tax amount could only add about 0.2 years to the project payback time. In general, it is possible to see that the production process would not be feasible at higher tax amounts.

## Conclusion

The economic effects of eight market variables for biodiesel production using a CaO catalyst were studied. Technically, the designed process route could provide fuel-quality biodiesel that could meet the American society for testing and materials (ASTM) standard. This is due to a combination of factors such as high reactivity and the heterogeneous character of the CaO catalyst as well as the efficiency of the selected downstream process equipment. Economically, the process can be feasible for feedstock costs lower than US$590 ton$^{-1}$.

The selected market variables exhibited various effects on the feasibility of the process. Obviously, their effect is largely dependent on their amount and relative market values. Feedstock purchasing costs had a pronounced effect on the feasibility of the business in comparison with the other market variables, with a very sharp decrease (US$24 502 000) in the NPV when the feedstock price is increased by 0.1UD$ kg$^{-1}$). The second strongest market variable affecting the profitability of the business is the ethanol purchasing cost. This suggests a need for further investigation into the economic benefits of ethanol production from cheap renewable resources, which can be done side-by-side with the biodiesel production business.

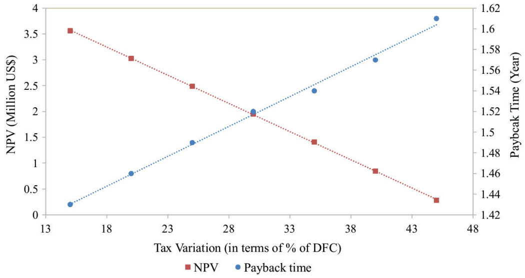


Figure 9. The effect of tax variation on payback time and NPV (●) and NPV (■).

For the selected production process, the minimum selling price of biodiesel for the business to be profitable is 0.775US$ kg$^{-1}$ (775US$ ton$^{-1}$). This price is broadly in agreement with the biodiesel selling price forecast in the Food and Agricultural Organization – Organization for Economic Co-operation and Development (FAO-OECD) Agricultural Outlook 2016–2025. The effect of the glycerol selling price is relatively less influential when compared with prices of oil feedstock and biodiesel. The labor cost and tax variations could also affect the viability of the business significantly. However, the effect in the change in equipment maintenance costs was found to be less, allowing for an increase in the amount allocated for routine maintenance activities to sustain the productivity of the process as much as possible.

This study is important because it included the eight most important market variables known to affect the economic feasibility of similar production processes. In this regard, the study could provide the cutoff values of the selected market variables at which the process could become profitable or not for a given market scenario. Moreover, this study can easily be extrapolated to other market scenarios, production capacities, and catalyst technologies if the process does not undergo major technical modifications.

## Disclaimer

Any decision made using the results of the process design is not the responsibility of the authors. The process design is only for research purposes. The authors can be contacted for further information regarding the limitations and scope of the process design.

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# Paper V

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# Biodiesel production through sulfuric acid catalyzed transesterification of acidic oil: Techno economic feasibility of different process alternatives

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ABSTRACT

Biodiesel is renewable fuel produced from fats and oils. When compared to conventional diesel fuel, it has considerable environmental benefits. However, its extensive use is hindered by high cost of production, mainly due to cost of feedstock. Among the different biodiesel production routes, acid catalyzed transesterification enables to use feedstock with higher free fatty acid content (cheaper feedstock). The absence of soap formation while using acid as a catalyst also simplifies the downstream separation and purification processes. In this study, a homogeneous sulfuric acid catalyzed transesterification of acidic oil is designed into four process scenarios based on four different downstream process routes.

The conceptual design and simulation of these process alternatives have been carried out using Super Pro and Aspen Plus software. These process models were used to evaluate the techno economic competitiveness of the four different scenarios. In the four process scenarios, all reactors for biodiesel production have been designed to have the same reaction conditions and the same amount of oil feedstock input. The difference of the scenarios was only on the arrangements and type of downstream process equipment required to get fuel grade biodiesel. The technical performances have been evaluated based on quality and quantity of products as well as the amount of biodiesel produced per feedstock consumed. The specific economic parameters considered were Unit Production Cost, NPV, IRR (after tax), and Payback time. The process scenario with ethanol recovery after catalyst neutralization and glycerol separation using decanting just before biodiesel purification has better technical and economic performances. Whereas the double reactor scenario shows much better technical performances with very low economic feasibility.

## 1. Introduction

The world energy demand is skyrocketing mainly due to economic growth and population expansion [1]. Such high demand together with the negative global environmental impacts of using fossil fuel for generations brings a question on dependability of the fossil fuel for sustainable economic growth. As a way out, the world is tending to depend more on renewables to secure the energy supply for extensive demands because of economic growth, improved standard of living and population expansion [2,3]. Among the promising renewable energy resources for substitution of fossil fuels are biofuels [4]. Biodiesel is one of these biofuels with significant advantages over its counterpart fossil diesel. It is produced from renewable resources like edible and non-edible oils, animal fats, and waste cooking oil. When compared to fossil diesel production, the process technologies usually employed to produce biodiesel are simpler and can easily be implemented in decentralized manner from small scale to large scale levels. The other major advantages are associated with its environmental and ecological benefits compared to the fossil diesel. It is biodegradable, non-toxic and free from sulfur and aromatics [5]. Combustion of biodiesel for energy releases less GHG, less air pollutants, and less particulate matters compared to the conventional fossil diesel, because it has relatively high amount of oxygen required for complete combustion of the fuel [6].

Biodiesel is a mono alkyl ester of long chain fatty acids produced mainly through the process of transesterification reaction. There are a number of possible process alternatives to accomplish transesterification reaction. Transesterification might be catalyzed or non-catalyzed. The catalyzed options are heterogeneous and homogeneous acid catalyzed, heterogeneous and homogeneous alkali catalyzed, and enzyme catalyzed transesterification reactions. The non-catalyzed option is usually supercritical methanol transesterification reaction taking place at higher pressure and temperature.

Depending on the characteristics of the feedstock used for biodiesel

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**Nomenclature**

| | |
|---|---|
| ASTM | American Society of Testing and Materials |
| CSTR | Continuous Stirred Tank Reactor |
| DG | Di-glyceride |
| DFC | Direct Fixed Cost |
| E | Ethanol |
| FAEE | Fatty Acid Ethyl Ester |
| FFA | Free Fatty Acid |
| G | Glycerol |
| GHG | Greenhouse Gas |
| IRR | Internal Rate of Return |
| MG | Mono-glyceride |
| NPV | Net Present Value |
| PC | Purchasing Cost |
| PCUE | Purchasing Cost of Unlisted Equipment |
| ROI | Return on Investment |
| TLC | Total Labor Cost |
| TG | Triglyceride |

production, each method has its own advantages and disadvantages. However, the commercially known technological route for biodiesel production is the homogeneous alkali catalyzed alternative [7–10]. This technology requires a feedstock with minimum FFA content, less than 0.5% [7,11,12]. Such oil feedstock are high quality oil like edible oil, which are usually expensive for biodiesel production.

The cost of biodiesel feedstock usually took the higher percentage share of the total manufacturing cost, affecting the unit cost of biodiesel production. In most cases, this cost share is greater than 80% [13,14]. Consequently, the unit cost of biodiesel production can directly be reduced while using the least cost feedstock alternatives [15,16]. Technically possible options to produce fuel grade biodiesel from such low quality feedstock types are acid catalyzed, enzyme catalyzed and supercritical transesterification routes [17–19]. Among them, supercritical route could give the least cost of materials as there is no any catalyst considered in the process. However, its higher pressure and temperature requirements result in bigger utility cost, making the alternative expensive [20,21]. The other alternative, enzyme catalyzed technology, is usually taken as a better choice for production of fuel grade biodiesel from low value feedstock [19]. However, the expensiveness of the catalyst is mentioned as the main drawback to use this option at industrial scale for production of biodiesel in economically competitive manner with that of fossil diesel [22].

One of the most viable options to produce biodiesel from low cost feedstock is the acid catalyzed transesterification reaction [23,24]. This is mainly because there is no additional pretreatment step required to reduce FFA, and the product separation and purification can be done with simple process steps as there is no soap formation [25,26]. Among the different possible types of acid catalysts for biodiesel production, sulfuric acid is the most studied one. It can catalyze the transesterification reaction at atmospheric pressure and relatively medium temperature range, from 55 °C up to 88 °C [27–29].

The study done by Michael et al. [29] evaluated alcoholysis of soybean oil using sulfuric, hydrochloric, formic, acetic, and nitric acids at different loading rates and found out that the sulfuric acid catalyst was the most effective. Their result showed that at 100 °C reaction temperature, 99% conversion of TG in soybean oil could be achieved in 8 h, when 0.5% sulfuric acid catalyst, and nine times methanol stoichiometry are used [29].

Farag et al. [30] studied the factors affecting production of methyl ester from mixed oil formed from 50% sunflower and 50% soybean oil using sulfuric acid as the catalyst. They found out that the optimum reaction conditions for the best conversion efficiency of 96.6%, was 6:1 M ratio of methanol to oil, 60 °C reaction temperature and, 2.5 wt.% of $H_2SO_4$ with respect to the oil feedstock [30].

In another study, Marchetti et al. [31], indicated that a conversion of 96% of acidic oil, with 10.684% FFA content, could be reached with an optimum reaction conditions of sulfuric acid amount of 2.5%, ethanol molar ratio of 6.1:1 and reaction temperature of 55 °C. However, while using sulfuric acid as a catalyst, excess amount of alcohol is usually recommended to get higher final conversion percentage [9,32,33].

The maximum conversion in an optimized transesterification reaction catalyzed by sulfuric acid could reach up to 96–99% [27,30,33]. Practically there are two main reactions taking place when acidic catalyst like sulfuric acid is used to catalyze the biodiesel production process using oil with higher FFA content. These are transesterification and esterification reactions. Transesterification is a reversible reaction between one mole of the triglyceride of the oil and three moles of alcohol in the presence of the catalyst to produce one mole of glycerol and three moles of ester. This happens in three consecutive reaction steps as depicted in Fig. 1. Esterification reaction takes place when one mole of FFA reacts with one mole of alcohol to produce one mole of ester and one mole of water as shown in Fig. 2.

$$TG + E \xleftrightarrow{Catalyst} FAEE + DG$$

$$DG + E \xleftrightarrow{Catalyst} FAEE + MG$$

$$MG + E \xleftrightarrow{Catalyst} FAEE + G$$

**Fig. 1.** Steps in transesterification reaction.

However, there might also be hydrolysis, depending on the amount of water in the feedstock and the amount of water formed during esterification.

A number of studies have been done to show how sulfuric acid catalyzed process is cost effective for biodiesel production from feedstock with high free fatty acid content [9,15,34]. Karmee et al. [15] compared the techno-economic performances of acid, base and enzyme catalysts for the production of fuel grade biodiesel from waste cooking oil. They found out that, the acid catalyst technology was the cost effective option by indicating better IRR compared to the two other options [15]. In another study Zhang et al. [34] compared the economic performances of producing biodiesel from waste cooking oil using alkali catalyzed and acid catalyzed processes and found out that the sulfuric acid catalyzed process was the most economically feasible alternative.

The techno-economic feasibility of the whole process of biodiesel production through sulfuric acid catalyzed transesterification can be further improved by using the most cost effective arrangement of equipment and selection of operation units for the major process steps. In this respect, there are a number of possible arrangement of alternative equipment for separation of the biodiesel from the glycerol as well as for purification of both the biodiesel product and the glycerol byproduct. Accordingly, this study is specifically targeted to sort out the most cost effective, technically efficient and economically sustainable biodiesel production route using sulfuric acid as homogeneous catalyst. To do so four different scenarios of sulfuric acid catalyzed biodiesel production processes have been simulated based on four different arrangement of operation units for major downstream processes. Eventually, the technical performances of the scenarios have been

$$FFA + E \xrightarrow{Catalyst} FAEE + WATER$$

**Fig. 2.** Esterification reaction.

compared in terms of the amount and quality of biodiesel and glycerol produced as well as the amount of product produced per unit of feedstock consumed. The economic evaluations, among the four scenarios, were also done based on total investment cost, unit cost of biodiesel production, IRR, NPV and payback time. The economic sustainability of the alternatives has been tested through sensitivity analysis over selected market variables. The sensitivity analysis was done to investigate how NPV and Payback time could be affected by change in market values of biodiesel selling price and oil purchasing cost so that to identify the most tolerant alternative to the global market fluctuations of the variables.

## 2. Process descriptions and methods

This study has been done on four process alternatives to produce biodiesel from acidic oil using homogeneous sulfuric acid as a catalyst. In all of the scenarios, since the amount of water in the biomass and amount of water produced during esterification is insignificant, hydrolysis has been neglected and the only dominant reactions considered are transesterification and esterification. Continuous stirred tank reactor is considered as the main reactor in all of the scenarios, for which the reaction temperature is set to be 55 °C. This is the optimum temperature for better biodiesel production from acidic oil using sulfuric acid catalyst [30,31,35].

### 2.1. Specifications of raw materials

The raw materials used in all process scenarios are the same in amount and quality. These include acidic oil feedstock, sulfuric acid catalyst, ethanol and calcium oxide. The oil feedstock is with 10% FFA content. This could represent most of second generation oil feedstock types from non-edible plants [36,37], which can have up to 14% FFA. The alcohol considered in the process designs is ethanol, which can be produced from renewable resources and which is also less toxic and safe to use. In all of the process scenarios, the ethanol is taken to be in 6.1:1 M ratio with the oil feedstock amount to encourage the forward reaction and get more conversion [30,31,35]. The acid catalyst used is sulfuric acid, with up to 98% concentration, as it is the most studied and effective acidic catalyst available for biodiesel production [23,38]. The relative optimum amount of sulfuric acid catalyst taken in all the processes is 2.1 wt.% of the oil feedstock [35]. The calcium oxide is included to totally neutralize the catalyst after the transesterification reaction. Calcium oxide is selected because it can be cheaply produced from waste materials like eggshells, mud scrap shells, and cockleshells among others. Eventually, the amount of each raw material has been determined based on their optimum allocations with respect to oil feedstock amount required for maximum conversion.

### 2.2. Design assumptions

The major assumptions considered for reasonable designing of the process scenarios are as follows:

- Oil feedstock capacities in all the scenarios are the same and equal to 41 million kg per year.
- The oil feedstock is assumed to be 100% free from solid particle.
- Oil feedstock input is assumed to be supplied throughout the whole year.
- Working hours per year is taken to be 7920 (330 working days per year).
- Pressure drop in all the process equipment is neglected.
- Moisture content of the feedstock is assumed to be very low and the water formed during esterification reaction is also considered negligible. Thus, the hydrolysis process is not considered in all of the scenarios.
- Transesterification and esterification are the only dominant reactions considered in all of the scenarios.
- Triolien represents the acidic oil with oil density of 907.8 kg/m$^3$, oleic acid represents the fatty acid with density of 895 kg/m$^3$ and ethyloleate represents biodiesel with density of 873.9 kg/m$^3$.
- As the property package for calculation of activity coefficient of the liquid phase in the simulations, the non-random two liquid (NRTL) thermodynamic model is selected due to the presence of polar compounds such as ethanol and glycerol in the process.
- Life time of the project is assumed to be 15 years
- The whole production processes are assumed to be run by own money without loan

### 2.3. Process alternative scenarios

Four possible process scenarios have been designed to investigate their techno economic feasibility so as to identify the most cost effective, technically efficient and economically reliable option(s) in producing biodiesel from low value oil feedstock using sulfuric acid as a catalyst. The scenarios are designed based on the various possible configurations of the six main downstream processes. These six main downstream processes are separation of biodiesel and glycerol, biodiesel purification, glycerol purification, excess ethanol recovery, catalyst neutralization, and separation of calcium sulfate. A number of possible unit procedures with different equipment types can be used to accomplish the six major downstream processes for production of fuel grade biodiesel. Accordingly, the four scenarios are designed by configuring technically viable as well as least cost equipment options as much as possible. The four process scenarios with their unit procedures and equipment types used for each process step are shown in Table 1.

Each process has been designed with a capacity of 41 million kg feedstock per year. Acidic oil with 10% FFA content is heated up to 55 °C and feed into the continuous stirred tank reactor at a rate of 5177.23 kg/h. At the same time, ethanol (1645.69 kg/h) and sulfuric acid catalyst (108.7 kg/h) are mixed in a simple two-way mixer, heated up to 55 °C and pumped into the continuous stirred tank reactor. The reaction condition in the stirred tank reactor is set to be isothermal at 55 °C and 1.013 bar pressure. The isothermal condition could be achieved using steam as heat transfer agent. The rate at which the product leaves the reactor is in such a way to attain 21 h residence time in the reactor. Because at the given reaction conditions (55 °C

**Table 1**
Process scenarios with required equipment for each process step.

| Process steps | Scenarios with unit procedures and equipment in each step | | | |
|---|---|---|---|---|
| | Scenario – I | Scenario – II | Scenario – III | Scenario – IV |
| 1 | Reaction (*CSTR – Single*) | Reaction (*CSTR – Single*) | Reaction (*CSTR – double*) | Reaction (*CSTR – Single*) |
| 2 | Ethanol recovery (*Distillation*) | Catalyst neutralization (*CSTR*) | Catalyst neutralization (*CSTR*) | Catalyst neutralization (*CSTR*) |
| 3 | Catalyst neutralization (*CSTR*) | $CaSO_4$ separation (*Centrifuge*) | $CaSO_4$ separation (*Centrifuge*) | $CaSO_4$ separation (*Centrifuge*) |
| 4 | $CaSO_4$ separation (*Centrifuge*) | Ethanol recovery (*Distillation*) | Ethanol recovery (*Distillation*) | Ethanol recovery (*Distillation*) |
| 5 | Glycerol separation (*Decanter*) | Glycerol separation (*Decanter*) | Glycerol separation (*Decanter*) | Biodiesel and glycerol purification (*Distillation*) |
| 6 | Biodiesel purification (*Distillation*) | Biodiesel purification (*Distillation*) | Biodiesel purification (*Distillation*) | Biodiesel and Glycerol separation (*Decanter*) |

temperature, 2.1 wt.% catalyst & 6.1:1 M ratio of the alcohol to oil) the conversion could reach at about 97.57% in 21 h [35]. All reaction conditions and everything else are made the same for all scenarios until this point.

The product from the reactor is then passed through the different downstream configurations to get fuel grade biodiesel. In all of the scenarios, the calcium sulfate salt formed during the neutralization of the acidic catalyst is removed using centrifugal decanter just after neutralization reactor. The excess ethanol is recovered using distillation column in all of the scenarios. In scenarios II, III & IV, the excess ethanol is recovered just after the salt is removed. However, in scenario I the excess ethanol recovery is done before the catalyst is neutralized. In scenario III, the reaction is carried out in two consecutive CSTR where there is a decanter in between them to separate the glycerol part after the first reactor. This double reactor configuration is the main difference between scenario II and III. In scenario IV, the separation of biodiesel from the glycerol is considered at the end after the unreacted oil is separated using distillation column. Whereas in scenarios I, II & III the final step is purification of the biodiesel using distillation column. This is very effective in separating the biodiesel from the unreacted oil remaining in the product. The other similar situation in all scenarios is neutralization of the acid catalyst. This is done by using CaO in a CSTR just after the main reactor(s) for biodiesel production in scenarios II, III & IV, whereas in scenario I, neutralization of the catalyst is considered after the excess ethanol is recovered.

The process flow sheets shown in this study are performed using Super Pro design software from Intellegin Inc.[39]. In order to verify their correctness, each process model has also been redesigned using Aspen Plus software from Aspentech [40]. This is because Aspen Plus has a broader choice in physical parameters and physical property methods to select for each specific process taken in the design. This would help to increase the viability of the results. Figs. 3–6 show the designed process flow sheets for each scenario.

### 2.4. Economic assessment

The economic performance evaluation of the studied process scenarios has been done considering latest and estimated costs of raw materials, labor, utilities and equipment as well as associated costs of equipment installation, auxiliary facilities and depreciation cost among others. The oil feedstock considered in these processes is the cheapest from non-edible oil plants, and estimated to cost in a range of 478–684 US$/ton [41,42]. We take the lower value 478 US$/ton to be the estimated cost of oil feedstock. The cost of other raw materials such as catalyst, ethanol and calcium oxide are based on latest market prices from different suppliers in Ethiopia and relevant literatures [43,44]. The labor cost is estimated based on the current wage indicator in Ethiopia [45], which is then extrapolated to scale it up to some amount. The calculation of the labor cost is based on detailed estimate using the basic rate allocated for each labor category. The other cost category included in the annual operating cost calculations is cost of utilities. The utilities considered in all of the studied scenarios are cooling water, steam, steam high and electricity, for which the cost estimations are entirely based on current market prices in Ethiopia and relevant literatures [46,47]. Table 2 shows estimated costs of raw materials, utilities and labor considered in the process alternatives.

The purchasing cost of each equipment designed in each process scenario is estimated using Peter and Timmerhaus method [48], where Chemical Engineering plant cost index of 591.335 for January 2018 is used [49]. This index denotes changes in the value of money due to inflation and deflation so that it helps to estimate the average cost of each equipment for the year 2018 based on previous year costs. The other components of the capital investment cost, such as installation, piping, electricity, instrumentation, and yard improvement are estimated based on the percentage allocation of the equipment purchasing cost for each cost item as shown in Table 3.

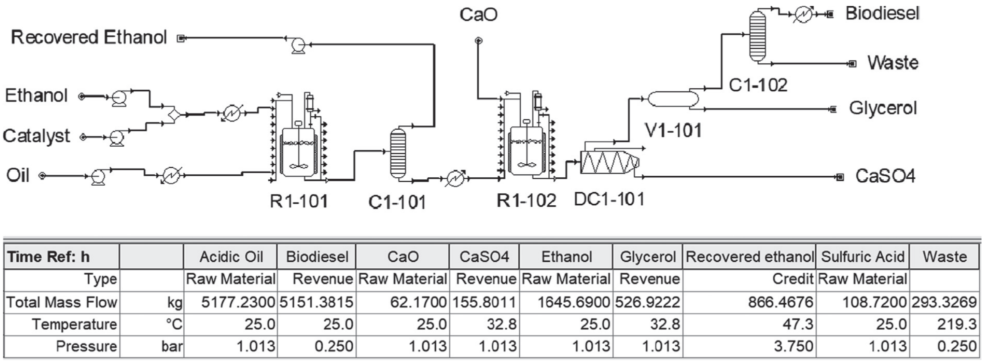
The cost estimation interface in the Super Pro design software gives options to allocate estimated percentage share of such cost categories as well as other associated costs like maintenance cost, depreciation, insurance and tax, during designing the processes. The percentage allocation of these type of costs are indicated in Table 4.

## 3. Results

Having optimized process conditions and determined equipment sizes, the material and energy balances of the four process alternatives have been carried out. Based on the results of the material and energy balances of each scenario as well as market values of input materials, labor and utilities the techno economics of the processes have been analyzed and presented as follows.

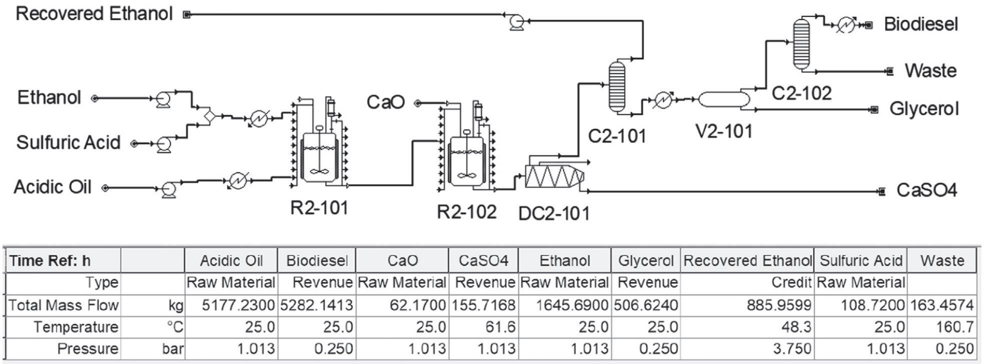
### 3.1. Technical performances

All four process scenarios are found to be technically feasible ways to produce biodiesel at required quality in accordance with ASTM standards. The technical performance results, such as biodiesel purity, glycerol purity and amount of biodiesel and glycerol produced per amount of feedstock used, are in agreement with those reported in other studies [15,51]. However, there is still a comparable difference among the scenarios in terms of these technical performances. For instance, scenarios II & III show better performance regarding the amount of biodiesel produced per amount of feedstock consumed. For scenario



| Time Ref: h | | Acidic Oil | Biodiesel | CaO | CaSO4 | Ethanol | Glycerol | Recovered ethanol | Sulfuric Acid | Waste |
|---|---|---|---|---|---|---|---|---|---|---|
| Type | | Raw Material | Revenue | Raw Material | Revenue | Raw Material | Revenue | Credit | Raw Material | |
| Total Mass Flow | kg | 5177.2300 | 5151.3815 | 62.1700 | 155.8011 | 1645.6900 | 526.9222 | 866.4676 | 108.7200 | 293.3269 |
| Temperature | °C | 25.0 | 25.0 | 25.0 | 32.8 | 25.0 | 32.8 | 47.3 | 25.0 | 219.3 |
| Pressure | bar | 1.013 | 0.250 | 1.013 | 1.013 | 1.013 | 1.013 | 3.750 | 1.013 | 0.250 |

**Fig. 3.** Scenario I: R1-101 CSTR for biodiesel production, C1-101 shortcut distillation column for ethanol recovery, R1-102 CSTR for catalyst neutralization, DC1-101 centrifuge decanter for $CaSO_4$ separation, V1-101 decanting tank for glycerol separation and C1-102 shortcut distillation column for biodiesel purification.



| Time Ref: h | | Acidic Oil | Biodiesel | CaO | CaSO4 | Ethanol | Glycerol | Recovered Ethanol | Sulfuric Acid | Waste |
|---|---|---|---|---|---|---|---|---|---|---|
| Type | | Raw Material | Revenue | Raw Material | Revenue | Raw Material | Revenue | Credit | Raw Material | |
| Total Mass Flow | kg | 5177.2300 | 5282.1413 | 62.1700 | 155.7168 | 1645.6900 | 506.6240 | 885.9599 | 108.7200 | 163.4574 |
| Temperature | °C | 25.0 | 25.0 | 25.0 | 61.6 | 25.0 | 25.0 | 48.3 | 25.0 | 160.7 |
| Pressure | bar | 1.013 | 0.250 | 1.013 | 1.013 | 1.013 | 0.250 | 3.750 | 1.013 | 0.250 |

**Fig. 4.** Scenario II: R2-101 CSTR for biodiesel production, R2-102 CSTR for catalyst neutralization, DC2-101 centrifuge decanter for $CaSO_4$ separation, C2-101 shortcut distillation column for ethanol recovery, V2-101 decanting tank for glycerol separation and C2-102 shortcut distillation column for biodiesel purification.

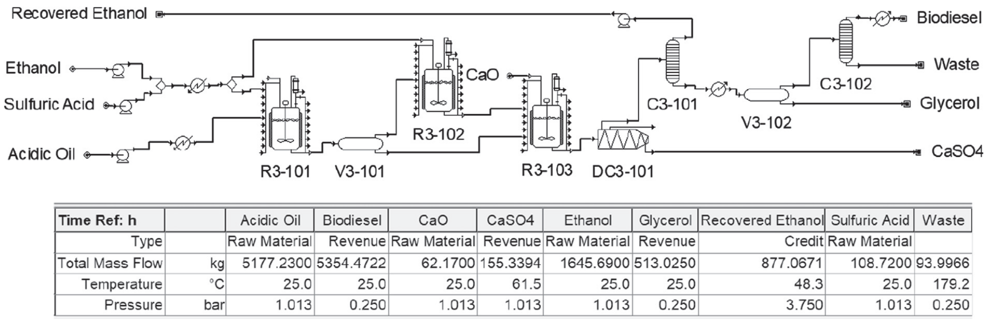
III, this is due to the double reactor configuration designed to improve the overall conversion of the oil into biodiesel. Whereas for scenario II, the higher performance might be due to arrangement of the downstream processes, where ethanol recovery is done after catalyst neutralization as well as biodiesel purification is done using distillation just after the glycerol separation by decanting. Such process arrangement helps to minimize the amount of biodiesel lost during biodiesel purification and waste separation through distillation. In contrary, the least performance is recorded in scenario IV, where, during separating the unreacted oil from the biodiesel in the second distillation process, considerable amount of the biodiesel could also be removed together with the unreacted oil. This might be due to the higher temperature of the reboiler required to separate the mixture of biodiesel and glycerol from the unreacted oil. Accordingly, the difference in amount of biodiesel produced among the scenarios could range up to 341 kg/h. This value specially indicates the product difference between scenario II and IV. In all of the scenarios, the biodiesel purity achieved is about 99.99%. This is mainly because of the fractional distillation employed to further purify the biodiesel after different arrangement of glycerol and calcium sulfate separation processes. As the main byproduct, glycerol could also be obtained at higher quality because a number of separation processes are employed in each scenario. Apparently, the higher glycerol product is recorded in scenario III, where two consecutive reactors are designed for higher conversion percentages. The purity of ethanol recovered in each scenario is the same. However, the amount recovered in scenario III is slightly less than the rest because a little more is consumed due to the second reactor.

The other crucial point that might improve the productivity of the whole production process is considering the production of more valuable byproducts for additional income generation. With this respect, a good quality calcium sulfate could be produced from all the scenarios with almost the same quantity. In all of the scenarios the separation of the calcium sulfate is done using centrifugal decanter as it is efficient in separating the solid calcium sulfate from the rest of the components. This is done just after the acid catalyst is neutralized so that to avoid the interference of the solid calcium sulfate to the liquid flow downstream afterwards. Calcium sulfate, as the second byproduct, can be used as a soil conditioner and if further calcined at required temperature, it can also be used in making tiles, wallboard, and various plasters among others [52]. Table 5 shows summary of technical performances of the studied process scenarios.

### 3.2. Economic performances

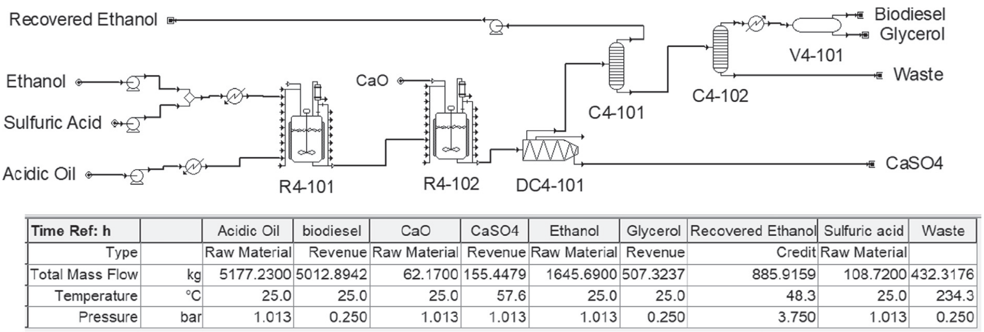
Having determined plant size, optimized reaction conditions and estimated costs for goods and services, it has been possible to compare the performances of the process alternatives in terms of some selected economic parameters. The economic parameters used for comparison are total investment cost, total annual operating cost, unit production cost, payback time, NPV, ROI, and after tax IRR. Summary of the economic performances of the alternative process scenarios is indicated in Table 6.

As shown in Table 6, scenario III is the most expensive alternative. This is mainly because of the double reactor scenario, which is



| Time Ref: h | | Acidic Oil | Biodiesel | CaO | CaSO4 | Ethanol | Glycerol | Recovered Ethanol | Sulfuric Acid | Waste |
|---|---|---|---|---|---|---|---|---|---|---|
| Type | | Raw Material | Revenue | Raw Material | Revenue | Raw Material | Revenue | Credit | Raw Material | |
| Total Mass Flow | kg | 5177.2300 | 5354.4722 | 62.1700 | 155.3394 | 1645.6900 | 513.0250 | 877.0671 | 108.7200 | 93.9966 |
| Temperature | °C | 25.0 | 25.0 | 25.0 | 61.5 | 25.0 | 25.0 | 48.3 | 25.0 | 179.2 |
| Pressure | bar | 1.013 | 0.250 | 1.013 | 1.013 | 1.013 | 0.250 | 3.750 | 1.013 | 0.250 |

**Fig. 5.** Scenario III: R3-101 first CSTR for biodiesel production, V3-101 first decanter for glycerol separation, R3-102s CSTR for additional biodiesel production, R3-103 CSTR for catalyst neutralization, DC3-101 centrifuge decanter for $CaSO_4$ separation, C3-101 shortcut distillation column for ethanol recovery, V3-102s decanting tank for glycerol separation and C3-102 shortcut distillation column for biodiesel purification.



| Time Ref: h | | Acidic Oil | biodiesel | CaO | CaSO4 | Ethanol | Glycerol | Recovered Ethanol | Sulfuric acid | Waste |
|---|---|---|---|---|---|---|---|---|---|---|
| Type | | Raw Material | Revenue | Raw Material | Revenue | Raw Material | Revenue | Credit | Raw Material | |
| Total Mass Flow | kg | 5177.2300 | 5012.8942 | 62.1700 | 155.4479 | 1645.6900 | 507.3237 | 885.9159 | 108.7200 | 432.3176 |
| Temperature | °C | 25.0 | 25.0 | 25.0 | 57.6 | 25.0 | 25.0 | 48.3 | 25.0 | 234.3 |
| Pressure | bar | 1.013 | 0.250 | 1.013 | 1.013 | 1.013 | 0.250 | 3.750 | 1.013 | 0.250 |

**Fig. 6.** Scenario IV: R4-101 CSTR for biodiesel production, R4-102 CSTR for catalyst neutralization, DC4-101 centrifuge decanter for $CaSO_4$ separation, C4-101 shortcut distillation column for ethanol recovery, C4-102 short cut distillation column for biodiesel purification and V4-101 decanting tank for glycerol separation.

**Table 2**
Estimated costs of raw materials, utilities and labor considered in all process scenarios.

| Raw material | |
|---|---|
| Oil | 0.478 US$/kg |
| Ethanol | 0.300 US$/kg |
| Sulfuric acid | 0.275 US$/kg |
| CaO | 0.120 US$/kg |
| *Utilities* | |
| Electricity | 0.021 US$/KW-h |
| Steam | 6 US$/MT |
| Steam high | 10 US$/MT |
| Cooling water | 0.025 US$/MT |
| *Labor (Basic rate)* | |
| Operator | 10 US$/h |
| Reactor operator | 15 US$/h |
| Supervisor | 15 US$/h |

**Table 3**
Direct plant cost categories and their percentage allocations with equipment cost [15].

| Cost category | % allocation with equipment cost |
|---|---|
| Piping | 20 |
| Instrumentation | 10 |
| Electrical | 15 |
| Insulation | 3 |
| Building | 15 |
| Yard improvement | 10 |
| Auxiliary facilities | 25 |
| Unlisted equipment | 20 |

**Table 4**
Cost estimation methods for components of capital investment and operating costs [50].

| Cost items | Estimation methods |
|---|---|
| *Capital Investment cost categories* | |
| Installation cost (for each equipment) | 0.2 X PC |
| Maintenance cost (for each equipment) | 0.1 X PC |
| Purchasing cost of unlisted equipment (PCUE) | 0.2 X PC |
| Installation cost of unlisted equipment | 0.5 X PCUE |
| *Operating cost categories* | |
| Insurance | 2 X DFC |
| Local tax | 15 X DFC |
| Factory expense | 5 X DFC |
| Laboratory and quality control | 30 X TLC |

supposed to improve the oil conversion efficiency and get more biodiesel produced. Because as the number of equipment increased, there would be associated increase in the total equipment cost, labor cost and utility cost. Even though this double reactor scenario could provide more biodiesel and glycerol compared to others, the overall economic performance indicated that it is not an economically feasible alternative. At optimum market values of goods and services, scenario III provides a very high unit cost of biodiesel production, negative NPV at 7% interest and higher payback time, implying that biodiesel produced should be sold at high price to get some profit. This makes the alternative economically unattractive.

Comparatively, scenario II is the least expensive alternative and the second scenario in providing more biodiesel amount. Even though it has the same type and number of equipment with scenario IV, the arrangement of the equipment in scenario II could provide more amount of biodiesel, making the alternative better in its economic performances through increasing the revenue. This might be due to the process arrangement where glycerol is decanted out before the biodiesel is purified using distillation column and thus the amount of biodiesel lost during glycerol separation is minimized. In addition, this process arrangement favors scenario II to have relatively less utility requirement because the reboiler in the distillation column works at relatively lower temperature compared to the one in scenario IV, which has the same type of equipment as well as the same process arrangement until the separation of the calcium sulfate byproduct. This decreases the over production cost. In terms of the economic terms, scenario II indicates higher NPV, less payback time and minimum unit production cost. Scenarios I and IV are the third and fourth alternatives respectively, in terms of their economic performances. Both show positive NPV, signifying that they are still feasible in the given market values of products.

In terms of the total capital investment cost, scenario III is the highest again because of the double reactor situation, which increases the equipment purchasing cost and the associated utility, installation and instrumentation costs. Among the other scenarios, scenario I is the second most expensive mainly due to larger volume of distillation column required to recover the excess ethanol before glycerol and calcium sulfate separation. Similarly, such larger column volume results in higher equipment, utility, instrumentation, and installation costs among others.

Because of the higher amount of biodiesel and glycerol produced, the superior revenue is recorded in scenario III, whereas scenario II shows the second larger revenue. Having the lower investment cost and second larger revenue, scenario II is the better alternative in terms of achieving lower unit production cost, higher ROI, and lower payback time.

**Table 5**
Summary of technical performances of the process scenarios.

| Technical performance indicators | Process scenarios with respective technical performances | | | |
|---|---|---|---|---|
| | Scenario I | Scenario II | Scenario III | Scenario IV |
| Annual Biodiesel production (kg/year) | 40,798,942 | 41,834,559 | 42,407,420 | 39,702,122 |
| Annual Glycerol production (kg/year) | 4,018,719 | 4,018,719 | 4,067,549 | 4,018,719 |
| Annual $CaSO_4$ production (kg/year) | 1,195,301 | 1,195,301 | 1,195,301 | 1,195,301 |
| Biodiesel purity (%) | 99.998 | 99.990 | 99.990 | 99.990 |
| Glycerol purity (%) | 96.20 | 99.98 | 99.95 | 99.86 |
| $CaSO_4$ purity (%) | 97 | 97 | 97 | 97 |
| Biodiesel produced per oil feedstock consumed (wt./wt.) | 0.995 | 1 | 1 | 0.968 |

**Table 6**
Summary of the economic performances of the studied process scenarios.

| Economic performance indicators | Scenario – I | Scenario – II | Scenario – III | Scenario – IV |
|---|---|---|---|---|
| Total capital investment cost (US$) | 22,359,405 | 21,865,163 | 31,542,376 | 21,869,629 |
| Total equipment purchasing cost (US$) | 4,372,471 | 4,346,531 | 6,477,990 | 4,271,634 |
| Direct fixed capital (US$) | 18,021,578 | 17,521,523 | 26,699,684 | 17,605,966 |
| Working capital (US$) | 3,436,748 | 3,467,564 | 3,507,708 | 3,383,365 |
| Total Annual operating cost (US$) | 44,081,688 | 44,262,764 | 47,811,814 | 43,353,794 |
| Total annual raw material cost (US$) | 23,805,788 | 23,805,788 | 23,805,788 | 23,805,788 |
| Labor dependent cost (US$) | 469,543 | 475,200 | 627,943 | 463,886 |
| Facility dependent cost (US$) | 6,026,595 | 5,867,002 | 8,928,640 | 5,887,610 |
| Laboratory, quality control & analysis (US$) | 140,863 | 142,560 | 188,383 | 139,166 |
| Utility cost (US$) | 13,528,900 | 13,862,214 | 14,151,061 | 12,967,345 |
| Annual revenue from Biodiesel (US$/year) | 46,917,850 | 48,090,537 | 48,752,243 | 45,641,805 |
| Annual revenue from Glycerol (US$/year) | 417,323 | 417,323 | 422,206 | 417,323 |
| Annual revenue from $CaSO_4$ (US$/year) | 153,173 | 153,173 | 153,173 | 153,173 |
| Total annual revenue (US$/year) | 47,488,346 | 48,661,033 | 49,327,622 | 46,212,301 |
| Unit production cost (US$/kg biodiesel) | 1.0805 | 1.0580 | 1.1274 | 1.0920 |
| NPV at 7% (US$) | 4,268,069 | 8,761,177 | −7,556,647 | 3,076,566 |
| ROI (%) | 19.02 | 22.19 | 12.47 | 18.01 |
| After tax IRR (%) | 9.92 | 12.73 | 2.89 | 9.14 |
| Gross margin (%) | 8.92 | 10.92 | 4.72 | 8.17 |
| Payback time in years | 5.26 | 4.51 | 8.02 | 5.55 |

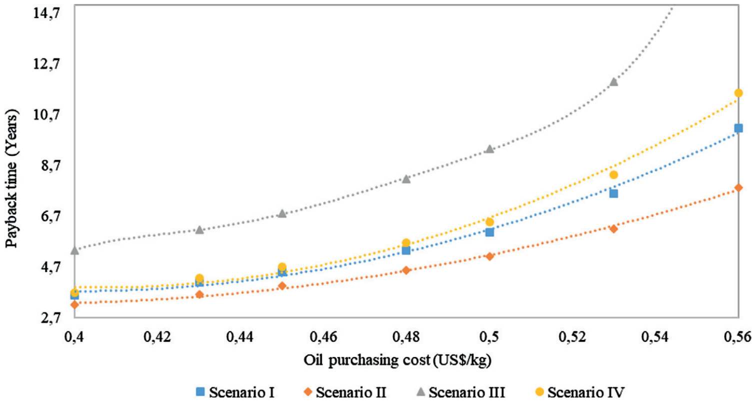


**Fig. 7.** Effect of change of oil purchasing cost on Payback time among the alternative scenarios.

### 3.3. Sensitivity analysis

The economic feasibility of a biodiesel production process can be dependable when there is a thorough analysis done on how fluctuation of values of market variables affect the profitability of the business. This is because such study would identify the market variables, which affect the profitability of the business more, so that we could take remedial measures, when necessary, to keep the business profitable. In addition, when such analysis is done among a number of alternative processes, it would help to identify the most reliable production alternative that could tolerate market fluctuations of inputs and outputs. Accordingly, in this study, the effects of change of market values of oil feedstock and biodiesel on profitability of the business have been analyzed and the results have also been compared and presented as follows. The

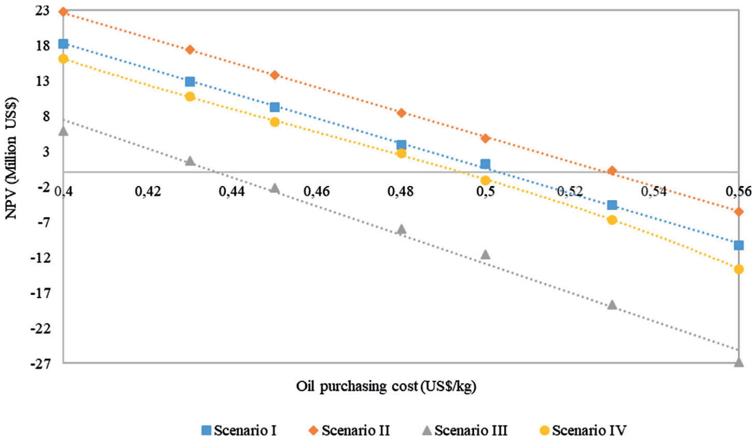


**Fig. 8.** Effect of change of oil purchasing cost on NPV among the alternative scenarios.

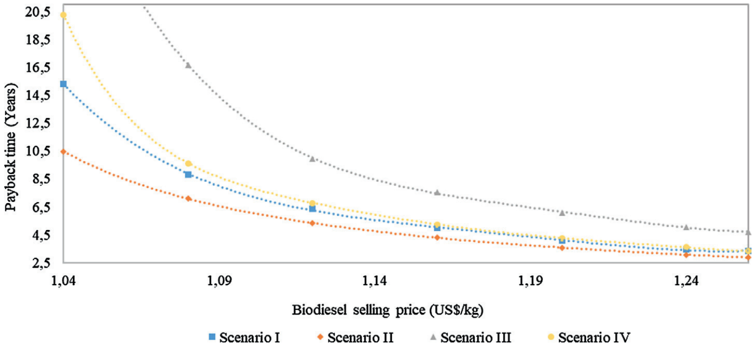


**Fig. 9.** Effect of change of Biodiesel selling price on Payback time among the alternative scenarios.

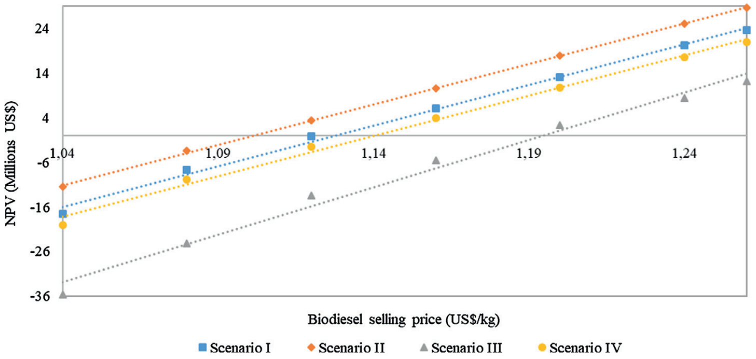


**Fig. 10.** Effect of change of Biodiesel selling price on NPV among the alternative scenarios.

economic indicators used to show the sensitivity of the business to changes in prices of the market variables are NPV at 7% interest and payback time.

### 3.3.1. Effect of change of oil feedstock purchasing cost

The oil feedstock took the higher share of the annual operating cost in all of the studied alternatives. This implies that a change in market price of the feedstock has a high probability in affecting the profitability of the business. To investigate how NPV and payback time change with change in feedstock cost among the studied scenarios, a price range of 0.45 up to 0.65 US$/kg of acidic oil feedstock was set. The effect of change of oil feedstock purchasing cost on NPV is shown in Fig. 5 and its effect on payback time is shown in Fig. 6.

Scenario III is the least dependable alternative for sustainable biodiesel production business. In this scenario, an increase in oil cost by 0.1 US$/kg could result in additional 4 years of payback time. At higher oil purchasing cost, above 0.53 US$/kg, the payback time would be beyond the lifetime of the project, making the alternative very sensitive to change to oil purchasing cost. Comparatively, scenario II indicates more tolerance to change in oil purchasing cost, in which the same price change (0.1 US$/kg) could increase the payback time by about 1.9 years.

The effect of change of oil feedstock purchasing cost on the profitability of biodiesel production business could be shown in a better way using NPV. Because NPV denotes the value of the investment calculated by adding the present value of expected future cash flows to the initial cost of the investment. Accordingly, the negative NPV attained in scenario III, as shown in Fig. 6, clearly suggests that the alternative is not economically feasible at even medium cost of oil feedstock (above 0.435 US$/kg). Consequently, feedstock has to be purchased with very minimum cost (less than 0.43 US$/kg) in order to be profitable using scenario III. The other less dependable option is scenario IV. It is unprofitable at moderately higher cost of oil feedstock (above 0.49 US $/kg). Comparatively, scenario II could provide positive NPV at higher cost of oil feedstock (up to 0.535 US$/kg), making it more economically dependable alternative for sustainable biodiesel production business.

### 3.3.2. *Effect of change of biodiesel selling price*

The other market variable considered to have an effect on the profitability of the alternative scenarios is the biodiesel selling price. Since biodiesel is the main product, its market value could have significant effect on the profitability of the production business. Similarly, NPV and payback time are the two economic indicators used to show how each scenario respond to change in selling price of biodiesel. The biodiesel selling price range of 0.96 up to 1.24 US$/kg is taken for the analysis. The effect of change of biodiesel selling price on NPV is shown in Fig. 7 and its effect on payback time is shown in Fig. 8.

Here again it is indicated that scenario III is the most sensitive for change in biodiesel selling price. Biodiesel price lower than 1.08 US $/kg would make the project payback time to go beyond its lifetime, making it less practical. The next sensitive alternative is scenario IV, which also required a biodiesel selling price of more than 1.14 US$/kg for its feasibility. Comparatively, scenario II is found to be the most tolerant to a considerable change in the market values of biodiesel selling price, allowing to consider minimum biodiesel price (up to 1.1 US$/kg) within the feasibility domain (see Figs. 9 and 10).

As shown in Fig. 9, the trend of change of NPV with change in biodiesel prices is the same for all scenarios. However, among them scenario III is found to be more sensitive and get no profit to the business even at higher prices of the biodiesel product. The next less dependable alternative is scenario IV, which indicates negative NPV starting from medium values of the biodiesel selling price (lower than 1.14 US$/kg). Scenario II is the better alternative in this respect, providing positive NPV at 7% interest even at lower values of biodiesel selling price (about 1.1 US$/kg).

## 4. Conclusion

Four process scenarios for biodiesel production from acidic oil using sulfuric acid as a catalyst were designed, analyzed and evaluated for their techno-economic performances. Accordingly, all scenarios are capable of producing fuel grade biodiesel and could also provide high quality calcium sulfate and glycerol byproducts for additional income. Scenario III, with double reactor, shows better technical performance with very low economic feasibility. In addition, scenario III is found to be the most sensitive alternative to change in market values of inputs and outputs.

Comparatively, scenario II is the cheapest alternative with less total investment cost, less unit cost of production, higher NPV and minimum payback time. It also indicates good technical performance and provides competitive amount of glycerol byproduct. In terms of sensitivity to change in market values of inputs and outputs, scenarios II is found to be more tolerant than the other scenarios.

Scenarios I and IV are relatively technically less efficient and scenario IV is the second most expensive alternative for having higher cost of biodiesel production, and less NPV among others. It is also the second most sensitive alternative to change in market values of inputs and outputs.

## Disclaimer

The authors do not have responsibility for a decision made based on the results of these process alternatives. The process designs indicated in this work are solely for research purposes. For specific applications, please contact the authors to get information about the limitations and scope of the process designs.

## Acknowledgements

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## Conflict of interest

All authors declare no conflicts of interest in this paper.

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# Paper VI

Modeling and Analysis

Biofpr
Biofuels Bioproducts & Biorefining

# Techno-economic performance of a bio-refinery for the production of fuel-grade biofuel using a green catalyst

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Abstract: The main challenge to the wider use of biodiesel as a transport fuel has been its high cost of production. Studies have been performed to obtain the cheapest methods for biodiesel production. The calcium oxide catalyzed transesterification reaction has shown better performance for fuel-grade biodiesel from cheaper feedstock. In this study, a calcium oxide catalyzed biodiesel production process is designed in four different scenarios based on different possible arrangements of the downstream processes.

The process flow diagrams of the different scenarios were designed using Aspen Plus and Super Pro software. These process simulations were used to evaluate the techno-economic performance of the process scenarios. Technical performance was been evaluated based on the quantity and quality of the biodiesel and glycerol produced, the amount of biodiesel produced per amount of feedstock consumed, and the amount of other valuable byproducts. Similarly, the economic performance of the process scenarios has also been assessed using parameters such as total investment cost, unit production cost, net present value, internal rate of return, payback time, and return on investment.

Each of these four scenarios was divided into two production capacity levels to investigate the effect of change in production capacity on the economic feasibility of the process scenarios.

The scenario with consecutive centrifugations for glycerol and soap separation, and distillation for biodiesel purification, evidenced poor technical performance, whereas the double reactor scenario provided more, and better quality, product, and the economic feasibility of this scenario was good when the oil supply rate was above 4600 kg $h^{-1}$. © 2019 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: CaO catalyst; biodiesel; technical performance; economic feasibility

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## Introduction

The world's energy supply relies mainly on conventional fossil fuels.[1] The ever increasing population together with economic activity, especially in developing countries, is creating a burden on the balance between the global energy demand and supply.[2] The use of conventional fossil fuels for many years proved to be the main cause of global warming through the emission of greenhouse gases (GHG).[3] A search for alternative and renewable energy resources, which can supply the world's growing energy demand and reduce global GHG emissions, is therefore inevitable. Among the major sectors of the economy, transport will remain the dominant sector for the next two decades in terms of world fuel oil demand. Diesel fuel demand took the larger share of this, at about 5.5 barrels per day.[4] This implies that substitution of this fossil diesel with renewable biodiesel could have a significant impact in cutting GHG emissions and in improving energy security in this sector. Biodiesel also has a number of advantages over conventional fossil diesel. It can be produced from renewable resources, which can be found anywhere, and its production technique is very simple. This indicates that biodiesel production process can be decentralized, making the fuel accessible everywhere in the world. As a fuel, biodiesel is non-toxic, biodegradable, and has a higher lubricant quality, thus considerably reducing engine wear. It has also more oxygen, which favors complete combustion of the fuel.[5]

High fuel-quality biodiesel is produced through the process of transesterification of oil or fat feedstock. This transesterification process can be catalyzed or non-catalyzed. In the catalyzed transesterification process, 3 mol alcohol (methanol or ethanol) react with 1 mol triglyceride of the oil or fat in the presence of a given catalyst to produce 3 mol fatty acid methyl or ethyl ester and 1 mol glycerol. This typical three-step catalyzed transesterification reaction is shown in Fig. 1.

In the non-catalyzed process, supercritical methanol is normally used to convert triglycerides into biodiesel and glycerol at a high temperature and under high pressure.

$$TG + E \overset{Catalyst}{\longleftrightarrow} BD + DG$$

$$DG + E \overset{Catalyst}{\longleftrightarrow} BD + MG$$

$$MG + E \overset{Catalyst}{\longleftrightarrow} BD + G$$

Figure 1. The three-step catalyzed transesterification for biodiesel production.

Among the major catalysts used for biodiesel production are homogeneous and heterogeneous acid catalysts,[6–8] homogeneous and heterogeneous base catalysts,[9–11] and enzyme catalysts.[12–14] Each of these routes has its own advantages and disadvantages depending on the type of feedstock used. Generally, acid-catalyzed transesterification requires relatively simple steps to produce fuel-grade biodiesel from feedstock with high free fatty acid content, such as waste cooking oil.[15,16]

On the other hand, conventional homogeneous base-catalyzed transesterification requires high-quality feedstock such as vegetable oil for the production of fuel-grade biodiesel.[17] This makes the biodiesel production process economically uncompetitive because it uses expensive feedstock as, in most of the cases, the cost of feedstock is more than 80% of the production cost.[18,19] However, heterogeneous base catalysts possess the advantage of being easily recovered and reused many times without considerable loss of catalytic activity.[20–22] Among such heterogeneous base catalysts in general, and from the alkaline earth metal oxides in particular, CaO catalysts display better catalytic activity,[10,21,23] least cost,[23,24] and ability to catalyze cheap feedstock, with considerable free fatty acid content, for the production of fuel-grade biodiesel.[25]

Research by Boey *et al.*[26] indicated that CaO from marine wastes was a good source of heterogeneous base catalyst for transesterification of waste cooking oil. In this study, a maximum conversion of 98% could be achieved with optimum reaction conditions at 5 wt% catalyst respected to oil fed methanol to oil molar ratio of 13:1 refluxing it for 3 hours.[26] This heterogeneous catalyst was prepared from waste mud crab shells and cockle shells with 1:1 mass ratio by calcining the mixture at 900 °C for 2 h.[26] In another study, Sasiprapha *et al.*[23] investigated the optimum reaction conditions required to obtain the maximum conversion in CaO catalyzed transesterification for biodiesel production. A 92.5% conversion could be achieved under optimum reaction conditions of methanol to oil molar ratio of 9:1, catalyst amount of 3 wt% within a total reaction time of 1 h.[23] The effectiveness of CaO catalyst produced from chicken manure was also tested by Maneerung *et al.*[25] and they found out that 90% fatty acid methyl ester (FAME) yield could be achieved at optimum reaction conditions of 65 °C, methanol to oil molar ratio of 15:1, and a catalyst amount of 7.5 wt% with respect to oil mass.[25] Correia *et al.*[27] also characterize the catalytic capacity of CaO prepared from two different natural sources – crab shell and eggshell. The CaO catalyst prepared from the eggshell resulted in greater conversion (97.75%) of the triglyceride into biodiesel under optimum reaction conditions. According to the authors' conclusion, such better catalytic performance of the calcined eggshell catalyst is due to the greater surface content of Ca for calcined eggshell than calcined crab waste.[27] A number of studies have been undertaken to investigate the catalytic effect of CaO prepared from different natural sources, each of them revealing the importance of the catalyst for the efficient production of biodiesel from oil feedstock with low up to medium free fatty acid (FFA) content.[28–30]

Significant economic benefits can be assumed while using a CaO catalyst for biodiesel production. The possibility of preparing the catalyst from waste materials with simple techniques, and its ability to catalyze cheap feedstock for biodiesel production, are the main points that could bring economic advantages. There are few studies focusing on the economics of biodiesel production using a CaO catalyst. In particular, there is no substantial research on the different possible arrangement of the unit procedures required to produce biodiesel and to study their economic effects. Hence, this study aims to investigate the techno-economic implications of the different process layouts and capacities of biodiesel production using a CaO catalyst. The assessment is entirely based on process simulations, which are designed using Aspen Plus and Super Pro software. Four scenarios of biodiesel production processes using a CaO catalyst have been designed based on the different possible arrangements of each unit procedure required to produce biodiesel from acidic oil. These four process scenarios have also been redesigned into two additional feedstock capacities (with a total of three feedstock capacities: 3106.34, 5177.23, and 7248.12 kg $h^{-1}$) to investigate the economic effect of variation of the oil feeding capacities and how each scenario responds to this. The technical parameters considered are the quality and quantity of the biodiesel and glycerol produced, and the amount of biodiesel produced per amount of feedstock consumed. The economic evaluations have been carried out using parameters such as total investment cost, unit production cost, gross margin, payback time, internal rate of return (IRR), and net present value (NPV).

## Process descriptions

This study considers the techno-economic effects of the process layouts and production capacities of biodiesel production using CaO as a catalyst. The dominant reaction, in all of the process scenarios, is transesterification between ethanol and oil with 10% free fatty acid content on a molar basis. However, there is also an inevitable saponification reaction due to the presence of a considerable amount of the free fatty acid and the CaO catalyst. In all of the four process scenarios, the oil feedstock and the alcohol are heated up to the required optimum temperature before each is let into the reactors. The optimum reaction conditions required for maximum conversion of the oil into biodiesel is entirely based on the literature. Accordingly, the reaction temperature of 75 °C, catalyst amount of 7% wt (with respect to oil amount), ethanol to oil molar ratio of 9:1 and reaction time of 2 h have been taken as the optimum conditions for the main CaO catalyzed transesterification reaction to attain the maximum conversion of 97.58%.[31] The optimum reaction condition for the pre-esterification reaction in the first reactor, in scenario II, is a reaction temperature of 55 °C, a sulfuric acid catalyst amount of 2.26% wt. (with respect to oil amount), and ethanol to oil molar ratio of 6.1:1 to attain 96% conversion of the FFA and 30% conversion of the triglycerides in 4 h.[32] The four process scenarios have been designed based on some important assumptions.

### Design assumptions

The basic assumptions considered during designing the process alternatives are as follows:

- For general techno-economic evaluation purposes, the oil feedstock capacity of 5177.23 kg $h^{-1}$ or 41 million kg per year is kept the same for all scenarios.
- Such oil feedstock is also assumed to be free from any solid particles and is expected to be supplied throughout the whole year.
- The feedstock is also considered to have very low moisture content and the water formed during esterification reaction in the first reactor in scenario II is negligible; hence the hydrolysis process is not taken into account.
- Triolien represents the acidic oil with oil density of 907.8 kg $m^{-3}$; the fatty acid is represented by oleic acid with a density of 895 kg $m^{-3}$ and the biodiesel is also represented by ethyloleate with a density of 873.9 kg $m^{-3}$.
- The number of working hours is 7920 (330 working days per year).
- In all of the process equipment, the reduction in pressure is ignored.
- As there are polar compounds involved in the processes, like ethanol and glycerol, the non-random two-liquid (NRTL) thermodynamic model is selected as the property package for the calculation of the activity coefficient of the liquid phase in the simulations.

- All process scenarios are assumed to be continuous processes to fulfill requirements for industrial-scale application.
- The lifetime of the project is taken to be 15 years.
- The project is expected to be fully funded Therefore loans from banks are not considered in the economic analysis.

### Raw materials

The raw materials in this study include acidic oil feedstock, alcohol, and catalysts. The acidic oil feedstock is assumed to have 10% free fatty acid content on a molar basis. This feedstock quality is typical of oils from most non-edible oil plants,[33] which can be produced at a lower cost than oils from edible oil plants. For each process scenario, the feedstock character is the same and the feeding rate is 5177.23 kg $h^{-1}$. The required amounts of alcohol and catalyst per hour are calculated using the feeding rate of the oil together with the optimum reaction conditions required to obtain the maximum conversion. The alcohol is ethanol. We took ethanol because it can be produced from renewable resources following very simple production routes and it is also safe to handle compared to methanol. The catalyst in all of the scenarios is heterogeneous CaO, which can be produced from waste materials like eggshell, mussel shell, and crab shell, among other substances. In addition to its least-cost character, we chose CaO catalyst because it can be recovered easily and can be reused many times without significant reduction in its catalytic activity.[22,34] There is also another catalyst, sulfuric acid, considered to catalyze the pre-esterification reaction in scenario II. We use sulfuric acid because it is the most effective and most studied acid catalyst for the esterification reaction. [6,7,35,36]

## Methods

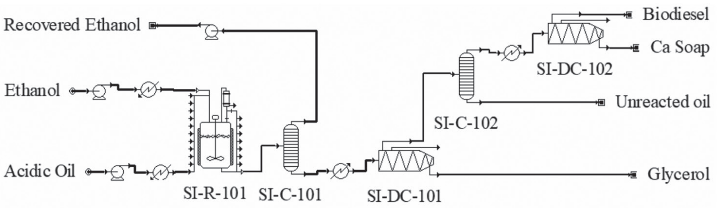
The techno-economic assessment of the proposed process alternatives is entirely based on process simulations using Aspen Plus software from Aspentech, Bedford, Massachusetts, United States [37] and Super Pro software from Intelligen Inc., Scotch Plains, New Jersey, US[38] to design the process alternatives. First, each scenario has been designed using Aspen Plus based on the design assumptions indicated above. Then each process flow has also been redesigned using Super Pro software, taking the results from Aspen Plus into consideration. We used Aspen Plus because it is very specific in the selection of property methods, thermodynamic methods, and pure component parameters according to the character of the chemicals and the specific reactions involved in the processes. The use of super pro is also helpful for the economic analysis of the scenarios as it is very convenient and flexible in acquiring meaningful cost data. Above all, using the two software together would make the result essentially accurate enough.

### Process alternative scenarios

The alternative process scenarios have been designed considering the various options of the downstream process units required to produce fuel-grade biodiesel from acidic oil using CaO as a catalyst. It is assumed that the differences in the arrangement and type of these unit procedures would result in a change in their techno-economic efficiency. The arrangement of the main unit procedures in each scenario and their distinctive differences are indicated as follows.

#### Scenario I

In scenario I, the oil feedstock (5177.23 kg $h^{-1}$) and the ethanol (2341.35 kg $h^{-1}$) are separately heated to 75 °C and pumped into the fixed-bed reactor (SI-R-101) packed with CaO catalyst, where the acidic oil is converted into biodiesel and glycerol. The crude product leaves the reactor at a rate that enables it to attain a residence time of 2 h in the reactor in accordance with the optimum reaction conditions from the literature.[31] This crude product is then taken out and let into a short-cut distillation column (SI-C-101), where the excess ethanol is recovered for reuse or to be considered for a credit calculation. This column is designed to have seven stages and a reflux ratio of 1.6 for maximum percentage of ethanol recovery. The bottom outlet from the distillation column mainly consists of biodiesel, glycerol, unreacted oil, and calcium soap (calcium oleate). It is cooled to an ambient temperature and passed to a centrifugal decanter (SI-DC-101) to separate the glycerol component from the rest easily. Finally, biodiesel purification is carried out in another short-cut distillation column (SI-C-102). This distillation column is made to have a 0.125 reflux ratio and 18 stages so that the maximum possible quality biodiesel can be attained. However, as there is a considerable amount of calcium soap in the biodiesel from this distillation column, it requires an addition step for further purification so that the fuel quality meets American Society of Testing and Materials (ASTM) standards. In doing so, the biodiesel from the distillation column is cooled and let into the second centrifugal decanter (SI-DC-102), where the calcium soap is separated from the biodiesel product. The design indicating the process flows in scenario I is shown in Fig. 2.



| Time Ref: h | | Recovered Ethanol | Ethanol | Glycerol | 99% unreacted oil | Acidic Oil | Biodiesel | Soap |
|---|---|---|---|---|---|---|---|---|
| Type | | Credit | Raw Material | Revenue | Credit | Raw Material | Revenue | Revenue |
| Total Mass Flow | kg | 1638.4262 | 2341.3500 | 496.0739 | 121.5453 | 5177.2300 | 5132.3045 | 147.9112 |
| Temperature | °C | 54.3 | 25.0 | 26.7 | 101.7 | 25.0 | 40.0 | 40.0 |
| Pressure | bar | 3.750 | 1.013 | 1.013 | 1.013 | 1.013 | 1.013 | 1.013 |

Figure 2. Process flows in scenario I: SI-R-101 fixed-bed reactor for biodiesel production; SI-C-101 first short-cut distillation for ethanol recovery; SI-DC-101 centrifugal decanter for glycerol separation; SI-C-102 second short-cut distillation for biodiesel purification, SI-DC-102 second centrifugal decanter for further purification of the biodiesel.

## Scenario II

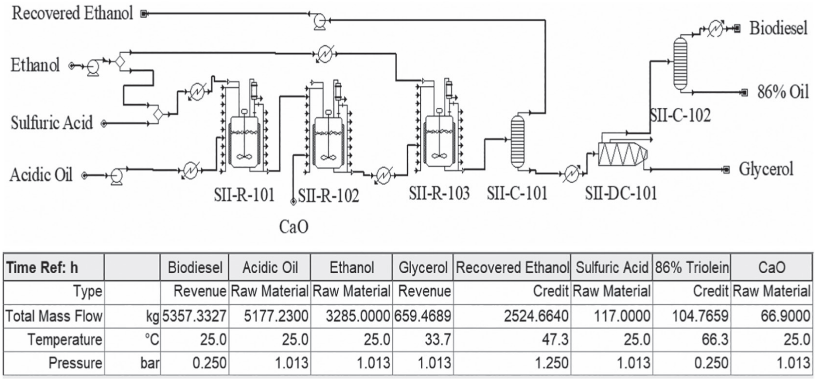
Scenario II has a different process arrangement from scenario I. This difference is mainly due to the inclusion of the preliminary reactor (SII-R-101) for the pre-esterification of the acidic oil to lower the FFA content as well as another continuous stirred tank reactor (CSTR) (SII-R-102) for neutralization of the sulfuric acid used to catalyze the pre-esterification reaction in the first reactor. The specified amount of oil feedstock (5177.23 kg h$^{-1}$), ethanol (1646 kg h$^{-1}$), and sulfuric acid (117 kg h$^{-1}$), which are determined based on the optimum reaction conditions, are heated up and let into the pre-esterification reactor, where 96% of the FFA and 30% of the triglycerides are converted.[32] The residence time in this reactor is 4 h according to the assumed reaction conditions from the literature.[32] Then the product from this reactor is taken to the second CSTR to neutralize totally the sulfuric acid, which could otherwise consume the CaO catalyst in the third reactor and lower the rate of the biodiesel production process if left to flow into the downstream process. The output from the neutralization reactor as well as a specified amount of heated ethanol (1639 kg h$^{-1}$) are let into the third reactor (SII-R-103), which is a fixed-bed reactor packed with CaO catalyst. In this third reactor, the dominant reaction is CaO-catalyzed transesterification where the remaining triglycerides are converted into biodiesel and glycerol. The product from this reactor is taken to the short-cut distillation column (SII-C-101) to recover the excess ethanol. This column has three stages and a reflux ratio of 1.5, which enables the maximum amount of ethanol to be recovered. The bottom outlet from this distillation column is cooled to the ambient temperature and is let into the centrifugal decanter (SII-DC-101) to separate the glycerol part easily. The remaining product from this centrifuge is then passed to another distillation column (SII-C-102) for further purification of the biodiesel, as in scenario I. The design indicating the process flows in scenario II is shown in Fig. 3.

## Scenario III

The process flows and the material inputs in scenario III are similar to those of scenario I, until the procedure required for glycerol separation. Their difference is mainly in the arrangement of the two procedures for purification of the biodiesel product. In scenario III, the crude product from the first centrifuge (SIII-DC-101) is let directly into second centrifuge (SIII-DC-102) for separation of the calcium soap from the rest of the product. However, because the biodiesel product from this second centrifuge has a considerable amount of unreacted oil, its quality cannot fulfill the ASTM biodiesel fuel standards' requirements in terms of minimum allowable percentage of unreacted oil in the fuel. Accordingly, the product from the second centrifuge is let into the second distillation column (SIII-C-102) for further purification of the biodiesel by separating it from the unreacted oil. The design indicating the process flows in scenario III is shown in Fig. 4.

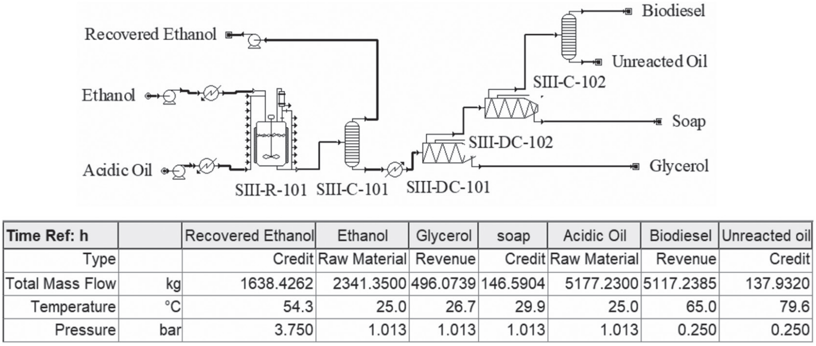
## Scenario IV

Scenario IV is a double reactor scenario, which involves two consecutive fixed-bed reactors packed with CaO catalyst for maximum possible conversion of the oil into



| Time Ref: h | | Biodiesel | Acidic Oil | Ethanol | Glycerol | Recovered Ethanol | Sulfuric Acid | 86% Triolein | CaO |
|---|---|---|---|---|---|---|---|---|---|
| Type | | Revenue | Raw Material | Raw Material | Revenue | Credit | Raw Material | Credit | Raw Material |
| Total Mass Flow | kg | 5357.3327 | 5177.2300 | 3285.0000 | 659.4689 | 2524.6640 | 117.0000 | 104.7659 | 66.9000 |
| Temperature | °C | 25.0 | 25.0 | 25.0 | 33.7 | 47.3 | 25.0 | 66.3 | 25.0 |
| Pressure | bar | 0.250 | 1.013 | 1.013 | 1.013 | 1.250 | 1.013 | 0.250 | 1.013 |

Figure 3. Process flows in scenario II: SII-R-101 first CSTR for pre-esterification; SII-R-102 second CSTR for acid neutralization; SII-R-103 third fixed-bed reactor for biodiesel production; SII-C-101 first distillation column for ethanol recovery; SII-DC-101 centrifugal decanter for glycerol separation; SII-C-102 second distillation column for biodiesel purification.



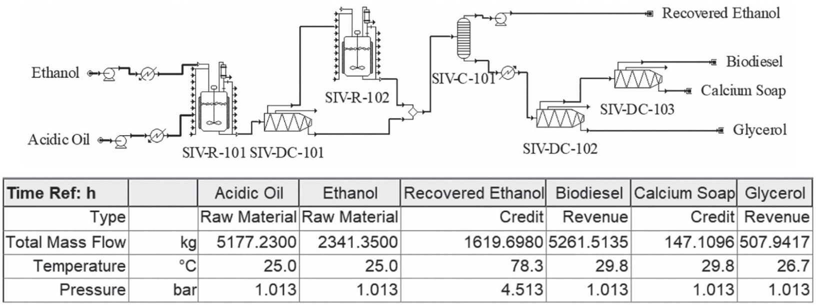
| Time Ref: h | | Recovered Ethanol | Ethanol | Glycerol | soap | Acidic Oil | Biodiesel | Unreacted oil |
|---|---|---|---|---|---|---|---|---|
| Type | | Credit | Raw Material | Revenue | Credit | Raw Material | Revenue | Credit |
| Total Mass Flow | kg | 1638.4262 | 2341.3500 | 496.0739 | 146.5904 | 5177.2300 | 5117.2385 | 137.9320 |
| Temperature | °C | 54.3 | 25.0 | 26.7 | 29.9 | 25.0 | 65.0 | 79.6 |
| Pressure | bar | 3.750 | 1.013 | 1.013 | 1.013 | 1.013 | 0.250 | 0.250 |

Figure 4. Process flows in scenario III: SIII-R-101 fixed-bed reactor for biodiesel production; SIII-C-101 first short cut distillation for ethanol recovery; SIII-DC-101 first centrifugal decanter for glycerol separation; SIII-DC-102 second centrifugal decanter for calcium soap separation and SIII-C-102 second short cut distillation for further purification of the biodiesel.

biodiesel. Oil feedstock and ethanol are heated to the optimum reaction temperature (75 °C) and are pumped into the first reactor (SIV-R-101), where most of the oil is converted into biodiesel. The product from this first reactor is then taken into a centrifugal decanter (SIV-DC-101) to separate the glycerol part so that the remaining crude product is let into the second packed-bed reactor (SIV-R-102) for further conversion of the unreacted oil into biodiesel. The outlet from this second reactor is then passed to a short-cut distillation column (SIV-C-101) for recovery of the excess ethanol used in the process. This column is designed to have 18 stages and a reflux ratio of 0.125 to recover the maximum possible amount of ethanol. The bottom outlet from this column is cooled to the ambient temperature and let into a centrifugal decanter (SIV-DC-101) for separation of the glycerol part from the rest of the product components. Finally, the remaining product is directed to another centrifugal decanter (SIV-DC-102) to purify the biodiesel. The design indicating the process flows in scenario IV is shown in Fig. 5.

## Techno-economic assessment

The techno-economic assessment considers both technical and economic performance, which is usually done to make the overall evaluation more realistic. This is because



| Time Ref: h | | Acidic Oil | Ethanol | Recovered Ethanol | Biodiesel | Calcium Soap | Glycerol |
|---|---|---|---|---|---|---|---|
| Type | | Raw Material | Raw Material | Credit | Revenue | Credit | Revenue |
| Total Mass Flow | kg | 5177.2300 | 2341.3500 | 1619.6980 | 5261.5135 | 147.1096 | 507.9417 |
| Temperature | °C | 25.0 | 25.0 | 78.3 | 29.8 | 29.8 | 26.7 |
| Pressure | bar | 1.013 | 1.013 | 4.513 | 1.013 | 1.013 | 1.013 |

Figure 5. Process flows in scenario IV: SIV-R-101 first fixed-bed reactor for biodiesel production; SIV-DC-101 first centrifugal decanter for glycerol separation; SIII-R-102 second fixed-bed reactor for further more biodiesel production; SIV-C-101 short-cut distillation for ethanol recovery; SIII-DC-102 second centrifugal decanter for glycerol separation and SIII-DC-103 third centrifugal decanter for calcium soap separation.

economic assessment without considering, for example, the quality of the biodiesel product, which is a technical parameter, would make the evaluation incomplete. The technical parameters considered in this study are therefore the quality and quantity of biodiesel and glycerol, and the amount of biodiesel produced per amount of oil feedstock consumed. Similarly, the economic parameters include total investment cost, unit production cost, internal rate of return, net present value, payback time, and return on investment (ROI).

Economic performance was evaluated using the recent market values of raw materials, labor, utilities, and the estimated costs of equipment including equipment-associated costs such as installation, auxiliary, instrumentation, and piping costs, among others. One of the raw materials is the oil feedstock with 10% FFA content on a molar basis. Such oil feedstock could represent most of non-edible plant oil, and it is cheap with an estimated cost of 478–684 US$ ton$^{-1}$.[39,40] We took the average of this cost range, 580 US$ ton$^{-1}$, to represent the cost of the oil feedstock assumed in the designs. Relevant literature[41] and information from suppliers in Ethiopia[42] were the main sources to obtain the current market values of the other raw materials, such as ethanol, sulfuric acid, and calcium oxide. The utilities considered while designing all of the process scenarios include electricity, steam, steam high, and cooling water, and their respective costs are entirely based on their current market price in Ethiopia as well as the relevant literature.[43,44] The labor cost calculation considers the latest amount of basic rate allocated for each labor category in the Ethiopian context. The information for this basic rate amount is based on the current wage indicator in Ethiopia.[45] Table 1 lists raw materials, utilities, and labor, including their respective costs.

The purchasing cost of the equipment involved in each scenario is estimated based on the Peter and Timmerhaus method.[46] For such cost estimation, the latest chemical engineering plant cost index used is 630.63 for July 2018.[47] Changes in cost of the equipment because of inflation and deflation are captured by this cost index, which enables the latest purchasing cost of the equipment to be estimated using its former cost. The estimated purchasing cost for the equipment is then used to estimate the value of the direct plant cost categories, such as instrumentation, auxiliary, electricity, piping, and yard improvement costs. This is carried out using the percentage allocation of the equipment purchasing cost for each cost category as shown in Table 2.

**Table 1. Raw materials, utilities, and labor with their respective cost.**

| Raw material | US$ kg$^{-1}$ |
|---|---|
| Oil | 0.580 US$ kg$^{-1}$ |
| Ethanol | 0.300 US$ kg$^{-1}$ |
| Sulfuric acid | 0.400 US$ kg$^{-1}$ |
| CaO | 0.120 US$ kg$^{-1}$ |
| *Utilities* | |
| Electricity | 0.09 US$ (KW-h)$^{-1}$ |
| Steam | 12 US$ MT$^{-1}$ |
| Steam high | 20 US$/MT$^{-1}$ |
| Cooling water | 0.05 US$ MT$^{-1}$ |
| *Labor (Basic rate)* | |
| Operator | 15 US$ h$^{-1}$ |
| Reactor operator | 20 US$ h$^{-1}$ |

**Table 2. Direct plant cost estimations based on equipment purchasing cost.**[15]

| Cost category | % allocation with equipment cost |
|---|---|
| Piping | 20 |
| Instrumentation | 10 |
| Electrical | 15 |
| Insulation | 3 |
| Building | 15 |
| Yard improvement | 10 |
| Auxiliary facilities | 25 |
| Unlisted equipment | 20 |

**Table 3. Relations to estimate capital investment and operating costs.**[48]

| Cost items | Estimation methods |
|---|---|
| *Capital investment cost categories* | |
| Installation cost (for each equipment) | 0.2 X PC |
| Maintenance cost (for each equipment) | 0.1 X PC |
| Purchasing cost of unlisted equipment (PCUE) | 0.2 X PC |
| Installation cost of unlisted equipment | 0.5 X PCUE |
| *Operating cost categories* | |
| Insurance | 2 X DFC |
| Local tax | 15 X DFC |
| Factory expense | 5 X DFC |
| Laboratory and quality control | 30 X TLC |

The other capital investment cost categories, like the equipment installation cost, maintenance costs, cost of unlisted equipment and depreciation, as well as insurance and tax estimates, are compiled as indicated in Table 3.

The effect of the variation in feedstock capacity on the economics of biodiesel production using CaO as a catalyst has also been tested. The change in feeding rate of the oil feedstock results in a change in the amount and the total cost of ethanol, calcium oxide, and sulfuric acid, as well as the cost of equipment. This is because the relative amounts of the raw materials are determined based on the amount of the oil feedstock, and their total cost depends on their total amount. Similarly, the cost of the equipment is affected by its size, which is directly related to the amount of oil feedstock considered in the process. We therefore compared three production capacities to see if variation in production capacity could have an effect on the economic efficiency of the production processes. These production capacities are specified by the feeding rate of the oil feedstock and they are 3106.34, 5177.32, and 7248.12 kg $h^{-1}$.

## Results

To evaluate the techno-economics of the processes, a material and energy balance was carried out for each scenario. This took the optimum reaction conditions, design assumptions, and equipment size into consideration. Then the results of this material and energy balance were used to measure the technical performance of the process alternatives. These results, together with the estimated costs of raw materials, labor, utilities, equipment, and current market values of products was also used to evaluate the economic performance of the process alternatives.

### Technical performance

The technical efficiency of the process alternatives was measured using the quality and quantity of biodiesel and glycerol as well as the production performance of the alternatives, expressed in terms of the amount of biodiesel produced per amount of feedstock consumed. The amount and purity / quality of ethanol recovered is also considered to measure their technical performance. In general, the technical performance of the scenarios, in terms of the amount of biodiesel per amount of oil feedstock as well as the quality of the products, are in agreement with the results found in other studies.[49,50] The numerical values of the performance parameters from this study are indicated in Table 4.

A higher biodiesel production amount is achieved in scenario II (5347 kg $h^{-1}$) and the smallest is in scenario III (5117 kg $h^{-1}$). In scenario II, the higher biodiesel amount is due to pre-esterification of the acidic oil to reduce the FFA content. This helps to omit totally the saponification reaction and produce an additional amount of biodiesel through the esterification of FFA. The second highest biodiesel amount is in scenario IV (5257 kg $h^{-1}$), which is apparently due to the presence of a double reactor to achieve a greater conversion of oil to biodiesel.

Even though all of the scenarios reached an acceptable level of biodiesel purity, scenarios II and IV accomplished this without additional purification processes, unlike scenarios I and III. The maximum purity in scenario IV is mainly due to the double reactors converting most of the oil, reducing the amount of unreacted oil in the biodiesel, and also due to the subsequent double centrifuges to separate glycerol and calcium soap from the biodiesel efficiently. Similarly, the absence of saponification together with the use of a short-cut distillation column for biodiesel purification could help to obtain greater purity in scenario II. The former would help to avoid calcium soap

**Table 4. Numerical values of technical performance parameters.**

| Scenarios | Biodiesel | | Glycerol | | Recovered ethanol | | Performance[a] |
|---|---|---|---|---|---|---|---|
| | Amount (kg h$^{-1}$) | Purity | Amount (kg h$^{-1}$) | Purity | Amount (%) | Purity | |
| **I** | 5132 | 99.99 | 496 | 99 | 67.5 | 96.4 | 0.99 |
| **II** | 5347 | 99.80 | 505 | 76 | 75.8 | 98.6 | 1.03 |
| **III** | 5117 | 99.99 | 496 | 99 | 67.5 | 96.4 | 0.98 |
| **IV** | 5256.6 | 99.90 | 507.8 | 99 | 66.7 | 96.4 | 1.02 |

[a] Biodiesel amount per oil amount.

**Table 5. Impurities percentage in the biodiesel from each scenario and their respective maximum allowable amount as per ASTM.**

| Scenarios | Biodiesel purity (mass %) | Percentage of impurities in the biodiesel product from each scenario | | | |
|---|---|---|---|---|---|
| | | Glycerol | Water | Triolein | Calcium soap |
| I | 99.99 | 0.002 | 0 | 0 | 0% |
| II | 99.80 | 0.07 | 0 | 0 | 0 |
| III | 99.99 | 0.002 | 0 | 0.012 | 0 |
| IV | 99.90 | 0.04 | 0 | 0.06 | 0 |
| **Max. allowable due to ASTM** | | **0.25** | **0.05** | **0.2** | **5 ppm (0.0005%)** |

impurity whereas the latter could efficiently separate the unreacted oil from the biodiesel. However, in scenarios I and III, the last unit procedures are additional process steps for further purification of the biodiesel to meet the fuel quality standard for the biodiesel produced.

The quality of the biodiesel product is the most important parameter; the biodiesel produced should have fuel-grade quality and fulfill international standards like ASTM and / or the European biodiesel standard. Such quality is determined by the relative percentage of glycerol, triolein, as well as total free glycerol, free fatty acids, monoglycerides and diglycerides. Table 5 indicates the percentages of the major impurities in the biodiesel from each scenario as well as the maximum allowable amounts according to the ASTM standard for comparison.

As shown in Table 5, biodiesel produced from all four scenarios could meet the ASTM standard's criteria in terms of the maximum amount of impurities. However, the high biodiesel fuel quality from scenarios I and III is mainly due to additional purification steps, which could incur additional costs and make the processes economically unattractive.

The amount of glycerol product is relatively higher in scenarios II and IV. However, the glycerol product from scenario IV is 2.8 kg h$^{-1}$ higher than that from scenario II. This is because the double reactor phenomenon in scenario IV encourages the conversion of more oil to biodiesel and glycerol. The purity of the glycerol is also lower in scenario II, where a considerable amount of calcium sulfate impurity is found in the glycerol due to the sulfuric acid neutralization reaction. There is also another economically valuable byproduct – calcium soap from scenarios I, III, and IV. Calcium soap can be used as a feed supplement for dairy cattle and other ruminants.[51]

## Economic performance

The economic performance evaluation requires the latest market values of inputs and outputs to be considered. In this study, recent and updated cost estimations for equipment, raw materials, utilities, and labor were taken from the relevant literature and suppliers in Ethiopia. The numerical values of the economic performance parameters for each process scenario are shown in Table 6.

Scenario II records a higher total investment cost, whereas scenario III is the cheapest among the process alternatives. This high cost of total investment in scenario II is due to the cost of equipment as it has three reactors: for pre-esterification, acid neutralization, and biodiesel production. The higher the equipment cost, the higher would be the direct costs associated with equipment such as installation, auxiliary costs, and instrumentation costs as well as cost of utilities. The higher cost of raw materials, due to a larger amount of ethanol (for pre-esterification and transesterification) and additional catalyst (sulfuric acid for esterification) may also be considered to be another reason for the high investment costs in scenario II. Even though scenario II could show a higher annual revenue, because of more biodiesel product, its unit production cost of biodiesel is higher than its unit production revenue. This results in negative NPV, a longer payback time, and less IRR and ROI, making the process economically infeasible.

Similarly, in scenario III the unit production revenue is slightly less than the unit production cost. In scenario

**Table 6. Results of economic performance of each process scenario.**

| Economic parameters | Process scenarios | | | |
|---|---|---|---|---|
| | I | II | III | IV |
| Total investment cost (US$) | 5 611 537 | 7 541 684 | 5 346 045 | 6 165 411 |
| Annual operating cost (US$ year$^{-1}$) | 32 620 354 | 36 562 306 | 32 422 148 | 32, 380 476 |
| Annual credit (US$ year$^{-1}$) | 4 311 526 | 6 396 949 | 4 416 524 | 3 965 946 |
| Total annual revenue (US$ year$^{-1}$) | 32 620 938 | 34 042 058 | 32 409 485 | 33 323 059 |
| Unit production cost (US$ kg$^{-1}$) | 0.8025 | 0.8617 | 0.800 | 0.7770 |
| Unit production revenue (US$ kg$^{-1}$) | 0.8025 | 0.8023 | 0.7997 | 0.7997 |
| Gross margin (%) | 13.22 | 11.39 | 13.59 | 14.73 |
| ROI (%) | 52.81 | 36.81 | 56.26 | 55.04 |
| Payback time (year) | 1.89 | 2.72 | 1.78 | 1.82 |
| IRR, after tax (%) | NA | NA | NA | 11.64 |
| NPV (US$) | –3 324 238 | –27 234 609 | –3 307 283 | 2 297 909 |

I the unit production revenue is almost equal to the unit production cost. These two options therefore have a negative NPV and are economically unproductive at the given market prices of inputs and outputs.

Scenario IV is the most promising and techno-economically feasible production process. Even though it has the second highest investment cost, the unit cost of biodiesel production is well below the unit production revenue. It therefore has a positive NPV, a higher percentage of IRR and ROI, and a relatively shorter payback time, and is economically very attractive.

## Effect of variation in oil feedstock supply rate (production capacity)

Each process scenario responds differently to a change in the oil feedstock supply rate. Unit production cost, payback time, and NPV have been used as the main parameters to assess the economic effect of such variation in production capacity.

### Effect of production capacity on unit production cost

Scenario II gave greater value in terms of unit production cost for all production capacities considered. The production cost changed only slightly (about 0.04 US$ kg$^{-1}$ or 4.6% change) when the production capacity was changed from 3106.34 to 7248.12 kg h$^{-1}$. For the same change in production capacity, scenario IV indicated a greater reduction from its already low unit production cost (about 6.5%). This makes scenario IV more economically feasible at higher production capacities when compared to scenario II. Scenarios I and III show almost the same pattern in the change of unit production cost due to the change in production capacity. Scenario I indicated a 7.3% decrease in unit production cost whereas scenario III indicated a 5.8% decrease when production capacity changed from 3106.34 to 7248.12 kg h$^{-1}$. However, scenario IV has the lowest unit production cost among the alternative production capacities considered. Figure 6 shows the effect of a change of production capacity on unit production cost for the four process scenarios.

### Effect of production capacity on payback time

In all of the cases, scenario II has the longest payback time compared to the other scenarios. However, it indicated a 4.7% change in payback time for a production capacity change from 3106.34 to 7248.12 kg h$^{-1}$. In comparison, scenario IV, could attain a 5.5% change in payback time for the same change in production capacity. For scenarios I and III the change pattern is more or less the same, with scenario I indicating a slightly higher reduction in payback time for larger production capacities. Figure 7 shows the effect of change of biodiesel production capacity on payback time for the process scenarios studied.

### Effect of production capacity on NPV

For scenarios I, III and IV, the higher the production capacity the more feasible the business would become in terms of positive NPV. Moreover, for scenario IV, the production business could be economically feasible at rela-

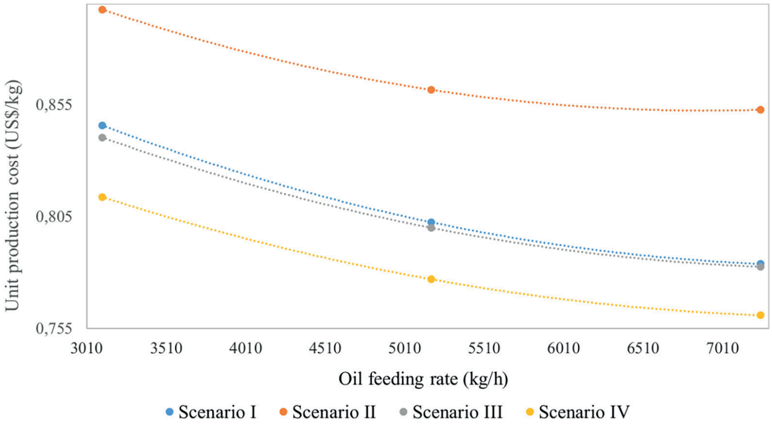


Figure 6. Effect of change of biodiesel production capacity on unit production cost.

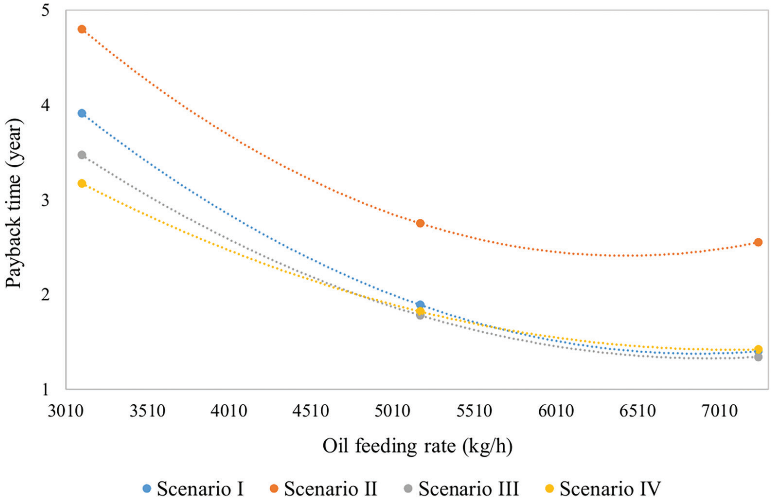


Figure 7. Effect of change of biodiesel production capacity on payback time.

tively lower production capacities of about 4600 kg $h^{-1}$ and above. However, for scenarios I and III the business can only be profitable when the oil feeding rate is above 6260 and 6050 kg $h^{-1}$, respectively.

Scenario II is more sensitive to change in production capacity, with a more negative NPV even for maximum production capacity. This might be due to the increase in the number of equipment units for the reactors required to accommodate the feedstock when the feeding rate is increased because, in scenario II, exceptionally, three reactors are designed. Moreover, two of the reactors are made of stainless steel because the reactions involve sulfuric acid. This causes the cost of the reactors to escalate as their capacity increases. Apparently, such an increase in equipment units and / or size results in higher equipment costs, utility costs, labor costs, and other equipment-associated costs such as auxiliary costs. For this reason, the total investment cost and operation cost increase so that the cash outflows exceed the cash inflows as production capacity increased. Figure 8 shows the effect of change in biodiesel production capacity on the NPV for all of the four process scenarios.

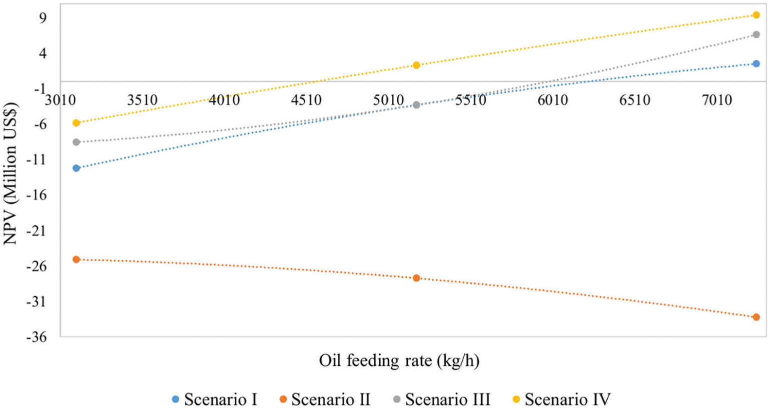


Figure 8. Effect of change of biodiesel production capacity on NPV.

## Conclusions

All four process scenarios could give fuel-quality biodiesel in accordance with the ASTM standards. In scenarios I and III, better quality biodiesel could be achieved with additional process steps considered to further purify the biodiesel. In general, in terms of overall technical performance, scenario IV is superior. It could attain biodiesel purity of 99.9%, provide the second highest amount of biodiesel (more biodiesel per given amount of oil feedstock), and provide the highest amount of glycerol, which would also be of higher quality. It could also provide another valuable byproduct – calcium soap – which could add an economic benefit to the process.

The economic performance evaluation indicated that scenario II is not economically feasible due to high investment costs, which result in a unit production cost that would be higher than revenue. This effect is more pronounced at higher production capacities. Comparatively good economic performance is indicated by scenario IV where the unit production cost is lower than scenario II by a magnitude of 0.09 US$/kg at optimum production capacity. However, at lower production capacity, scenario IV is not economically feasible as it indicated a negative NPV. A production capacity with oil feeding rate more than 4600 kg $h^{-1}$ could make scenario IV more dependable in terms of economic returns.

## Acknowledgements

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## Conflict of interest

The authors declare no conflicts of interest in this paper.

## Disclaimer

The authors are not responsible for any decision made based on the results of this study. The process designs indicated in this work are solely for research purposes. For specific applications, please contact the authors to obtain information about the limitations and scope of the process designs.

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# Paper VII

*energies*

Article

# Techno-economic performance of different technological based bio-refineries for biofuel production

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**Abstract:** There are different technologies for biodiesel production each having its own benefits and drawbacks depending on the type of feedstock and catalyst used. In this study, the techno-economic performances of four catalyst technologies have been investigated. The catalyst are bulk calcium oxide (CaO), enzyme, nano calcium oxide and ionic liquid. The study is mainly based on process simulations designed using Aspen Plus and Super Pro software. The quantity and quality of biodiesel and glycerol as well as the amount of biodiesel per amount of feedstock are the parameters to evaluate technical performances. The parameters for economic performances are total investment cost, unit production cost, Net Present Value (NPV), Internal Return Rate (IRR) and Return over Investment (ROI). Technically all the studied options provide fuel quality biodiesel and high purity glycerol. However, under the assumed market scenario, the process using bulk CaO catalyst is more economically feasible and tolerate to the change in market values of major inputs and outputs. In contrary, the enzyme catalyst option is very expensive and economically infeasible for all considered ranges of cost of feedstock and product. The result of this study can be used as a basis to do detail estimates for practical implementation of the efficient process.

**Keywords**: Biodiesel, CaO catalyst, Nano catalyst, Ionic liquid catalyst, economic analysis

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## 1. Introduction

According to the recent report from the World Energy Outlook 2018 [1], 93% of the world's carbon capacity is already in use up to 2040. Consequently, there is very narrow space for development of fossil fuel projects over this period without contradicting international objectives about climate change. This implies that it is becoming inevitable to push on the development of alternative and renewable energy resources for the supply of reliable and environmentally efficient energy to the growing economic activities around the world. Among such alternative sources are biofuels [2], which are mainly preferred for their carbon neutral character, their renewability as well as the fact that they can be produced in decentralized manners from abundant and versatile resources. Biodiesel is one of the promising biofuels to substitute the conventional fossil diesel. It has a number of environmental and technical benefits over the conventional fossil diesel. Environmentally, biodiesel is non-toxic, biodegradable, and its greenhouse gas (GHG) emission is very low compared to the conventional fossil diesel [3, 4]. The technical benefits are associated with its use for fuel, like for example, its possession of more oxygen to favor complete combustion and its better lubricating character to reduce engine wear [5].

Biodiesel can be produced from different oil and fat resources, which are found everywhere. Such feedstock include edible and non-edible plant oil, animal fat as well as waste oils and fats. The production of fuel quality biodiesel from oil and fat feedstock mainly involve the transesterification reaction with alcohol in the presence of some kind of catalyst or without catalyst at supercritical condition. The transesterification reaction catalyzed by homogeneous base catalyst like NaOH and KOH is the conventional way of producing biodiesel at industrial scale [6], which requires relatively better quality feedstock like edible oil with very low free fatty acid (FFA) content [7, 8]. Such high quality feedstock is usually associated with high price. In addition, it creates food versus energy controversies. These reasons altogether have been making biodiesel the expensive alternative fuel compared to its counterpart – fossil diesel, because cost of feedstock can take up to 80% of the total cost of biodiesel production [9, 10]. Comparatively, the heterogeneous alkali catalyzed transesterification reaction has advantages of easy catalyst recovery and reuse for multiple times [11, 12]. Unlike the homogeneous ones, the heterogeneous alkali catalyzed transesterification can tolerate considerable amount of FFA in the feedstock. For instance, Avhad et al. [13] reported that using glycerol-enriched calcium oxide as heterogeneous alkali catalyst, a 96.1% of crude *Jatropha curcas* oil containing high free fatty acid could be converted into biodiesel within 7h. In addition, most of such heterogeneous base catalyst types can be easily prepared from cheap resources, indicating a potential to reduce biodiesel production cost. For example, industrial wastes (red mud, slag, ash) and biological wastes (chicken eggshells, mollusk shells, animal bones) have huge potential towards developing cheap catalyst for low-cost biodiesel production [14]. Among the heterogeneous alkali catalysts developed for biodiesel production, the main ones include basic zeolites, alkaline earth metal oxides and hydrotalcites [15].

The conventional chemical catalyst options also include homogeneous and heterogeneous acid catalysts. In general, acid catalyzed transesterification is very efficient in production of biodiesel from feedstock with very high FFA content [16, 17]. However, the problem usually associated with the use of acid catalysts are high reaction temperature, longer reaction time and corrosion of the equipment due to the acid catalyst [10]. There are some substantial advantages of solid acid catalysts over the homogeneous ones. This includes ease of catalyst separation from the reaction media, which lowers product contamination, ease of catalyst regeneration and reuse, as well as much-minimized equipment corrosion [18]

The other most promising technologies for production of biodiesel from least cost feedstock involve CaO based catalysts, enzyme catalysts, ionic liquid (IL) catalysts and nano particle catalysts. Calcium oxide, as a catalyst has such advantages as abundance occurrence, better catalytic property, easy separation from the product stream, reusability for multiple times, nontoxicity, and least cost character for feasible production of biodiesel from lower quality feedstock [19, 20]. Boey et al. [21] did a study on the production of biodiesel from waste cooking oil using a CaO catalyst derived from waste sources like mud crab shells and cockleshells. They calcined the CaO obtained from these wastes at 900°C for 2h separately and mix them in a 1:1 mass ratio to catalyze transesterification of the oil. According to their result, a 98% conversion could be achieved within 3h for optimum reaction conditions of 5wt.% catalyst and a methanol to oil molar ratio of 13:1 at methanol refluxing temperature [21]. In another study, Sasiprapha et al. [22] assessed the production of biodiesel from used oil using CaO catalyst derived from river snail shell. For optimum reaction conditions of methanol to oil ratio of 9:1, catalyst amount of 3 wt.% and reaction temperature of 65°C, they could achieve 92.5% conversion of oil to biodiesel within 3h [22].

Even though the enzyme-catalyzed approach for biodiesel production is the expensive option, primarily due to cost of enzyme, the technical performance of most enzyme catalysts for production of fuel quality biodiesel is very significant. Enzyme for catalysis of biodiesel production has such advantages over the chemical catalysts as being less energy intensive, allowing easy recovery of glycerol from the product stream and efficient conversion of acidic oil (oil with high FFA content) to biodiesel [23, 24]. A study done by Cervero´ et al. [25] indicated that a 95% conversion of soybean oil to biodiesel could be reached within 24h using Novozyme 435 enzyme catalyst at optimum reaction conditions of 5wt.% enzyme load, 3:1 molar ratio of ethanol to oil, and a temperature of 37°C. Ketsara et al. [26], also studied the production of biodiesel from used palm oil using mixed enzymes in a solvent free environment. The studied mixed enzyme contains *Pseudomonas fluorescens* and *Candida rugose*. According to their result, 89% conversion could be realized within 12h for optimum reaction conditions of 3:1 ethanol to oil molar ratio, 10% enzyme dosage, 2% water content of the oil feedstock and a 45°C reaction temperature [26].

The other group of promising catalysts for biodiesel production are ionic liquids, which are generally known as solvents and green catalysts in chemical processes. A number of ionic liquids are being used for catalysis of biodiesel production from various low cost feedstock alternatives. The use of such ionic liquids for biodiesel production provide considerable advantages over most other catalyst categories. Some of such advantages are low corrosion of equipment, ease of separation, recyclability, and less wastewater production [27]. In addition, the lower reaction time together with the ability to produce good quality biodiesel from low cost feedstock could make ionic liquid catalysis better alternative than most of the catalyst options for biodiesel production. Feng et al. [28] studied the transesterification process to produce biodiesel from palm oil using Brønsted acidic ionic liquid as catalyst. They found out that a conversion of 98.7% of the oil to biodiesel could be achieved within 2.5h when the optimum reaction conditions are: methanol to oil molar ratio of 21:1, catalyst dosage of 3 wt.%, and reaction temperature of 120°C [28]. In another study Ullah et al. [29] investigated the production of biodiesel from waste palm cooking oil using acidic ionic liquid as a catalyst. They used specific ionic liquid butyl-methyl imidazolium hydrogen sulfate ($BMIMHSO_4$) as catalyst and the highest biodiesel yield of 95.6% could be achieved with optimum reaction conditions of 5 wt.% of $BMIMHSO_4$, methanol to oil molar ratio of 15:1, 1h reaction time at 160°C reaction temperature and agitation speed of 600 rpm [29].

Similarly, nano catalysts are also becoming very interesting for the production of biodiesel from low quality feedstock as they do have higher catalytic activity due to having large pore size and large surface area. Having large pore size and large surface area means possessing more active catalytic surface, because active surface of a catalyst, which is its vital property, increases when the size of the catalyst is reduced [30]. Such higher catalytic character enables to use smaller amount of the catalyst compared to other catalyst options and this has considerable economic benefits for large-scale production processes. Generally, by using nano catalysts better conversion of oil feedstock to biodiesel can be achieved at relatively medium temperature and shorter reaction time. The study done by Bet-Moushoul et al. [31] indicated that oil conversion range of 90-97% could be attained within 3h using CaO-based gold nanoparticles as heterogeneous catalyst for transesterification of sunflower oil with methanol. For this conversion, the optimum reaction conditions were a reaction temperature of 65°C, methanol to oil molar ratio of 9:1, and a catalyst loading of 3wt.% [31]. **Table 1** shows some of the recent studies done on the optimum reaction conditions required to produce biodiesel from different feedstock types using bulk CaO, Ionic liquid, Enzyme and Nano particle catalysts.

**Table 1: Optimum reaction conditions for biodiesel production from different feedstock using four different catalyst categories: Bulk CaO, Enzyme, Ionic Liquid and Nano-particle catalysts**

| Catalyst | Feedstock | Alcohol | Optimum reaction conditions | | | Conversion (%) | Time (h) | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | | Alcohol molar ratio | Catalyst amount (Wt.%) | Temperature (°C) | | | |
| Glycerol-enriched CaO | Jatropha oil | Methanol | 9:1 | 15 | 65 | 93.5 | 7 | [13] |
| CaO | Vegetable oil | Methanol | 6:1 | 3 | 65 | 100 | 1.25 | [32] |
| Activated CaO | Sunflower oil | Methanol | 13:1 | 3 | 60 | 94 | 1.67 | [33] |
| CaO from river snail shell | WCO[d] | Methanol | 9:1 | 3 | 65 | 92.5 | 1 | [22] |
| CaO from chicken manure | WCO | Methanol | 12:1 | 7.5 | 65 | 93 | 6.5 | [34] |
| CaO from WBCS[e] | WCO | Methanol | 12:1 | 7 | 65 | 94.25 | 1 | [35] |
| Novozyme 435 | Soybean oil | Ethanol | 3:1 | 5 | 37 | 95 | 24 | [25] |
| Mixed Enzyme[a] | Used Palm oil | Ethanol | 3:1 | 10 | 45 | 89 | 12 | [26] |
| Immobilized lipase | Canola oil | Methanol | 6:1 | 2.15 | 40 | 90 | 24 | [36] |
| *Pseudomonas fluorescens* enzyme | Waste frying oil | Methanol | 3:1 | 5 | 45 | 63 | 24 | [37] |
| [Bmim]Im[b] | Vegetable oil | Methanol | 6:1 | 6 | 60 | 95 | 1 | [38] |
| 4B[c] | Vegetable oil | Ethanol | 9:1 | 5 | 60 | 94.3 | 5 | [39] |
| [Hnmm]OH[d] | Soybean oil | Methanol | 8:1 | 4 | 70 | 97 | 1.5 | [40] |
| [CyN1,1PrSO3H][p-TSA] | Palm oil | Methanol | 24:1 | 3 | 120 | 98.7 | 2.5 | [28] |
| Imidazole-based IL | Tung oil | Methanol | 21:1 | 5 | 120 | 98 | 2 | [41] |
| Iron doped zinc oxide Nano catalyst | Castor oil | Methanol | 12:1 | 14 | 55 | 91 | 0.833 | [42] |
| CaO/Au nanoparticles | Sunflower oil | Methanol | 9:1 | 3 | 65 | 90-97 | 3 | [31] |
| Functionalized CaO nanoparticles | Canola oil | Methanol | 9:1 | 3 | 65 | 97 | 8 | [43] |
| KF/CaO catalyst | Tallow seed oil | Methanol | 12:1 | 4 | 65 | 97.5 | 2.5 | [44] |

[a] *Mixture of Pseudomonas fluorescens and Candida rugose;* [b] *Ionic liquid: 1-butyl-3-methylimidazolium imidazolide;* [c] *Ionic liquid: 1-benzyl-1H-benzimidazole;* [d] *Ionic liquid: 1-butyl-3-methyl morpholine hydroxide;* [e] *WBCS - White bivalve clamshell;* [d] *WCO - Waste Cooking Oil*

Even though these four catalyst categories are technically capable of producing fuel quality biodiesel from various feedstock options, the relative economic feasibility of each production alternative remains unclear, as there are no such considerable studies performed so far to investigate the economic competitiveness of the alternatives. Accordingly, this study is aimed at evaluating the techno-economic performances of bulk CaO, enzyme, ionic liquid and nano particle catalyst technologies to produce biodiesel fuel from low quality and cheap oil feedstock. The study will compare the proposed catalyst technologies in terms of their technological efficiencies and economic feasibilities. Such approach would give complete view on the practicability of the process routes for sustainable production of biodiesel fuel. In addition, the study can be used as preliminary estimate of the whole set up of the projects based on which detail estimates for actual implementation of the efficient and affordable production process could be carried out. As to our knowledge, there are no similar investigations and comparisons performed among the catalyst technologies mentioned in this study.

The study is entirely based on process simulation involving all the unit procedures required to produce fuel quality biodiesel. These process simulations are designed using two commercial software - Aspen Plus and Super Pro. The technical performance evaluation has been done based on the relative amount and purity of the product biodiesel and the byproduct glycerol as well as the relative amount of biodiesel produced per amount of oil feedstock. Whereas the economic performance assessment has been performed using such economic parameters as Total Investment Cost, Unit Production Cost, Net Present Value (NPV), Internal Rate of Return (IRR), Return over Investment (ROI), and Gross Margin. The sensitivity of the technology options towards the change in market values of oil purchasing cost, catalyst purchasing cost and biodiesel price has also been assessed using NPV as a parameter.

## 2. Materials and Methods

### *2.1 Description of raw materials*

The raw materials used in all of the technological options include acidic oil feedstock, ethanol and four catalyst types such as bulk CaO, enzyme (Novozyme 435), ionic liquid (1-benzyl-1H-benzimidazole based IL) and nano CaO (Zinc doped CaO Nano particle). We took acidic oil with 10% FFA content to represent the oil from most of non-edible plants [45, 46], which are cheap and found everywhere. The alcohol considered is ethanol because it is non-toxic (thus easy to handle) and can be produced from renewable resources; making the biodiesel produced to be entirely from renewable resources.

The four catalyst categories considered in this study are proved to achieve significant conversion of low quality oil to biodiesel [25, 39, 47, 48]. The bulk CaO based catalyst can be prepared using cheap resources through very simple process steps like calcination [22]. Thus, we consider this catalyst because it is very cheap and can be easily prepared from waste materials. It can also be reused 13 times [49], favoring considerable reduction of the total cost required for catalyst purchase. Concerning the nano particle catalyst category, we took Zinc doped nano CaO catalyst, because it does have additionally better catalytic activity due to its higher surface area [30, 50]. Kumar et al. [48] found out that Zink doped CaO nano catalyst can catalyze transesterification of oil with 8.4 wt % FFA content for its complete conversion. The third catalyst category considered is enzyme, which is well known for its technical efficiency in producing fuel quality biodiesel from feedstock with very high FFA content [51, 52]. In this study, we consider the commercial enzyme, Novozyme 435, produced from *Candida antarctica*. Li Deng et al. [53] studied the performances of different lipases with different alcohols for production of biodiesel from sunflower oil; and found out that Novozyme 435 is preferable enzyme catalyst for highest yield of fatty acid alkyl esters (with more than 90% yield) using methanol, ethanol, 1-propanol. Even though, the cost of the enzyme is very high, the greater reusability rate of such catalysts would reduce the total cost required to purchase the enzyme catalyst. According to Andrade et al. [54], immobilized enzymes like Novozyme 435 can be reused 300 times favoring reduction of the total cost. The fourth catalyst considered is ionic liquid catalyst, which is very well known to achieve higher conversion within relatively short reaction time when compared to most of the catalyst types used for biodiesel production [27, 29, 41]. In this specific study, we prefer to take the Bronsted acid Ionic Liquid, *1-benzyl-1H-benzimidazole,* because this catalyst is proved to be one of the highly efficient catalyst compared to other ionic liquid catalysts [39]. This catalyst can be reused 8 times without considerable reduction in its catalytic activity [39].

### *2.2 Design assumptions*

The process flow diagrams of all the production technology options are designed based on the following assumptions

- ✓ Feeding rate of the oil feedstock is kept the same for all technological options and it is 5177.23 kg/h. This value is assumed to represent large-scale production capacity considering that the oil feedstock has 10% FFA in molar basis; in that case, the feedstock consists of 5000 kg triglyceride and 177.23 kg FFA.

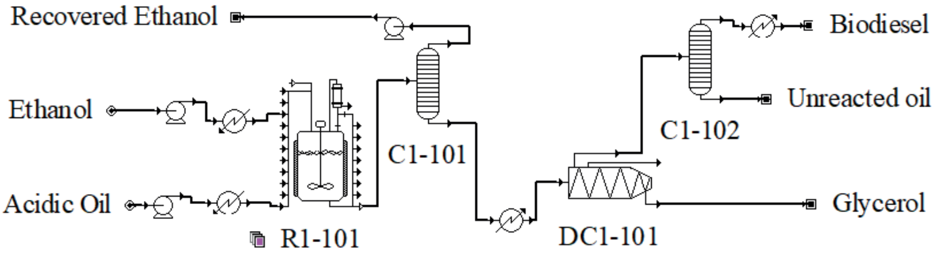
- ✓ It is assumed that there is no solid particle in the oil feedstock.
- ✓ The oil supply is continuous throughout the year.
- ✓ 7920 working hours or 330 working days per year are considered.
- ✓ In all of the equipment, the pressure drop is neglected.
- ✓ The triglyceride is represented by triolein with density of 907.8kg/m$^3$, the FFA is denoted by oleic acid with density of 895kg/m$^3$ and the pure biodiesel is denoted by ethyloleate with density of 873.9kg/m$^3$.
- ✓ Due to the presence of polar compounds such as ethanol and glycerol in all of the processes considered, the non-random two liquid (NRTL) thermodynamic model is selected as the property package for calculation of activity coefficient of the liquid phase in the simulations.
- ✓ The total project lifetime is assumed to be 15 years.
- ✓ There is no loan considered for all the projects.In each process option, the reusability of the catalysts is considered in the calculation of the total cost of catalyst.

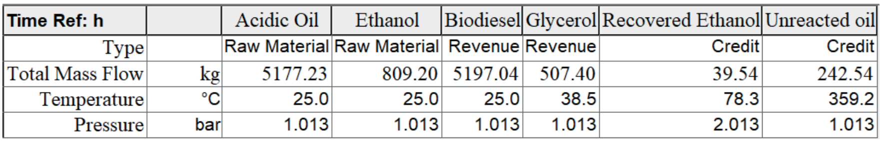
### *2.3 Description of the technology options for biodiesel production*

Four different catalyst options for biodiesel production from acid oil have been considered in order to examine their techno-economic performances while producing fuel quality biodiesel from cheap oil. ***Technology option I***: Enzyme catalyzed transesterification and esterification; ***Technology option II***: Bulk CaO catalyzed transesterification; ***Technology option III***: Ionic liquid catalyzed transesterification; and ***Technology option IV***: Nano-CaO catalyzed transesterification. Recently, these catalyst technology options are getting more emphasis by researchers for efficient and eco-friendly production of biodiesel from cheap resources. In all of the process alternatives, transesterification is the dominant reaction; however, there are also other possible side reactions that may occur based on the oil quality and the type of the catalyst used. The dominant reactions, the optimum reaction conditions, the amount and specific type of input materials as well as the whole flow of the processes involved in each catalyst technology are indicated as follows.

#### 2.3.1 Technology option I

This option is designed to investigate the techno-economic performance of the enzyme catalyzed biodiesel production process by involving all the equipment necessary to get fuel quality biodiesel. **Figure 1** indicates the process flow diagram of the enzyme catalysis technology option.





| Time Ref: h | | Acidic Oil | Ethanol | Biodiesel | Glycerol | Recovered Ethanol | Unreacted oil |
|---|---|---|---|---|---|---|---|
| Type | | Raw Material | Raw Material | Revenue | Revenue | Credit | Credit |
| Total Mass Flow | kg | 5177.23 | 809.20 | 5197.04 | 507.40 | 39.54 | 242.54 |
| Temperature | °C | 25.0 | 25.0 | 25.0 | 38.5 | 78.3 | 359.2 |
| Pressure | bar | 1.013 | 1.013 | 1.013 | 1.013 | 2.013 | 1.013 |

**Figure 1**. Technology option I: R1-101 Continuous Stirred Tank Reactor (CSTR) to produce biodiesel, C1-101 first short cut distillation column to recover unreacted ethanol, DC1-101 centrifugal decanter to separate glycerol, C1-102 second short cut distillation column to purify biodiesel

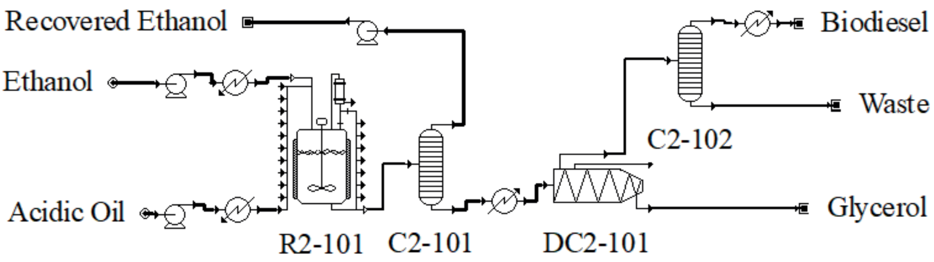
The dominant reactions involved in enzyme catalyzed processes are transesterification and esterification. There is also hydrolysis of the triglyceride by water produced from esterification reaction. Therefore, enzyme catalyzed biodiesel production is comprised of two processes, namely: direct alcoholysis of triacylglyceride in one-step reaction and a two-step hydrolysis of triacylglyceride followed by an esterification [25].

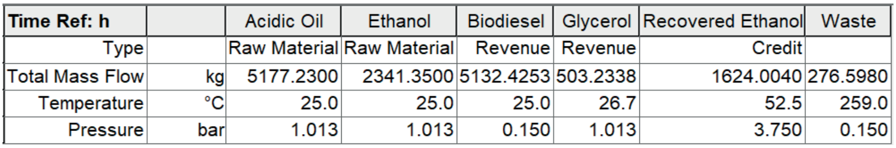
The optimum reaction condition is taken to be 3:1 ethanol to oil molar ratio, 5 wt.% Novozyme 435 catalyst, and 37°C reaction temperature to attain about 95% oil conversion within 24h [25]. The alcohol to oil molar ratio considered here is the exact stoichiometric amount (3:1) because excess amount of alcohol in the reaction could hinder the activity of the enzyme [25, 55]. Especially when methanol is used as the reacting alcohol, the effect is more pronounced [25] and it is always recommended to perform stepwise (2 or 3 steps) addition of the alcohol to the reaction [51, 56]. However, concerning ethanol alcohol, the effect is not that much significant and one-step addition of the stoichiometric amount does not significantly affect the enzyme activity. This might be due to the lower amount of undissolved alcohol in the substrate when we use ethanol than methanol, because it is much amount of undissolved alcohol that inhibits the enzyme activity [57]. Thus, since ethanol is more soluble in oil than methanol [58], enzyme inhibition effect is very low when we use ethanol than methanol. Cervero´ et al. [25] also indicated that at maximum reaction time, the conversion of soybean oil to biodiesel is almost similar for both single step and multiple step addition of ethanol to the reaction. Accordingly, one-step addition of the ethanol is considered in this process flow. This could also avoid the need to include more reactors, which would otherwise be if the alcohol is added in multiple steps.

Both the oil (5177.23 kg/h) and ethanol (809.35 kg/h) are heated up to 37°C and pumped separately to a continuous stirred tank reactor (R1-101), which has a total volume of 33.6 $m^3$ and packed with Novozyme 435 catalyst. The reactor is designed to have constant temperature of 37°C and work continuously in such a way that the oil conversion of 95% could be achieved within a residence time of 24h based on the optimum reaction conditions taken from literature [25]. The produce from the reactor is then directed to the first distillation column (C1-101) to recover the unreacted ethanol for possible reuse and to improve the biodiesel quality too. The bottom outlet from this distillation column is cooled down and directed into a centrifugal decanter (DC1-101) to separate the glycerol. The upper output from this centrifugal decanter is then taken to the second short cut distillation column (C1-102) to purify the biodiesel. This distillation column is designed to have 11 number of stages and 0.125-reflux ratio for which the maximum possible biodiesel purification can be attained.

### 2.3.2 Technology option II

The second technological option considers the application of bulk CaO catalyst to produce biodiesel through transesterification of acidic oil by involving all unit procedures required to get high quality fuel. **Figure 2** indicates the flow diagram of the whole processes involved to produce biodiesel fuel using CaO catalyst.





| Time Ref: h | | Acidic Oil | Ethanol | Biodiesel | Glycerol | Recovered Ethanol | Waste |
|---|---|---|---|---|---|---|---|
| Type | | Raw Material | Raw Material | Revenue | Revenue | Credit | |
| Total Mass Flow | kg | 5177.2300 | 2341.3500 | 5132.4253 | 503.2338 | 1624.0040 | 276.5980 |
| Temperature | °C | 25.0 | 25.0 | 25.0 | 26.7 | 52.5 | 259.0 |
| Pressure | bar | 1.013 | 1.013 | 0.150 | 1.013 | 3.750 | 0.150 |

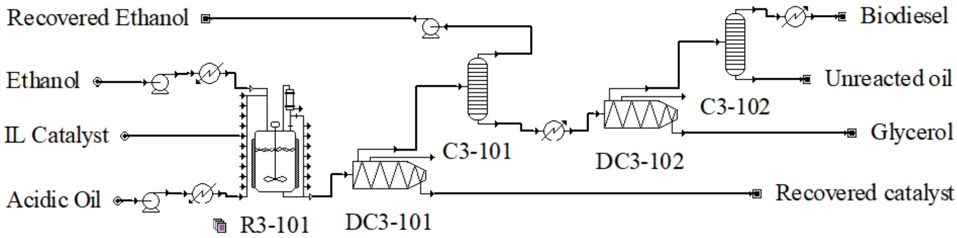
**Figure 2**: Technology option II: R2-101 CSTR for production of biodiesel, C2-101 first short cut distillation column to recover excess ethanol, DC2-101 centrifugal decanter to separate the glycerol, C2-102 second short cut distillation column to purify the biodiesel.

In this technology option, the dominant reaction is CaO catalyzed transesterification reaction for which excess amount of ethanol is used to favor forward reaction for more biodiesel production [20, 32]. There is also an unavoidable saponification reaction between the FFA and the catalyst, which could not be dominant due to relatively lower amount of FFA. The reactor designed is a continuous stirred tank reactor packed with bulk CaO catalyst. The optimum reaction conditions taken into consideration are oil to ethanol molar ratio of 9:1, catalyst loading of 7wt.% with respect to oil and reaction temperature of 75°C; and at such reaction conditions, 97.58% oil conversion could be achieved within 2h [47].

Oil amount at 5117.23 kg/h and ethanol amount at 2341.35 kg/h are heated up to 75°C separately and pumped into the continuous stirred tank reactor (R2-101), which has a total volume of 18.9 m$^3$ and packed with bulk CaO catalyst. The reactor is designed to have 75°C constant temperature. The outlet from the reactor is directed to the first distillation column (C2-101) to separate the excess ethanol for reuse. Seven number of stages and 2-reflux ratio are the optimum values taken in the design of this distillation column to recover the maximum possible ethanol left after the reaction. The lower pipe from this distillation column is directed to centrifugal decanter (DC2-101) for glycerol separation from the product mixture. The upper outlet from this centrifugal decanter is then directed to the second distillation column (C2-102) for purification of the biodiesel product. This distillation column is designed to with 4 number of stages and 3 reflux ratio, beyond which there could not be further purity of the biodiesel attained. The waste stream from this process is composed of unconverted oil and calcium soap, which is non-toxic and rather useful if further purification is included. However, such additional purification unit procedure incur considerable cost and would increase the overall production cost, making the technology option economically unattractive.

### 2.3.3 Technology option III

In this technology option, ionic liquid catalyzed biodiesel production process has been designed for techno-economic evaluation of the possible arrangement of all equipment required to produce fuel quality biodiesel. **Figure 3** indicates the whole flow diagram required to produce fuel quality biodiesel using specific type of ionic liquid catalyst.



| Time Ref: h | | Acidic Oil | Ethanol | Ionic Liquid Catalyst | Biodiesel | Glycerol | Recovered ethanol | Recovered Catalyst | Unreacted oil |
|---|---|---|---|---|---|---|---|---|---|
| Type | | Raw Material | Raw Material | Raw Material | Revenue | Revenue | Credit | Credit | Credit |
| Total Mass Flow | kg | 5177.2300 | 2428.0700 | 89.0000 | 5104.1441 | 490.1182 | 1674.3256 | 89.0761 | 336.7259 |
| Temperature | °C | 25.0 | 25.0 | 25.0 | 25.0 | 26.7 | 78.3 | 60.0 | 101.0 |
| Pressure | bar | 1.013 | 1.013 | 1.013 | 1.013 | 1.013 | 4.513 | 1.000 | 1.013 |

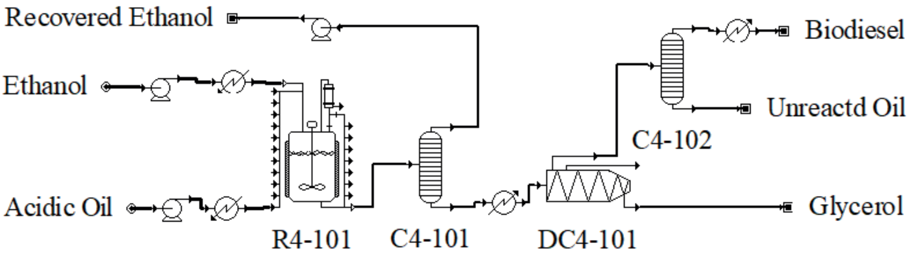
**Figure 3**. Technology option III: R3-101 CSTR for production of biodiesel, DC3-101 first centrifugal decanter to recover the catalyst, C3-101 first distillation column to recover excess ethanol, DC3-102 second centrifugal decanter to separate the glycerol and C3-102 second short cut distillation to purify the biodiesel.

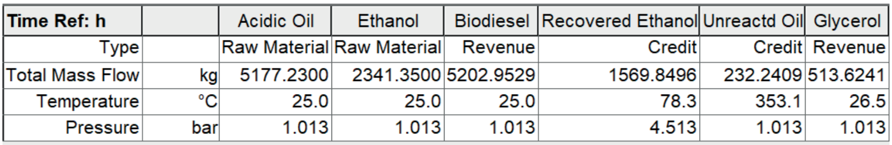
Transesterification is the dominant reaction considered here, even though there is also esterification reaction due to the presence of FFA in the oil. The optimum reaction condition taken for this process option is 9:1 ethanol to oil molar ratio, 5% (based on mmol of oil) catalyst, and 60°C reaction temperature to attain a maximum conversion (94.3%) of the oil with in 5h [39].

Oil with a rate of 5177.23 kg/h and ethanol with a rate of 2428.07 kg/h are heated up to 60°C separately and pumped into CSTR (R3-101), which has a total volume of 23.7 m3 and to which a Brønsted acid ionic liquid (1-benzyl-1H-benzimidazole) catalyst is also supplied at a rate of 258.86 kg/h. The reactor is designed to work at 60°C as constant temperature. The product from this reactor is directed into the first centrifugal decanter (DC3-101) for separation of the catalyst from the remaining product mixture. The upper outlet from this centrifugal decanter is let into the first short cut distillation column (C3-101) to recover the leftover ethanol for recycle. This column is designed to have 5 number of stages and 3.5-reflux ratio, above which there is no change in amount and quality of ethanol recovered. The bottom output from this first distillation column is then directed to the second centrifugal decanter (DC3-102) to separate glycerol. The upper outlet from the second centrifugal decanter is let into the second distillation column (C3-102) for purification of the biodiesel product. This distillation column is designed to have 7 number of actual stages and 0.125 reflux ratio by which the maximum possible purity could be attained.

### 2.3.4 Technology option IV

As the fourth technology option, nano-CaO catalyzed process has been designed to assess the techno-economic performance for production of fuel quality biodiesel. **Figure 4** indicates the whole process flow diagram of producing fuel quality biodiesel using Zinc doped CaO nano catalyst.





| Time Ref: h | | Acidic Oil | Ethanol | Biodiesel | Recovered Ethanol | Unreactd Oil | Glycerol |
|---|---|---|---|---|---|---|---|
| Type | | Raw Material | Raw Material | Revenue | Credit | Credit | Revenue |
| Total Mass Flow | kg | 5177.2300 | 2341.3500 | 5202.9529 | 1569.8496 | 232.2409 | 513.6241 |
| Temperature | °C | 25.0 | 25.0 | 25.0 | 78.3 | 353.1 | 26.5 |
| Pressure | bar | 1.013 | 1.013 | 1.013 | 4.513 | 1.013 | 1.013 |

**Figure 4.** Technology option IV: R4-101 CSTR for production of biodiesel, C4-101 first short cut distillation column to recover excess ethanol, DC4-101 centrifugal decanter to separate the glycerol, C4-102 second distillation column to purify the biodiesel.

Transesterification is the dominant reaction using nano CaO catalyst. According to the study done by Kumar et al. [48], the existence of saponification reaction among the specific catalyst, Zinc doped CaO, and the FFA in the oil is negligible. The optimum reaction condition for 99% conversion of the oil within 1h is taken to be molar ratio of ethanol to oil of 9:1, catalyst amount of 5 wt.% with respect to oil, and 65°C as the reaction temperature [48].

The oil at a feeding rate of 5177.23 kg/h and ethanol at a rate of 2341.35 kg/h are heated up to 65°C separately and driven into the continuous stirred tank reactor (R4-101), which has a total volume of 9.4 m$^3$ and packed with Zinc doped CaO nano catalyst. The rector is designed to work at a constant temperature at 65°C. The produce coming out of the reactor is directed into the first distillation column (C4-101) to distill out the excess ethanol for reusing. This column is designed to have 4 number of stages and 1 reflux ratio for maximum possible recovery of the excess ethanol. The bottom outlet from the first distillation column is cooled down to ambient temperature and directed to centrifugal decanter (DC4-101) for separation the glycerol from the rest of the mixture. Finally, the upper outlet from this centrifugal decanter is directed into the second short cut distillation column (C4-102) to purify the biodiesel from impurities such as unreacted oil and remaining glycerol. This distillation column is designed to have 7 number of stages and 0.2 reflux-ratio at which the maximum possible purity of the biodiesel product could be achieved.

In all of the production technology options, the storage tanks for raw materials and output are not involved, because the raw materials are considered to be used immediately and the outputs could also be used as soon as they are produced without the need to store them. In most of the process options, there is no waste stream from the production, except in technology option II, where the waste stream is composed of unreacted oil and calcium soap. This waste stream can be purified further to get reusable oil and economically valuable calcium soap. Calcium soap is vital as fat supplements for ruminants because it comprises high concentration of fat and calcium and both are beneficial for ruminants [59].

### *2.4 Techno-economic assessment*

The technical performances of the technology options are evaluated based on the relative amount and purity of biodiesel product and glycerol byproduct while using the same amount and quality of oil feedstock. The other important parameter considered is the quantity of biodiesel that can be produced from a kilogram of the oil feedstock. Such technical performance assessment depends on the material and energy balance, which is done using Aspen plus V10 considering optimum reaction conditions of the dominant reactions in each technology option.

The economic analysis of the processes has been carried out using Super Pro software. By using financial input data, the program calculates the internal return rate (IRR) (before and after tax), NPV (at 7% interest rate), Gross Margin, Unit Production Cost, and annual revenue among other important economic parameters. The latest market values and the estimated cost of raw materials, utilities, labor and equipment are used as the basis for evaluating the economic performances of the studied technology options. The other considerable cost categories for such evaluation are equipment installation cost, auxiliary facilities cost and depreciation cost among others. The feedstock taken is non-edible and cheap oil with estimated cost in a range of 478 - 684US$/ton [45, 46, 60]. In this specific study, feedstock cost of 580US$/kg was taken as the average value, because it is very cheap to produce such oil in Ethiopian context; even though there is no formal market to buy or sell non-edible oil in the country. The delivered cost of the other raw materials such as the four catalysts and ethanol are based on latest market prices taken from various sellers in Ethiopia as well as from relevant literature [54, 61].

The costs of all the required labor categories are according to the current wage indicator in Ethiopia [62], for which the conversion to US$ was done based on the rate at the time of referring the database. The labor cost is calculated using the basic rates allocated for each labor category. In doing so, the basic rate is multiplied by the sum of the benefit, supervision, supplies and administration rates as well as the total labor hours. In all of the technology options the percent of work time dedicated to process-related activities, which is used to estimate the labor time, is taken to be 70% considering that the technology options involve continuous processes. The utilities considered in all of the technology options include electricity, steam, steam high and cooling water; and their cost estimations are taken according to the current market prices in Ethiopia as well as from relevant literatures [63, 64]. **Table 2** shows estimated costs for utilities, labor and raw materials considered in all of the technology options.

**Table 2: Estimated cost of raw materials, labor and utilities used in the four technology options**

| | |
|---|---|
| *Raw materials* | |
| Oil | 0.478US$/kg |
| Ethanol | 0.300US$/kg |
| Bulk CaO | 0.120US$/kg |
| Ionic Liquid | 50.5US$/kg |
| Enzyme (Novozyme 435) | 1000US$/kg |
| Nano CaO | 6.5US$/kg |
| *Utilities* | |
| Electricity | 0.021US$/KW-h |
| Steam high | 10US$/MT |
| Steam | 6US$/MT |
| Cooling water | 0.025US$/MT |
| *Labor (Basic rate)* | |
| Reactor operator | 15US$/h |
| Operator | 10US$/h |

The cost of every equipment involved in all technology options is estimated using Peter and Timmerhaus method [65]. For such estimation, the Chemical Engineering Plant Cost Index of 691.8 for February 2019 is used [66]. This index signifies the money time value due to deflation and inflation by which the average cost of each equipment can easily be calculated for the year 2019 using previous year cost values. For the estimation of the other components of the capital investment cost like instrumentation, piping, electricity, installation, and yard improvement, a method involving allocation of percentage of total equipment purchasing cost is used based on literature as shown in **Table 3**.

**Table 3: Direct plant cost categories and their percentage allocation with equipment cost [67]**

| Cost category | % allocation with equipment |
|---|---|
| Piping | 20 |
| Instrumentation | 10 |
| Electrical | 15 |
| Insulation | 3 |
| Building | 15 |
| Yard improvement | 10 |
| Auxiliary facilities | 25 |
| Unlisted equipment | 20 |

These capital investment cost categories can directly be used in Super pro because its cost estimation interface gives options to assign estimated percent of total equipment cost for each direct plant cost category. The other equipment-associated costs such as insurance, depreciation, maintenance cost, and tax can also be put in the software based on the percentage allocation of their costs as indicated in **Table 4**.

**Table 4: Cost estimation methods for components of capital investment and operating costs**

| Cost items | Estimation method |
|---|---|
| Capital investment cost categories | |
| Installation cost (for each equipment) | 0.2 X PC[h] |
| Maintenance cost (for each equipment) | 0.1 X PC |
| Purchasing cost of unlisted equipment (PCUE) | 0.2 X PC |
| Installation cost of unlisted equipment | 0.5 X PCUE |
| Operating cost categories | |
| Insurance | 2 X DFC[i] |
| Local tax | 15 X DFC |
| Factory expense | 5 X DFC |
| Laboratory and quality control | 30 X TLC[j] |

*[i]DFC- Direct Fixed Cost; [h]PC-Equipment Purchasing Cost; [j]TLC-Total Labor Cost*

## 3. Results & Discussion

The material and energy balance of the four technology options has been carried out based on determined equipment size and the optimum reaction conditions taken for each dominant reaction in the processes. Using the results from material and energy balance together with the latest prices of raw materials, utilities, labor and equipment the techno-economic performances of the technology options have been evaluated and presented as follows.

### *3.1 Technical performances*

All the process options could provide fuel quality biodiesel and pure glycerol proving that the catalysts used together with the unit procedures involved in separation and purification of the crude biodiesel can attain high quality product. Accordingly, the biodiesel from all technology options fulfil the American Society for Testing and Materials (ASTM) standards for biodiesel fuel quality. However, there is a slight variation in the amount of biodiesel and glycerol produced. In terms of biodiesel product, technology option IV has the highest performance with about 98.98 kg/h product variation from the least performing one. This is mainly owing to the high catalytic activity of the nano CaO particles, which favors high conversion of the oil into biodiesel within relatively short reaction time. It might also be due to negligible occurrence of the saponification reaction when Zinc doped nano CaO catalyst is used [48], which also minimizes the likely of the catalyst being used by the FFA in the process of saponification. Relatively the least performance in terms of biodiesel product is indicated in Ionic liquid catalyst option. This is due to the lower conversion percentage achieved in the given optimum reaction conditions taken from literature [39].

Similarly, the higher glycerol production amount is attained in technology option IV, with product variation of 23.43 kg/h glycerol from the least performing option. This is again due to the variation in the achievement of oil conversion percentage according to required optimum reaction conditions. Consequently, option I and IV do have relatively highest performance as they provide more amount of biodiesel product from the same amount of feedstock used. Table 5 indicates the relative technical performances of the technology options studied.

**Table 5: Summary of technical performances of the technology options**

| Indicators | Technology options | | | |
|---|---|---|---|---|
| | Option I | Option II | Option III | Option IV |
| Biodiesel amount (kg/h) | 5191.26 | 5132.16 | 5103.64 | 5202..62 |
| Biodiesel quality (% mass) | 99.9 | 99.9 | 99.9 | 99.9 |
| Glycerol amount (kg/h) | 507.47 | 503.06 | 489.98 | 513.41 |
| Glycerol quality (% mass) | 99 | 99 | 99 | 99 |
| Performances (biodiesel/oil) | 1 | 0.991 | 0.986 | 1 |
| *Impurities in biodiesel** | | | | |
| Glycerol (% mass) | 0.11 | 0 | 0.01 | 0.00 |
| Triolein (% mass) | 0 | 0 | 0 | 0 |

**The maximum allowable amount of impurities according to ASTM, are Glycerol 0.25% mass and Triolein 0.20% mass*

The catalysts from all of the technology options can be recovered and reused for a number of times. This would help to reduce a considerable amount of money which otherwise could be spent to purchase the extra catalyst. The other advantage of the processes is that in all of the process options, except technology option II, there is no waste produced. In option II, the waste stream is composed of unreacted oil and calcium soap that can be further purified for economic benefits. The unreacted oil from technology option I and option III can be recycled directly to the processes, whereas the one from technology option IV should pass through a treatment step before it is reused in order to reduce the FFA content. This is because 76% of the unreacted oil from this process is composed of FFA, which is left unreacted in the Nano catalysis process.

### *3.2 Economic performances*

Technology option I is the most expensive alternative mainly due to the very high cost of the enzyme, Novozyme 435. Even though this catalyst can be repeatedly used for more than 200 times [54] and the process can give the second higher biodiesel product, the higher total investment cost of the option could not make it economically feasible for production of biodiesel fuel. The higher production cost in option I is also attributed to its relatively larger reactor volume required due to longer reaction time. Because the larger the equipment volume, the higher would be the costs of equipment, facilities and utilities.

The second expensive option is the technology option III. Its total investment cost is almost half of that of option I and 37% higher than the least cost option, which is option II. This is mainly because of second larger volume of reactor required due to longer reaction time as well as because of additional centrifugal decanter required to separate the catalyst. The larger and the more equipment we use, the higher would be the utility cost and the other equipment-associated costs. Technology option II has the least total capital investment cost because it requires smaller equipment sizes due to minimum reaction time and the catalyst involved is the cheapest among the catalyst options studied.

Even though technology option IV is the second cheapest option, the higher cost of the nano CaO catalyst could still make it economically infeasible at the optimum market prices of raw materials and outputs. Similarly, option III is also economically infeasible at the current market prices of raw materials and outputs. However, for the optimum market values of inputs and outputs considered, option II is the most feasible option with positive NPV, lower unit production cost, higher IRR, ROI and Gross margin. **Table 6** summarizes the economic performances of the technology options. It highlights the comparative economic performances of the process options for the given market scenario. The first part indicates the total investment cost followed by expenditures in cost categories. The calculated revenues from the product & byproduct as well as the value of the calculated economic parameters are also indicated in the table.

**Table 6: Summary of the economic performance of the technology options**

| Economic performance parameters | Catalyst technology options | | | |
|---|---|---|---|---|
| | Option I | Option II | Option III | Option IV |
| Total capital investment cost (US$) | 13,200,448 | 4,608,642 | 6,319,464 | 4,744,425 |
| Total equipment purchasing cost (US$) | 1,629,303 | 432,295 | 674,025 | 403,033 |
| Direct Fixed Capital (US$) | 6,716,375 | 1,781,747 | 2,778,061 | 1,682,115 |
| Working Capital (US$) | 6,148,254 | 2,737,807 | 3,402,499 | 2,978,204 |
| Total Annual operating cost (US$) | 71,304,387 | 31,224,324 | 39,050,943 | 33,824,494 |
| Total annual raw material cost (US$) | 66,706,623 | 29,372,952 | 36,670,506 | 32,010,394 |
| Labor dependent cost (US$) | 624,549 | 364,320 | 390,343 | 364,320 |
| Facility dependent cost (US$) | 3,376,225 | 889,148 | 1,396,347 | 844,949 |
| Laboratory, Quality Control &Analysis (US$) | 187,365 | 109,296 | 117,103 | 109,296 |
| Utility cost (US$) | 299,626 | 378,608 | 366,644 | 385,535 |
| Annual revenue from Biodiesel (US$/year) | 32,087,761 | 31,704,748 | 31,529,636 | 32,140,209 |
| Annual revenue from Glycerol (US$/year) | 1,607,422 | 1,594,245 | 1,552,758 | 1,627,161 |
| Total Annual Revenue (US$/year) | 33,695,184 | 33,298,993 | 33,082,394 | 33,767,370 |
| Unit production Revenue (US$/kg) | 0.8186 | 0.8192 | 0.8184 | 0.8194 |
| Unit production cost (US$/kg biodiesel) | 1.7323 | 0.7681 | 0.9660 | 0.8208 |
| NPV at 7% (US$) | -349,847,116 | 9,736,266 | -57,834,235 | -3,217,935 |
| ROI (%) | 26.11 | 84.66 | 71.48 | 103.69 |
| After tax IRR (%) | -100 | 32.73 | -100 | -100 |
| Gross Margin (%) | 13.79 | 17.53 | 20.19 | 21.93 |

The higher amount of biodiesel product and glycerol byproduct for nano CaO catalyzed option results in relatively higher value of total annual revenue incurred as shown in **Table 6.** The lowest total annual revenue is recorded for ionic liquid catalyzed option with about 684,976US$/year lower than the revenue from the nano catalyzed option. The enzyme catalyzed option scored the highest unit production cost with about 0.964US$ increment per kilogram of biodiesel product compared to the bulk CaO catalyzed option. Positive after tax IRR is recorded only for bulk CaO catalyzed option. For the enzyme-catalyzed option, the Gross Margin, ROI, and NPV are the lowest, followed by the ionic liquid catalyzed option.

Concerning the relative economic performances of the technologies, divergent results might be obtained if calculations are done in a different market scenario or using market values of inputs and outputs, which are not comparable to what has been used in this study. This implies that such performances are expected to be different for countries with different market scenarios.

### *3.3 Sensitivity Analysis*

The economic feasibility of the studied technology options are very divers mainly due to the cost variation among the catalysts as well as the number and size of equipment required to attain fuel quality biodiesel. Thus, it seems reasonable to test how sensitive the technology options are towards the change in market values of the inputs and outputs. Among the various economic variables, oil cost and catalyst cost comprise the higher percentage of the raw materials' cost. Similarly, biodiesel is the main product to get the desired revenue from the projects. Therefore, in this study, the economic effect of variations of oil purchasing cost, biodiesel selling price and catalyst purchasing cost has been evaluated in terms of NPV (at 7% interest rate); and the results among the technology options are compared and presented as follows. We considered biodiesel price since biodiesel is the main product and its price fluctuation could have direct effect on the feasibility of the businesses. We considered oil cost because cost of feedstock took the higher share of raw material cost. In addition, we took cost of catalyst for sensitivity analysis in order to indicate how the respective cost of the studied catalysts affect the businesses as well as to indicate the maximum possible cost of each catalyst for economic feasibility of the businesses.

#### 3.3.1 Effect of change of oil cost on NPV

The trend at which the technology options respond towards change in oil purchasing cost is almost similar. However, option I is found to be economically infeasible for all ranges of the oil purchasing cost considered. For option III, the maximum cost of oil feedstock has to be about 0.39 US$/kg, beyond which the option would be economically infeasible. Option II is found to be more tolerant to the market variation of oil cost. It can still be economically feasible up to 0.59US$/kg of oil purchasing cost. In comparison, option IV is also the second most tolerant to market fluctuations of oil purchasing cost. Nevertheless, it can be economically feasible for oil purchasing cost less than 0.51US$/kg. **Figure 5** indicates the effect of the change in oil purchasing cost on NPV of the technology options.

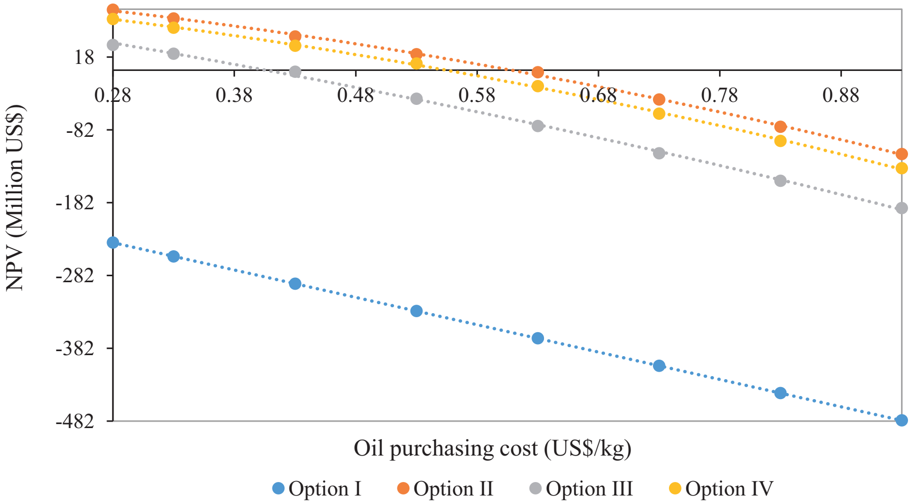


**Figure 5**. Effect of change of Oil purchasing cost on NPV

### 3.3.2 Effect of change of biodiesel selling price on NPV

The changing trend of the technology options towards the variation of the market values of biodiesel price is almost similar. Option I is unprofitable for the considered ranges of biodiesel selling prices. For this option to be economically feasible, the biodiesel should be sold at very high price (1.8US$/kg), which is practically impossible. In contrary, technology option IV can be economically feasible with almost half of this price (0.97US$/kg). This designates that the production of biodiesel fuel using technology option I should be subsidized to make the fuel economically competitive with fossil diesel in the market. For the biodiesel selling price range considered, option II is found to be more tolerant to the possible fluctuation of biodiesel price and can still be economically feasible at a biodiesel price as low as 0.77US$/kg. **Figure 6** indicates the effect of variation of biodiesel selling price on NPV of the technology options.

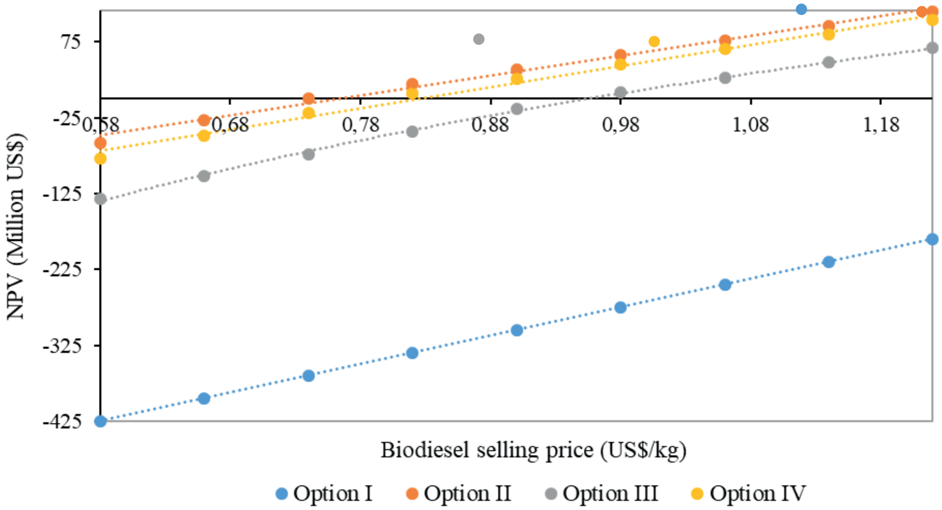


**Figure 6.** Effect of change of Biodiesel selling price on NPV.

### 3.3.3 Effect of change of catalyst purchasing cost on NPV

The entire techno-economic comparison is among these four catalyst technologies. Thus evaluating the effect of the market values of the four catalyst types could give a reasonable ground for selecting the technology option that is more tolerant to fluctuating cost of materials in the market. The trend at which the NPV changes with the catalyst cost is almost the same for all technological options. However, some get negative NPV at very low cost values and some at relatively higher values. For instance, option I could still be economically feasible for about 61US$/kg cost of enzyme catalyst. This is mainly due to its higher reusability that can reduce the total cost of the catalyst. Nevertheless, this higher price, indicated here, is not enough to buy the very expensive enzyme catalysts, especially immobilized ones [54]. This demands more investigation on enzyme catalysts, which could be produced with a cost as low as 60US$/kg while possessing the same catalytic performance as indicated here. Option III is the most sensitive towards a change in the value of catalyst purchasing cost. It is economically feasible for a catalyst cost of less than 4.1US$/kg. Option IV gets its negative NPV for a catalyst cost of more than 5US$/kg. The cheapest catalyst is the bulk CaO catalyst in option II. It can be prepared from wastes such as eggshell, crab shell, and river snail shell among others. The cheap cost of and higher reusability of the CaO catalyst makes option II be more tolerant for the possible fluctuations of catalyst purchasing cost in the market. It gets its negative NPV for a catalyst cost more than 7US$/kg, which seems to be far from its current market value as indicated in **Table** 2. **Figure 7** shows the effect of variation of catalyst cost on NPV of each technology option.

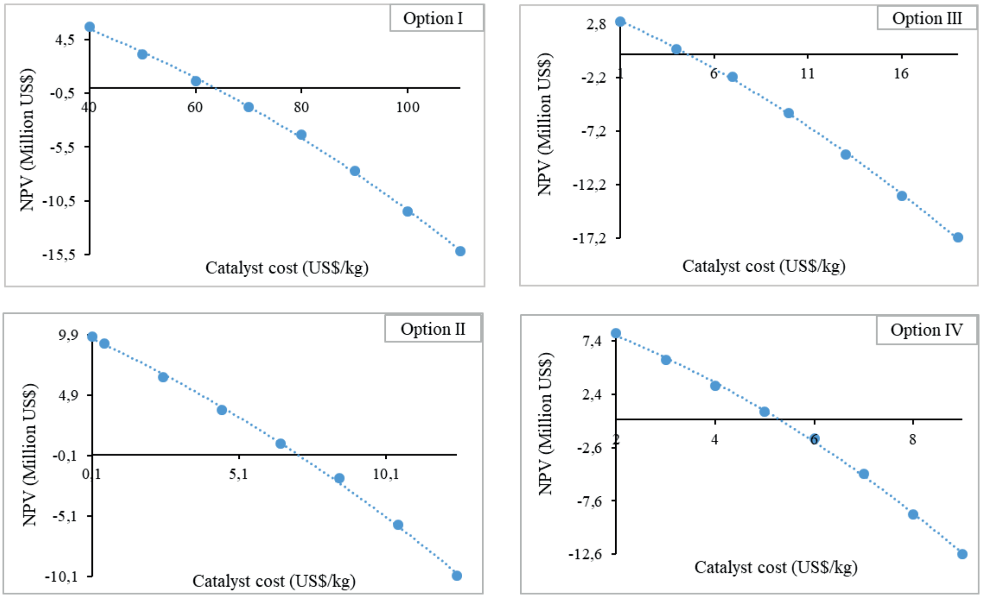


**Figure 7.** Effect of change of catalyst purchasing cost on NPV of each production technology option

## 4. Conclusions

All the studied technology options can produce fuel quality biodiesel and pure glycerol. Their technical performance with regard to the quantity of biodiesel per amount of oil feedstock is almost the same. Economically the enzyme-catalyzed option is not feasible mainly due to very high cost of the enzyme catalyst and larger volume of reactor. The second expensive technology is the ionic liquid catalyzed option. This is because it has the second largest reactor volume and more number of equipment required to get fuel quality biodiesel. The bulk CaO catalyzed option is the most efficient in economic terms as it attains higher positive NPV, higher IRR, higher Gross margin, higher ROI and minimum total capital investment cost. The enzyme-catalyzed option is not economically feasible for all possible ranges of biodiesel price and oil cost considered. The enzyme catalyst has to be bought for less than 60US$/kg for the process to be economically feasible at all. The bulk CaO catalyzed option is the most tolerant towards the change in price of biodiesel, oil cost and catalyst cost. It indicates profitability at a biodiesel price as low as 0.74US$/kg, oil purchasing cost as high as 0.70US$/kg and catalyst cost as high as 7US$/kg.

**Disclaimer**: The authors are not responsible for any decision that might be made using results from the process options. The process options specified in this study are merely for research purposes. If anyone needs further clarification or wants to use the result for specific applications, please contact the authors for more information concerning the limitations and scope of the designs.

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