Norwegian University of Life Sciences
Faculty of Science and Technology

Philosophiae Doctor (PhD)
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- *Dedicated to my beloved family*

“I will give thanks to the LORD because of his righteousness; I will sing the praises of the name of the LORD Most High”.
Psalm 7:17

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Summary

Energy is basic for development and its demand increases due to population growth, urbanization, and the improvement of living standards in most parts of the world. Nowadays, the energy sector faces dual challenges, the need to meet the ever increasing energy demand and at the same time the concern for environment, particularly, reducing the carbon emissions. Fossil fuels are the main sources of energy and they will continue to dominate the other energy sources although they have negative impacts on the global climate and are non-renewable. The negative effects on the global climate and the uncertainty of the petroleum reserves has increased interests to search for alternative sources of energy which are renewable and have less pollution potential and carbon emission. One of such alternative sources of energy is the biodiesel, which is ecofriendly, renewable, biodegradable and nontoxic. Biodiesel can be produced from vegetable oils, animal fats, waste oils and microalgae. Production of biodiesel from edible vegetable oils resulted in food vs fuel debate, and thus, nowadays production of biodiesel from the oil of non-edible crops such as jatropha seeds is preferred. Jatropha seed oil has been considered as a promising biodiesel feedstock as it is non-edible due to the presence of a toxic compound (the phorbol ester) in it and the oil content of the seed is high. The oil contents of jatropha seeds and seed kernel vary from 20-60% and 40-60%, respectively.

The primary objective of the present thesis is to determine the oil contents of different jatropha seed collections and optimize biodiesel production using reusable and low cost heterogenous catalysts. For this purpose, the thesis attempted to identify the suitable conditions for jatropha seed drying for oil extraction in order to determine the oil contents of different jatropha seed collection. Some physco-chemical properties of the oils were also evaluated to determine whether the oils could be used for biodiesel production or not. Moreover, to search for low cost and more sustainable methods of biodiesel production, renewable alcohols and reusable and low cost heterogenous catalysts were used to produce biodiesel at different reaction conditions, and to optimize the reaction process.

The present PhD thesis is based on six scientific papers that systematically presented interrelated research activities that included the investigation of different biodiesel feedstocks and various oil extraction methods, techniques of seed drying for oil extraction, extraction of oil from different

jatropha seed collections and biodiesel production using renewable alcohols, and reusable and low cost heterogenous catalysts. The research activities in this thesis are interrelated and stepwise activities, and the results obtained from the preceding works were used as the bases and/or inputs for the next activities. Accordingly, the research work was started with the review of the state of art of relevant literature to evaluate the advantages and limitations of using different biodiesel feedstocks and oil extraction methods from different oil sources in general, and from plant seeds in particular (**Paper I**). From a thorough examination of the literature reports, it was understood that oils from non-edible crops such as jatropha was identified as a promising feedstock for biodiesel as using such oils does not compete with human consumption. Moreover, jatropha seeds have high oil content and the plant has great adaptation potential to various climates. Solvent extraction method was also selected for oil extraction from the seeds due to its efficiency in oil extraction and its simplicity and affordability.

The experimental part of the study began with drying a selected jatropha seed collection at storage conditions for oil extraction as the moisture in a seed can affect the oil yield and the quality of the oil. The pretreated crushed seeds and non-pretreated whole seeds were dried at five different temperatures (40, 50, 60, 70 and 80 ºC) to identify the temperature and the pretreatment that could reduce the seed moisture to its minimum (**Paper II**). From this experiment, it was concluded that drying the whole seeds of jatropha at 80 ºC for 2880 minutes produced the dried seed with suitable residual moisture (0.34%) for oil extraction. The moisture ratios calculated from the systematically recorded moisture loss from the drying seeds indicated above were adjusted to four semi-theoretical drying mathematical models (Lewis, Henderson and Pabis, Page and Avhad and Marchetti models) to determine the model that best fitted to the experimental drying kinetics of the seeds (**Paper III**). Among the employed mathematical models, Avhad and Marchetti model showed the best fitting to the experimental data. In **Paper IV**, after drying the seeds using the previously determined techniques, thirteen different jatropha seed collections were extracted with a Soxhlet extractor using hexane as solvent and cotton or thimble as filter to determine the seed collection that could give the largest percentage of oil. The physco-chemical properties of the sample from mixed oil (a mixture formed from oils from thirteen jatropha seed collections) and oil of Chali seed collection were also determined in order to use these oils for biodiesel production. Moreover, the heat contents of the de-oiled seed residues were determined as using such residues as an energy source can contribute to a reduction of the biodiesel production costs. In the extraction with cotton, Dana seed collection gave the largest oil yield (48.29%) while in the extraction with thimble, the largest oil yield (45.79±0.54%) was obtained from Chali seed collection. The results from the physco-chemical analyses of both oil samples suggested that the oils can be used for biodiesel production. Furthermore, since the average gross calorific value of the de-oiled jatropha seed residues after oil extraction was found to be about 19.64 MJ kg^{-1}, the residues can be used as the source of heat.

Two transesterification reactions were performed to produce biodiesel using renewable alcohols and reusable heterogenous catalyst at different reaction conditions to optimize the reaction processes. In the first reaction, the mixed oil (mixture of oils extracted from thirteen different seed collections) was reacted with ethanol using Amberlyst A26 (OH), anion ion exchange resin, at various reaction temperature, ethanol: oil molar ratio and catalyst percent to optimize the oil conversion and biodiesel yield (**Paper V**). From this study, it was found that the reaction temperature highly affected the reaction process. The maximum oil conversion (38.12%) and ester yield (36.81%) were experimentally obtained at an optimum temperature of 55 °C, alcohol: molar ratio of 35:1 and catalyst amount of 15%. Based on results obtained from the first experiment, it was suggested that upscaling of the oil conversion and biodiesel yield by using an integrated reaction factors, as well as reducing the amount of alcohol employed is needed.

In the second transesterification reaction, glycerol enriched non-calcined calcium oxide was employed to catalyze the reaction of the oil of the Chali seed collection (Chali oil) with butanol at different temperatures and butanol: oil molar ratio by employing a constant amount of catalyst (15%wt) and glycerol (15%wt of the catalyst) (**Paper VI**) to optimize the process. From this study, it was found that the reaction temperature significantly affected the reaction process ($p \leq 0.05$). Moreover, the maximum oil conversion of 98.16% was predicted to be obtained at the optimum temperature of 87.35 °C and butanol: oil molar ratio of 9.13:1. The maximum butyl ester yield of 95.79 % was also estimated to be found at the optimum temperature of 90.48 °C and butanol: oil molar ratio of 13.24:1. Furthermore, the butyl ester yield of 95.64% was experimentally obtained at the predicted optimum conditions for the ester yield. From the results of the second reaction, it was suggested that glycerol enriched non-calcined commercial calcium oxide can be used as a good alternative catalyst for biodiesel production using butanol.

Sammendrag

Energi er grunnleggende for all utvikling og etterspørselen øker på grunn av befolkningsvekst, urbanisering og forbedring av levestandarden i de fleste deler av verden. I dag står energisektoren overfor doble utfordringer, behovet for å imøtekomme det stadig økende energibehovet og samtidig bekymringen for miljøet, spesielt for å redusere karbonutslippene. Fossilt brensel er de viktigste energikildene, og de vil fortsette å dominere over de andre energikildene, selv om de har en negativ innvirkning på det globale klimaet og ikke er fornybare. De negative effektene på det globale klimaet og usikkerhetene omkring petroleumsreservene har økt interessen for å søke etter alternative energikilder som er fornybare og har mindre forurensningspotensiale og karbonutslipp. Biodiesel er en slik alternativ kilde til energi; den er miljøvennlig, fornybar, biologisk nedbrytbar og ikke-giftig. Biodiesel kan produseres fra vegetabilske oljer, animalsk fett, avfallsoljer og mikroalger. Produksjon av biodiesel fra spiselige vegetabilske oljer resulterte i mat vs drivstoffdebatt, og i dag foretrekkes nå produksjon av biodiesel fra olje som kommer fra fra ikke-spiselige vekster, slik som jatrophafrø. Jatropha har blitt sett på som et lovende råstoff for biodiesel, ettersom oljen er ikke spiselig på grunn av tilstedeværelsen av en giftig forbindelse (phorbolesteren), og oljeinnholdet i frøet er høyt. Oljeinnholdet i jatropha frø og frøkjernen varierer fra henholdsvis 20-60% og 40-60%.

Hovedmålet med den herværende oppgaven er å bestemme oljeinnholdet i forskjellige jatrophafrø innsamlet i Etiopia og optimalisere biodieselproduksjon ved å bruke gjenbrukbare og rimelige heterogene katalysatorer. Med dette formålet forsøker avhandlingen å identifisere egnede betingelser for tørking av jatrophafrø for å ekstrahere olje, for deretter å bestemme oljeinnholdet i de forskjellige jatrophafrøkildene. Noen fysisk-kjemiske egenskaper av oljene ble også evaluert for å bestemme om oljene kunne brukes til biodieselproduksjon. For å finne de laveste kostnadene og mer bærekraftige metoder for biodieselproduksjon, ble dessuten fornybare alkoholer og gjenbrukbare og rimelige heterogene katalysatorer brukt til å produsere biodiesel ved forskjellige reaksjonsbetingelser, og for å optimalisere reaksjonsprosessen.

Den nåværende doktorgradsavhandlingen er basert på seks vitenskapelige artikler som systematisk presenterte sammenhengende forskningsaktiviteter som inkluderte utredning av forskjellige biodiesel råstoff og forskjellige oljeekstraksjonsmetoder, teknikker for frøtørking for oljeekstraksjon, ekstraksjon av olje fra forskjellige jatrophafrøsamlinger og biodieselproduksjon

ved bruk av fornybare alkoholer, samt gjenbrukbare og rimelige heterogene katalysatorer. Forskningsaktivitetene i denne avhandlingen henger sammen og trinnvis, og resultatene oppnådd fra de foregående arbeidene ble brukt som baser og / eller innspill til de neste aktivitetene. Følgelig ble forskningsarbeidet startet med en gjennomgang av den aktuelle teknikk for relevant litteratur for å evaluere fordelene og begrensningene ved å bruke forskjellige biodieselråstoff og oljeekstraksjonsmetoder fra forskjellige oljekilder generelt, og fra plantefrø spesielt (**Artikkel I**). Fra den detaljerte gjennomgangen av litteraturen ble det antydet at oljer fra ikke-spiselige avlinger som jatropha er identifisert som et lovende råstoff for biodiesel ettersom bruk av slik olje ikke konkurrerer med matproduksjon direkte. Dessuten har jatrophafrø høyere oljeinnhold, og planten har stort tilpasningspotensial til forskjellige klima. Oppløsningsmiddelekstraksjonsmetode ble også valgt for oljeekstraksjon fra frøene på grunn av dens effektivitet i oljeekstraksjon og dens enkelhet og rimelig kostnad.

Den eksperimentelle delen av studien ble startet med tørking av en valgt jatrophafrøsamling etter lagring. Lagringstilstand før oljeekstraksjon kan ha betydning for oljeutbyttet og kvaliteten på oljen, siden fuktigheten i et frø påvirker dette. De forbehandlede knuste frøene og ikke-forbehandlede hele frøene ble tørket ved fem forskjellige temperaturer (40, 50, 60, 70 and 80 °C) for å identifisere temperaturen og forbehandlingen som kunne redusere frøfuktigheten til sitt minimum (**Artikkel II**). Fra dette eksperimentet ble det konkludert med at tørking av hele frøene av jatropha ved 80 °C i 2880 minutter ga det tørkede frøet med passende restfuktighet (0,34%) for oljeekstraksjon. Fuktighetsforholdene beregnet ut fra det systematisk registrerte fuktighetstapet fra tørkefrøene som er angitt ovenfor, ble justert til fire semi-teoretiske tørkende matematiske modeller (Lewis, Henderson og Pabis, Page og Avhad og Marchettis modeller) for å bestemme hvilken modell som passet best til forsøket tørkingskinetikk av frøene (**Artikkel III**). Av de anvendte matematiske modellene viste Avhad og Marchetti-modellen seg best tilpasset til eksperimentelle data. I **Artikkel IV** ble tørrinnsamling av jatrophafrøekstrakt med Soxhlet-ekstraktor ved bruk av de tidligere optimale teknikker, og ved å anvende heksan som løsningsmiddel, og bomull eller fingerbøl som filter, for å finne den frøsamlingen som kunne gi den største prosentvise oljen. De fysisk-kjemiske egenskapene til prøven fra blandet olje (en blanding dannet av oljer fra tretten jatrophafrøsamlinger) og olje fra Chali-frøsamlingen ble også analysert for å bruke disse oljene til biodieselproduksjon. Videre ble varmeinnholdet i frørestene etter oljeutvinning bestemt fordi bruk av slike rester som energikilde kan bidra til med å redusere de totale investeringskostnadene for biodieselproduksjon. I ekstraksjonen med bomull ga Dana-frøsamlingen det største oljeutbyttet (48,29%), mens i ekstraksjonen med fingerbøl ble den største mengden olje (45,79 ± 0,54%) oppnådd fra Chali-frøsamlingen. Resultatene fra den fysisk-kjemiske analysen av begge oljeprøvene antydet at oljene kan brukes til biodieselproduksjon. Siden de gjennomsnittlige brutto brennverdiene av jatrophafrørestene etter oljeekstraksjon var ca. 19,64 MJ kg^{-1}, kan restene brukes som varmekilde.

To transesterifiseringsreaksjoner ble utført for å produsere biodiesel ved bruk av fornybare alkoholer og gjenbrukbar heterogen katalysator ved forskjellige reaksjonsbetingelser for å optimalisere reaksjonsprosessene. I den første reaksjonen ble den blandede oljen (blanding av oljer ekstrahert fra tretten forskjellige frøsamlinger) omsatt med etanol ved bruk av Amberlyst A26 (OH), anionionbytterharpiks, ved forskjellige reaksjonstemperaturer, etanol: olje-molforhold og katalysatorprosent for å optimalisere oljeomdannelse og biodieselutbytte (**Artikkel V**). Fra denne studien ble det funnet at reaksjonstemperaturen påvirket reaksjonsprosessen sterkt. Maksimal oljeomdannelse (38.12%) og esterutbytte (36.81%) ble eksperimentelt oppnådd ved en optimal temperatur på 55 ^{o}C, alkohol: molforhold på 35:1 og katalysatormengde på 15%. Basert på resultater oppnådd fra det første eksperimentet, ble det antydet at oppskalering av oljekonvertering og biodieselutbytte ved bruk av integrerte reaksjonsfaktorer, samt reduksjon av anvendt alkoholmengde er nødvendig.

I den andre omesterifiseringsreaksjonen ble glyserolanriket ikke-kalsinert kalsiumoksyd anvendt for å katalysere reaksjonen fra oljen fra Chali frøsamlingen (Chali olje) med butanol ved forskjellige temperaturer og butanol: olje (i et molært forhold) ved å bruke en konstant mengde katalysator (15% vekt) og glyserol (15 vekt% av katalysatoren) (**Artikkel VI**) for å optimalisere prosessen. Av denne studien fant vi at reaksjonsprosessen ble betydelig påvirket av reaksjonstemperaturen ($p \leq 0,05$). Videre ble den maksimale oljekonvertering på 98,16% forventet å være oppnådd ved en optimale temperatur på 87,35 ^{o}C og et butanol: olje-molforhold på 9,13:1. Det maksimale butylesterutbytte på 95,79% ble også beregnet til å bli oppnådd ved en optimal temperatur på 90,48 ^{o}C og butanol: olje-molforhold på 13,24:1. Vi viste eksperimentelt et butylesterutbyttet på 95,64% ved de forutsagte optimale betingelsene for esterutbyttet. Av resultatene fra den andre reaksjonen er det mulig at glyserolanriket ikke-kalsinert kommersielt kalsiumoksyd kan brukes som et god alternativ katalysator for biodieselproduksjon ved bruk av butanol.

List of Articles

Paper I

Keneni YG, Marchetti JM . Oil extraction from plant seeds for biodiesel production. *AIMS Energy*. 2017; 5: 316-340. https://doi.org/10.3934/energy.2017.2.316

Paper II

Keneni YG, Marchetti JM. Temperature and pretreatment effects on the drying of different collections of *Jatropha curcas* L. seeds. *SN Applied Sciences*. 2019; 1:943 | https://doi.org/10.1007/s42452-019-0969-3.

Paper III

Keneni YG, Hvoslef-Eide T, Marchetti JM. Mathematical modelling of the drying kinetics of *Jatropha curcas* L. seeds. *Industrial Crops and Products*. 2019; 132:12-20. https://doi.org/10.1016/j.indcrop.2019.02.012.

Paper IV

Keneni YG, Bahiru LA, Marchetti JM. Effects of different extraction solvents on the amount of oil extracted from Jatropha seeds from Ethiopia and the potential of de-oiled seed residues as a heat provider. Submitted to *BioEnergy Research*.

Paper V

Keneni YG, Hvoslef-Eide T, Marchetti JM. Optimization of the production of biofuel from Jatropha oil using a recyclable anion-exchange resin. *Fuel*. 2020;278:118253. https://doi.org/10.1016/j.fuel.2020.118253.

Paper VI

Keneni YG, Marchetti JM. Butanolysis of Jatropha oil using glycerol enriched non-calcined calcium oxide: optimization of the process. Submitted to *Fuel*.

Additional Scientific contributions

Oral presentations

Keneni YG, Marchetti JM. Mathematical modelling of the drying kinetics of *Jatropha curcas* L. seeds collected from Ethiopia. 2nd World Congress on Wind and Renewable Energy & 5th World Congress and Expo on Green Energy, June 14-16, 2018, London, UK. DOI: 10.4172/2090-4541-C3-056.

Keneni YG, Bahiru LA, Marchetti JM. Effects of different extraction solvents on the amount of oil extracted from Jatropha seeds and the potential of de-oiled seed residues as a heat provider. Summary was accepted by the 24th International Congress of Chemical and Process Engineering, CHISA 2020, August 23-27, 2020, Prague. *(However, this conference is postponed due to Covid-19 pandemic).*

Poster presentations

Yadessa GK, Jorge MM. Temperature and pretreatment effects on the drying of different collections of *Jatropha curcas* L. seeds from Ethiopia. The 23rd International Congress of Chemical and Process Engineering, CHISA, August 25-29, 2018, Prague, Czech Republic.

Keneni YG, Hvoslef-Eide T, Marchetti JM. Biodiesel production from Jatropha oil using recyclable an anion-exchange resin: optimization of the process. Summary was accepted by the 24th International Congress of Chemical and Process Engineering, CHISA 2020, August 23-27, 2020, Prague. *(However, this conference is postponed due to Covid-19 pandemic).*

Articles

Santaraite M, Keneni YG, Marchetti JM, Sendzikiene E. New lipase-catalyzed in situ transesterification of Jatropha oil for direct production of B10. (Under preparation).

Santaraite M, Keneni YG, Sendzikiene E, Marchetti JM. Feasibility study to use spent coffee grounds for the production of biodiesel using the lipase-catalyzed in situ transesterification process. (Under preparation).

List of abbreviations

CCD	central composite design
CCDm	modified central composite design
CS	Crushed seeds
DGs	Diglycerides
FFA	Free fatty acids
EMC or M_e	Equilibrium moisture content
MAE	Mean absolute error
MBE	Mean bias error
M_e	Equilibrium moisture content
M_f	Final moisture loss
MGs	Monoglycerides
M_0	Initial moisture content
MR	Moisture ratio
M_t	Moisture content at time t
PSCS	Particle sizes of the crushed seeds
R^2	coefficient of determination
R_{MSE}	Root mean square error
RSM	Response surface methodology
TGs	Triglycerides
WS	Whole seeds
wt%	Weight percentage
X^2	chi-square test
X_{JO}	Jatropha oil conversion
X_{JOB}	Jatropha oil conversion with butanol
X_{JOE}	Jatropha oil conversion with ethanol
Y_{FABEs}	Yield of fatty acid butyl esters
Y_{FAEEs}	Yield of fatty acid ethyl esters
Y_{FAEs}	Yield of fatty acid esters

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1. Introduction

1.1. General introduction

Energy is required to meet basic human needs and its demand is expected to increase due to rapid population growth, expanding urbanization and better living standards [1]. Recently, in the released International Energy Outlook 2019 [2], it has been reported that world energy consumption will grow by nearly 50% between 2018 and 2050, and transportation energy consumption will increase by nearly 40%. Moreover, the residential energy consumption in Africa grows by an average of 2.5% per year from 2018 to 2050 which is faster than the continent's population growth of 1.9% per year [2]. Fossil fuels remain the dominant source of energy [3] and will continue to provide over two-thirds of global primary energy until 2040 [4] though it is non-renewable and has negative impacts on global climate [5].

Ethiopian national energy mainly depends on traditional biomass and fossil fuels, and the contribution of renewable energy such as hydropower, wind power, solar energy and biofuel is very small [6]. It was reported that in 2010, the energy from biomass accounting for about 92% of total energy consumption of the country out of which about 89% was for household cooking and baking both in the urban and rural regions. The remaining energy share is from petroleum (7%) and hydropower generated electricity (1%) [7, 8]. The Ethiopian energy sector faces the dual challenges: limited access to modern energy and heavy reliance on traditional biomass energy sources to meet the growing demand. The demand of energy in the country rapidly increases due to fast economic and population growth [9]. The projected energy demand of the country for the year 2030 is estimated to be 180 Petajoule (PJ) from which the shares of biomass, petroleum and electricity are 71.6, 22.6 and 5.8%, respectively [7, 10].

Ethiopia entirely depends upon imported petroleum products to supply the ever-growing energy demand. The imported fossil fuel, with fluctuating price, puts high pressure on foreign currency reserves of the country [11, 12]. The yearly import of petroleum products accounts for more than one third of the annual export products of the country [12]. The petroleum import increased by about 7.14% in the 2015/2016 fiscal year, and the fuel import accounts for 16.4% of total imports of goods and services. During the fiscal year (FY) 2013/14, a total of about 2.63 million tons of petroleum products worth 47.6 billion Ethiopian Birr (2.49 billion USD) was imported. About 82% of the petroleum is used for transportation, followed by 12% and 6% usage by the residential and industrial sectors, respectively. Petroleum accounts for 99.8% of the transportation fuel and the rest is produced from biofuel, particularly bioethanol. Ethiopia started blending of ethanol with gasoline in October 2008 with 5% blending and increased to E10 (10% blending) in 2012. Currently, the country uses blended bioethanol for city vehicle fuel consumption [13].

The Ethiopian National Energy Policy recognized the urgent need of alternative and renewable energy sources and the rationale energy mixes to reduce the burden on the unsustainable use of woody biomass resources. This includes utilization of biomass fuels such as biogas, biodiesel, briquetted fuels, and bioethanol. In order to avoid the undesirable impacts of biodiesel production on food security at a country level, the national biofuels development strategy discourages the use of food crops as feedstock for biofuel production [13]. While the ethanol target of 10% blending requirement was successfully reached in 2012 in major cities of the country, progress regarding the biodiesel target is meager. Moreover, the government manages a well-coordinated ethanol production system while biodiesel is left largely to private operators [13] .

The Ethiopian government has made large efforts to create a better environment for bio-energy production to attract investors to the sector. For example, tax exemption for the first five years of production, importing machinery without tax and providing free land for the cultivation of bioenergy crops were some of the motivations. Since 2007, the government has given great attention to biofuels, particularly, biodiesel production from jatropha and bioethanol from sugarcane molasses [10].

Reducing the dependence on fossil fuels is a crucial requirement for sustainable development, and biofuels are seen as a possible alternative to fossil fuels, especially in the transport sector [14]. For developing countries such as Ethiopia, utilization of alternative renewable energy sources such as biodiesel is both the panacea for higher fossil oil prices and a bridge towards becoming a little bit more dependent on themselves rather than on others [15]. The country also has a large underutilized labor force, a vast arable land area and a suitable climate for the cultivation of biodiesel crops [16].

The Ethiopian Biofuel Development and Utilization Strategy that was prepared in 2007 targeted towards increasing fuel utilization efficiency, and substituting fossil fuel demand by biofuel produced from locally available feedstock, without affecting the country's food self-sufficiency [16]. Jatropha, palm tree and castor bean were identified in the strategy as promising biodiesel bearing plants [16, 17]. By using weighted overlay analysis for biophysical suitability factors evaluation using spatial modeling method (taking elevation, climate and water logging as the main limiting factors), Tadesse [17] also identified that 15.07% (166,082 km^2) and 76.57% (844,040 km^2) of land in Ethiopia is highly and moderately suitable for jatropha production, respectively.

According to Portner, *et al*. [14], jatropha was introduced into Ethiopia, particularly to the Bati districts of the north-central Ethiopia, four decades ago, and the plant has been used for living fences, land rehabilitation and soil and water conservation. However, promoting jatropha plantation as biodiesel feedstock and the efforts to support such investments has begun to emerge in 2005 with the facilitation of the government and involvement of private investors. Then, in 2007, the "Biofuel Development and Utilization Strategy" was prepared to manage the involvement of the well-motivated foreign and domestic private investors in the area by the Ethiopian government [16, 18]. However, both the motivations from the government to attract the investors and the involvement of the investors in jatropha cultivation and biodiesel production has been interrupted at its infant stage. Some of the factors contributed to the interruption of jatropha cultivation by the investors in the country might be due to the knowledge gap on the characteristics of jatropha plant to manage its cultivation and lack of research-based knowledge regarding the oil extraction and biodiesel production methods [19]. Concerning this, Shete and Rutten [20] reported that biofuel production is relatively new to Ethiopia, and there was very little expertise, few trained and skilled staff and limited technology to support the domestic investors. Particularly, the lack of suitable technology that processes and converts biofuel feedstock to liquid fuel is a great challenge that was faced by the domestic private investors.

The initiatives of the Ethiopian government to support the investors that produce alternative liquid biofuels, particularly biodiesel from non-edible jatropha oil, to contribute to the country's energy demands is very important and one of the key priorities in the energy sector the country. However, the actual scientific research-based information concerning the biology, ecophysiology and life cycle assessment of jatropha in Ethiopia, and the available technology that processes and converts jatropha seed oil to biodiesel was limited. These uncertainties can be one of the reasons that investors are less attracted towards the cultivation of jatropha and biodiesel production from its seeds compared to what is expected by the government.

The methods of jatropha seed processing for oil extraction, oil extraction techniques used, and the technology used to convert the oil to biodiesel may determine the quantity and quality of the oil and the cost of the final product. Therefore, the present thesis focused on the investigations of:

i) Easy and more affordable techniques of jatropha seed drying for oil extraction,

ii) Efficient method of oil extraction from the dried seeds for biodiesel production, and

iii) Biodiesel production methods using renewable alcohols and cost effective and reusable heterogenous catalysts.

1.2. Research objectives

With the exception of few reports on the extraction of jatropha oil using hexane and/or petroleum ether, no study has been reported on the effects of pretreatments of seeds for oil extraction, extraction of oil from different seed collections using different solvents and characterization of the oil, and biodiesel production using different heterogenous catalysts. Accordingly, the primary objectives of the current thesis include:

i) Identification of appropriate oil extraction methods from oilseeds in general, and from jatropha seeds in particular **(Paper I)**,

ii) Determination of the effects of temperature and seed pretreatments on the drying of jatropha seeds for oil extraction **(Paper II** and **III)**,

iii) Identifying jatropha seed collection that gives the largest amount of oil using different extraction solvents **(Paper IV)**, and

iv) Selecting the affordable and effective heterogenous catalysts for biodiesel production from jatropha oil and optimization of the reaction process **(Paper V** and **VI)**.

1.3. Organization of the thesis

Stepwise accomplishments of tasks were performed to achieve the overall objectives of the present thesis and the specific objectives were addressed in the six publications arranged in the thesis. The description of the contents of each publication is outlined below.

Paper I presents a review of the state of the art of the last publications concerning the oil extraction methods from plant seeds for biodiesel production. The paper focused on reviewing various oil sources for biodiesel production, different oil extraction methods that have been practiced, the pros and cons of using different biodiesel feedstocks, and the advantages and disadvantages of using different oil extraction methods. The paper also summarizes the easily available and cheap oil sources for biodiesel production and tries to identify the most preferable oil extraction methods. Accordingly, in this review paper, the most suitable plant seed oils for biodiesel production and the most preferable method to extract the largest percentage of oil from the oilseeds are identified.

In **Paper II,** we presented the effects of pretreatment and different temperatures on the drying of different collections of jatropha seeds for oil extraction. The paper presents the results of drying non-pretreated seeds (whole seeds) and pretreated seeds (crushed seeds) of jatropha at different temperatures using a heating furnace prior to oil extraction to reduce the moisture content of the seeds. In this paper, the suitable pretreatment and drying temperature to minimize the moisture of the seeds for oil extraction were identified.

Paper III has focused on the mathematical modeling of the drying kinetics of the whole and crushed jatropha seeds. The experimental drying data at different temperatures were fitted to selected semi-theoretical mathematical models, and the model that best fitted to the experimental drying curves was identified to describe the drying kinetics of the seeds with great accuracy.

In **Paper IV,** the oil contents (wt%) of different jatropha seeds collections from Ethiopia were determined using an experimentally selected organic solvent, and the seed collection that produced the largest amount of oil (%) was identified. The article also provides the heat contents of the de-oiled jatropha seed residues remaining after oil extraction.

Biodiesel production by the reaction of jatropha oil with ethanol using an alternative recyclable anion-exchange resin, Amberlyst A26 (OH) wet, as catalyst as well as the optimization of the process was presented in **Paper V.** In this article, the effects of reaction temperature, ethanol to oil molar ratio and the catalyst amount (wt%) on the oil conversion and the yield of the esters were presented. The maximum conversion and yield obtained at the optimum reaction conditions were also presented in this article.

Paper VI presents the effects of the reaction temperature and butanol to oil molar ratio on the transesterification of jatropha oil using glycerol enriched non-calcined calcium oxide as a solid catalyst. The optimum conditions needed for the maximum oil conversion and biodiesel yield were also presented in this article.

2. Research background

2.1. Biodiesel

Biodiesel is defined as the mono-alkyl ester of long chain fatty acids derived from renewable lipid feedstock such as vegetable oils and animal fats [21, 22]. It is typically produced through the transesterification reactions of a vegetable oil or animal fat with short-chain alcohols (typically methanol or ethanol) in the presence of a catalyst to yield methyl or ethyl esters (biodiesel) and glycerin [23-25].

Biodiesel is considered as a promising alternative to diesel fuel as it is produced from renewable biological sources and more environmentally friendly compared to petroleum diesel [26, 27]. Biodiesel is biodegradable, nontoxic and has lower emission profiles and better lubricity properties compared to petroleum diesel [28-30]. Biodiesel has similar properties to petroleum diesel and thus, it can be used in the transport sector as an alternate fuel [31, 32]. As biodiesel does not contribute to a net rise in the level of carbon dioxide in the atmosphere, its utilization leads to minimize the intensity of greenhouse effect [28, 32].

In addition to its environmental benefits, biodiesels that can be produced within the petroleum importing countries will enable these countries to be less dependent upon the imported fossil oil [33]. Moreover, well designed and organized biodiesel production system can create employment opportunities for rural people and thus, it contributes to the improvement of the domestic economy [23, 30, 33]. This could also reduce immigration from villages to cities, which is a big problem for developing countries [23, 30]

2.2. Potential feedstocks for biodiesel production

Biodiesel can be produced from different feedstocks such as vegetable oils, waste frying oils and fats, soap-stock and algae [30]. However, the physico-chemical properties of different biodiesel feedstocks vary and this significantly affects the fuel properties of the biodiesel produced [30, 34]. According to Singh *et al*. [26], the selection of biodiesel feedstock depends on the physico-chemical properties of the feedstock in general and on top of that, the properties related to the fatty acid profile in particular. The chemical composition of fatty acids in vegetable oil is also based on oilseed species, oil extraction techniques and processing conditions [26, 35].

For the satisfactory replacement of petroleum diesel with biodiesel, two basic requirements should be fulfilled. Firstly, biodiesel must be easy accessible and environmentally acceptable and secondly, the price of the biodiesel should be reasonable [36]. Different countries have different potential biodiesel feedstocks [37] as the availability of biodiesel resources depends on the regional climate, geographical location, local soil conditions and agricultural practices of a country [27, 38]. It has been reported that the price of biodiesel mainly depends on the cost of the feedstocks which makes up about 75% of the total production cost [27, 39, 40]. Hence, minimizing the cost of biodiesel production should be the main agenda for biodiesel to be competitive with the fossil-based fuels [32, 41].

Based on the origin of the feedstocks, biodiesels can be broadly classified into four generations [25, 42, 43]. Biodiesel that are produced from edible oils are termed as the first generation while those from non-edible oils, waste oil and animal fats are the second generation [25, 27]. Third generation biodiesels are produced from algae [25, 27, 43] whereas the fourth generation biodiesel are drawn from man-made biological tools such as photobiological solar fuels and electro-fuels, and is at the infancy level of fundamental research [26, 42]. According to Mahmudul *et al*. [37], oil crops are the main pillar for biodiesel production. Globally, more than 350 oil-bearing crops (both edible and non-edible) have been identified as the promising feedstocks of biodiesel [27, 44]. The availability of a wide range of feedstocks is one of the most significant factors that enable the sustainable production of biodiesel [45-47].

2.2.1. First generation biodiesel

First generation biodiesels are produced from edible oil resources such as rapeseed oil, soybean oil, coconut oil, corn oil, palm oil, mustard oil, olive oil and rice oil [27, 32, 42]. More than 95% of the world biodiesel has been produced from edible oils: rapeseed oil (84%), sunflower oil (13%), palm oil (1%), soybean oil and others (2%) [27, 32, 48]. However, continuous large-scale usage of edible plant oils for biodiesel production raises many concerns. These include the food versus fuel crisis and major environmental problems such as deforestation and the destruction of vital soil resources, and the conversion of farm lands to oil bearing plants [27, 42, 49]. The prices of vegetable oil has also increased dramatically in the last few decades and this will affect the economic viability of the biodiesel industry [27, 49, 50]. Furthermore, the use of such edible oils to produce biodiesel is not feasible in the long term due to the growing gap between demand and supply [27]. These drawbacks have initiated the users to search for alternative feedstocks for biodiesel production [42, 51]. One of the possible solutions to reduce the use of edible oil for biodiesel production is using non-edible oils instead.

2.2.2. Second generation biodiesel

Non-edible oils are regarded as the second generation biodiesel feedstocks. Animal fats, waste oils and grease are also considered as the second generation feedstocks [27], and using these types of feedstocks eliminates the cost of their disposal in addition to contributing to the supply of biodiesel [27, 46]. The main non-edible plant oils that have been used as the feedstock of biodiesel include the oils of jatropha, karanja, nagchampa, mahua, *calophyllum inophyllum*, jojoba, linseed and rubber seeds [42, 51]. Non-edible plant oils have been considered as a promising substitute for the oils of traditional edible food crops because of the high oil content of their seeds, their easy availability, and having the advantage that the plants could be grown on land which is not suitable for agriculture [27, 52]. Non-edible oil bearing plants could also be grown with less intensive attention; thus, reducing the cost of cultivation [27, 36, 52, 53]. Therefore, production of biodiesel from non-edible oils is an effective way to overcome the associated problems with edible oils [52].

During the selection of plant seeds for biodiesel feedstock, the amount of oil that can be obtained from the seeds and the physco-chemical characteristics of the oils are very important parameters to be considered [52, 53]. The oil crops with a higher oil yield are more preferable in the biodiesel industry as this contributes to a reduction in the overall biodiesel cost [54]. In the reviews that have investigated the oil contents of some selected non-edible oil bearing plants, it was reported that jatropha gave the highest oil yield, and this was followed by *Pongamia pinnata* (karanj) [54, 55].

2.2.3. Third generation biodiesel

Third generation biodiesels are produced from microalgae [55, 56]. Biodiesel production from microalgae is more feasible compared to that from the first and second generations feedstocks [57]. It overcomes some difficulties faced in the utilization of first and second generation feedstocks such as availability, economic feasibility, food versus fuel debate and the problem of adaptability to some climatic conditions [51]. Microalgae can be grown in undeveloped land and water which is not suitable for food production. They also have high growth rates and ability to sequester CO_2 from the flue gases [56, 58]. Moreover, microalgae can give the highest oil yield per unit area of land compared to other conventional biodiesel feedstocks [58]. However, the requirement of large investment, the necessity of sunlight, issues of production at a large scale and difficulties in oil extraction are some of the disadvantages of using microalgae as biodiesel feedstock [55]. At present, the production of biodiesel from algal biomass is being researched to enhance the process of oil extraction and biodiesel production [42].

2.2.4. Fourth generation biodiesel

Photobiological solar biodiesel and electro-biofuels are considered as the fourth-generation biodiesels [42]. In this generation, raw materials that are inexhaustible, cheap and widely available are used to convert solar energy to solar biofuels [42, 56, 59]. The biggest scientific breakthroughs are expected to rely on the synthetic biology which involves the design and creation of new biological parts, redesign of the existing ones and devising of the natural biological systems for efficient and direct conversion of solar energy to fuel [56, 59]. For instance, bioengineering of photosynthetic microorganisms towards direct solar fuel production, the fuel production without a biomass phase, is a recently emerged area of research [59]. Similarly, a mixture of photovoltaic or inorganic water-splitting catalysts with metabolically engineered microbial fuel production pathways (electro-biofuels) is a powerful emerging technology for efficient production and storage of liquid fuels [42, 59]. The benefits of using fourth generation biodiesel resources include more lipid content, more CO_2 absorbing ability, high energy content and rapid growth rate. The drawbacksof this generation are the requirement of high initial investment and limited knowledge as the research in this area is at its infancy [42, 59].

2.3. Jatropha and its potential as biodiesel source

2.3.1. Biology and ecology of jatropha

The term jatropha is derived from the Greek term, ‘iatros’ meaning doctor and ‘trophe’ meaning food [60], which incorporates the historical medicinal uses of this plant [61]. Genus *Jatropha* belongs to family Euphorbiaceae and includes about 175 species from which *Jatropha curcas* L., is the most common [62]. Jatropha (*J. curcas* L.) is a poisonous semi-evergreen perennial tree or shrub that reaches a height of up to 6 meters [63], but can attain a height of 8-10 meters under favorable conditions [64]. Jatropha plant can start fruiting from the second year of planting but giving larger yield staring from fifth year onward [65]. The life span of the plant is up to 50 years [66].

It is believed that jatropha is native to Central America and has naturalized to many tropical and subtropical areas including Asia, Africa and North America [62, 67]. Originating from the Caribbean region, jatropha has spread as a useful hedge plant to Africa and Asia by Portuguese merchants [63, 64, 67], and now the plant is found abundantly in many tropical and sub-tropical regions of the world [64] including Ethiopia [68].

Jatropha can be cultivated in various soil conditions, including dry, stony and shallow, soils with low to high fertility and with mineral deficiency. It is believed to have outstanding adaptation power to a variety of environments and has a huge ability to absorb and make use of nutrients even in poor soils [62]. However, like other crops, to produce higher yield the plant needs soil with an optimum amount of nutrients and moisture [69]. Jatropha grows in tropical and sub-tropical regions, with cultivation limits at 30ºN and 35ºS [69, 70]. The optimum elevation for growth and productivity of the plant ranges from sea level to 1500 m above sea level [17, 69] while altitudes from1500 to 2150 m above sea level are moderately suitable [17]. Jatropha grows under conditions where the temperature ranges between 15 and 40 °C[61], and the optimum temperature is 25 to 35 ˚C [62]. The optimal annual rainfall for jatropha cultivation is between 1000 and 1500 mm and the plant needs a minimum annual rainfall of 600 mm to produce fruits [17, 69].

2.3.2. Jatropha oil as biodiesel feedstock

Jatropha is considered as a multipurpose plant as its different parts have different uses [60, 71, 72]. It has the potential to be used as the source of biodiesel, cleaning agents, cosmetics, dyes, organic fertilizers and different medicines [60, 72]. Jatropha seeds contain a high amount of oil that is not edible due to the presence of a toxic compound, the phorbol ester, and this makes the oil of the plant a very attractive source of biodiesel [73]. Production of biodiesel from non-edible seed oils such as jatropha has been given due consideration in the past decade as these oils are renewable, biodegradable and a non-toxic alternative to fossil fuels [52, 74]. Using these oils as biodiesel feedstock also eliminates the food versus fuel debate that occurred in the case of using edible oils for biodiesel [52].

The amount of oil that could be extracted from jatropha seed and seed kernel could vary from 20-60% and 40-60%, respectively [53, 75]. The oil contents of jatropha seeds may vary from provenance to provenance [68] and for different agro-ecological zones [76]. The study on various physical and chemical properties of the jatropha oil has shown that the oil is suitable for biodiesel production [62]. However, jatropha oil has a wide range of fatty acid compositions and percentages of FFAs [77]. In many literatures it has been reported that the main fatty acids found in jatropha oil are oleic acid (18:1), linoleic acid (18:2), palmitic (16:0) and stearic acid (18:0). For instance, Akbar *et al*. [78] reported that oleic acid (44.7%), linoleic acid (32.8%), palmitic acid (14.2%), stearic acid (7.0%) and palmitoliec acid (0.7%) were the main fatty acids found in jatropha oil from Malaysia. Oleic acid (42.8-51.4%), linoleic acid (21.73-25.43%), stearic acid (10.9-19.3%) and palmitic acid (10.62-15.91%) were also determined for the oils from different jatropha seed collections from Ethiopia [79]. As jatropha oil contains only a very small percentage of the fatty acid with triple bonds, linolenic acid (18:3), and no fatty acid with four double bonds, it is suitable for biodiesel [78]. According to the European standard, EN 14214, the concentration of linolenic acid and fatty acid containing four double bonds in fatty acid methyl ester should not exceed the limit of 12% and 1%, respectively [80] .

The FFA content of jatropha oil may vary depending on the origin of the oil, the pre-extraction seed processing and the post extraction oil processing and storage. When the percentage of the FFA of jatropha oil is higher, it is not suitable to use alkaline catalysts for the transesterification reaction to produce biodiesel [77]. In such cases, one of the methods to favor the biodiesel production process is the pretreatment of the oil with acidic catalyst to reduce the FFA to below 1% before employing the alkaline catalyst for transesterification [77, 81].

2.3.3. Jatropha seed collection and processing

Knowledge of the maturation stage of a fruit contributes to the establishment of the ideal time to harvest when seeds have a better physiological quality [82]. Jatropha seed harvesting time is one of the critical steps as the seed oil content is related to the fruit maturity stages [82, 83].

Fructification of jatropha plant is uneven where growth of last fruits continues after ripening of the first ones in the same inflorescence. Therefore, classification of fruits based on the fruit color has an economic and logistical application to obtain the seed with higher quality [82] .

During the maturation process of jatropha fruits, seeds undergo physical and chemical changes that determine the quality of the oil [82]. Accordingly, jatropha fruits change in color gradually from green to green yellow, yellow, yellow brown and finally to brown dry. From the study of the influence of fruit maturity stages on the properties of seed oil and its derived biodiesel, by using seeds from green yellow, yellow, yellow brown and brown dry fruits, it was found that seeds from yellow fruits resulted in the highest oil yield, oil with the least FFA level, and biodiesel with the highest energy content [83]. It has also been reported that maximum physiological quality and lipid content of jatropha seeds occur at physiological seed maturity stage, which corresponds to seeds obtained from yellow fruits [84, 85]. Therefore, collection of jatropha seeds when the fruits turn to yellow is very important.

After jatropha fruit has been collected, the seeds should be removed from the fruit shells by hand, by crushing with a wooden board or by using a mechanical decorticator [69]. Then, the seeds should be properly dried to reduce its moisture content for storage or further processing [69, 86]. According to Almeida *et al*. [87], due consideration should be given to the seed moisture content during storage as this parameter affects seed chemical composition and the speed of seed metabolic activities. Moisture content of oilseeds is also one of the important parameters that determine the quantity of oil which can be obtained from the seeds [88]. Thus, attention should be given to the seed moisture content during postharvest processing which includes seed handling, storage, milling and oil extraction from the seeds [89]. Accordingly, the collected jatropha seeds should be shade dried for sowing but dried in the sun for oil production to reduce the moisture content to around 6-10% for storage. If kept dry and stored at optimum conditions, the seeds may be stored for up to 12 months without loss of oil content [69].

2.4. Oil extraction from plant seeds

2.4.1. Preparation of seeds for oil extraction

In industry, oil seeds undergo several preparation steps prior to oil extraction. These may include seed cleaning, moisture conditioning, deshelling, crushing and heat treatment [86]. Oil seeds should be cleaned to remove foreign material such as plant stalk, debris or damaged seed. Moisture conditioning of seeds is used to increase the plasticity and adjusts the moisture content of the seed to the optimum level for extraction. Decreasing the particle size of the seed by grinding/crushing can also increase the surface area of oil-bearing cells that interacts with the extraction solvent [86].

2.4.1.1. Seed drying for oil extraction

Drying could be defined as the process of moisture removal as a result of heat and mass transfer between the biological product and the drying air through evaporation, and generally caused by temperature and air convection forces [90]. Seed drying is an important step to achieve the desired moisture content of the seeds. Knowing the drying characteristics of oilseeds is essential in the handling of the seed, and to preserve its contents in its current form [91]. Drying oilseeds such as jatropha seeds to a lower moisture content, particularly to the moisture content for oil extraction and/or in situ biodiesel production, and keeping it up at this moisture content in the storage is impractical [92]. Thus, drying the seeds at storage prior to oil extraction and/or in situ biodiesel production may be needed.

Lower jatropha seed moisture contents compared to the normal seed storage moisture content were recommended by several researchers in order to obtain higher oil yield, and quality oil and biodiesel. For instance, in the study of oil extraction from soybean using hexane as solvent, Lawson *et al*. [93] obtained the oil yield of 15% and 11.81% from seeds with moisture content of 10% and 20%, respectively. In the extraction of jatropha oil from ground kernel with a moisture content of 0.912%, using a Soxhlet extractor and hexane as solvent, Kadry [94] obtained a maximum of 45% oil that contained 0.9% free fatty acids. It was also reported that the oil obtained by this method did not need pretreatment with acid to carry out basic catalyzed biodiesel production [94] as its FFA is less than 1% [95, 96]. Moreover, in biodiesel production from jatropha seeds through in situ transesterification by alkaline catalyst, seeds with moisture content less than 1% was used to prevent saponification [97]. Furthermore, drying of oilseeds could reduce the amount of chemical input during in situ biodiesel production process. For example, Haas and Scott [98] found that a reduction of 60% methanol and 56% sodium hydroxide input when soybean flakes with moisture contents of 7.4 % were dried to the lowest moisture content (to around 0%) before in situ transesterification.

As the measurement of oilseed moisture content and its adjustment is a vital process at different levels of seed processing [89], determining the physical properties of seeds and their relation to the seed moisture content enables the improvement of the design of the equipment used for seed harvesting and postharvest processing [60]. The development and improvement of machinery for seed drying, simulation and gathering of theoretical information on the behavior of each product during reduction of moisture content become essential [99]. Accordingly, the mathematical modeling of the drying process of the seeds could help to predict the behavior of moisture removal from the seeds, reduce the time and costs of seed drying, and helps in the invention of appropriate drying equipment [99, 100].

2.4.1.2. Crushing of seeds for oil extraction

Before oil extraction using solvents, reducing the particle size of the oilseeds by grinding is important to ease the extraction process. Grinding of the seeds facilitates oil extraction by increasing the surface area of the seed particles that come in contact with a solvent and by decreasing the distance that the oil will have to travel to reach the particle surface [86]. As the particle sizes of the pulverized seeds can affect the percentage of oil extracted for a particular solvent [94], due consideration should be given to it during oil extraction.

2.4.2. Oil extraction methods

One of the most important steps in biodiesel production from oilseeds is oil extraction. The three most commonly employed conventional oil extraction methods are mechanical, chemical/solvent and enzymatic extraction methods [32, 52]. Besides these, accelerated solvent extraction, supercritical fluid extraction and microwave-assisted extraction methods are frequently used [32]. For commercial oil extraction, solvent extraction and mechanical pressing are the most commonly used methods [52]. Mechanical press method of oil extraction is the most conventional technique for which a manual ram press or an engine driven screw press can be used [32]. The oil extracted by both methods needs filtration and degumming in order to produce a more pure raw material [52, 101]. Another problem associated with conventional mechanical presses is that the design of mechanical extractor is suited only to the seeds of some oil crops. Therefore, the oil yield is affected if that mechanical extractor is used for seeds that it is not suited to [32, 52, 101]. Solvent extraction is the process in which the oil is removed from a solid materials by means of a liquid solvent, and it is termed as leaching [32]. Generally, compared to mechanical press, solvent extraction results in higher oil yields [102].

Each oil extraction method has its own advantages and limitations. For instance, extraction of oil from jatropha seeds using n-hexane as solvent results in the largest percentage of oil yield compared to mechanical and enzymatic extractions. However, using hexane as extraction solvent has negative environmental impacts compared to extraction with ethanol and enzymes [52, 103]. Oil extraction with enzymatic method is ecofriendly, but it takes a longer time as the rate of oil extraction by this method is very slow compared to that of the solvent extraction methods [104]. Moreover, in supercritical fluid extraction, oil produced has a very high purity and the time needed is also very short; however, the operating and investment cost is higher to use this extraction method [105].

In solvent extraction of oil, several solvents can be used to extract oil individually or as a mixture of solvents. Some of the most commonly used solvents include hexane, petroleum-ether, diethyl ether, ethanol, n-heptane, isopropanol, acetone, chloroform, methanol and 1-butanol [105-110]. Compared to other solvents, it has been found that oil extraction using n-hexane results in the highest oil yield, and this makes it the most commonly used solvent [52]. The oil extraction efficiency, environmental impacts and renewability of different solvents vary. Different extraction solvents could also yield in extracts with different composition from a particular material [111]. Therefore, selection of a solvent for oil extraction is one of the most important steps in oil extraction by chemical methods, particularly, in the most commonly used Soxhlet extraction method [112].

Soxhlet extraction is one of the most traditional techniques still being used to extract oil from solid samples using different volatile solvents [111]. It has been a standard technique for over a century, and the methods based on it remain the primary references against which the performance of new leaching methods is measured [113, 114]. It is also used as a reference for several existing modern oil extraction techniques [111]. However, compared to the newly developed modern oil extraction techniques such as supercritical fluid extraction, microwave-assisted extraction and accelerated solvent extraction, Soxhlet extraction is an older extraction technique [114].

2.5. Biodiesel production techniques

The most common problems associated with using crude vegetable oils in diesel engines are high viscosity, low volatility and polyunsaturated characters of the oils [38]. There are four main methods by which raw vegetable oil and/or animal fat can be made suitable for use as substitute fuel in diesel engines, namely direct use and blending, micro-emulsion, pyrolysis (thermal cracking) and transesterification [115, 116]. Direct use of oils and fats, particularly in diesel engines, could produce serious damage due to high viscosity, FFA content/acidity, gum formation, oxidation and polymerization during storage and combustion [117]. Biodiesel obtained by pyrolysis and microemulsion methods is related to the incomplete combustion due to a low cetane number [118]. Therefore, transesterification (alcoholysis) is the most widely used over the other methods for industrial production of biodiesel from vegetable oils and animal fats as it has the advantages of easier production technology and results in better yield [45, 118]

2.5.1. Transesterification for biodiesel production

As it is already mentioned, transesterification is a chemical reaction between triglyceride and alcohol in the presence of catalyst to produce fatty acid ester (biodiesel) and glycerol. It consists of three consecutive reversible reactions where TGs are converted to DGs, then, DG to MG followed by the conversion of MG to glycerol. In each step, an ester is produced and thus, three ester molecules are produced from one molecule of triglycerides [116]. A general reaction of transesterification is shown in Figure 2.1.

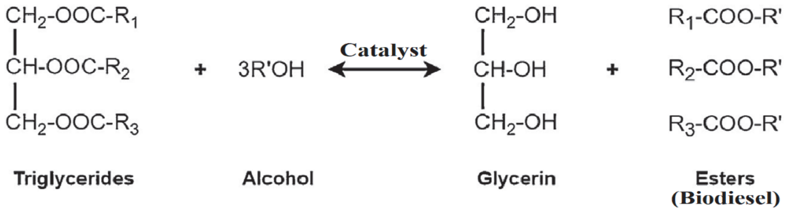

Figure 2.1: Transesterification reaction for biodiesel production (R_1, R_2 and R_3 are fatty acid chains).

The alcohols commonly used in transesterification includes methanol, ethanol, propanol, butanol and amyl alcohol, but methanol and ethanol are predominantly used [119]. Generally, transesterification is a reversible reaction that requires a catalyst to increase the reaction rate and ester yield; excess alcohol is also needed to shift the equilibrium to the product side [120].

2.5.2. Factors affecting transesterification process

Several factors can influence the transesterification process and the biodiesel yield. These factors include the type of catalyst used, alcohol to oil molar ratio, catalyst loading, reaction temperature, moisture and FFA content the oil, and the reaction time [38, 121].

2.5.3. Catalysts for biodiesel production

Generally, alcohol and triglycerides (vegetable oil and animal fat) are not miscible to form a single phase of mixture, and this poor surface contact between the two reactants causes transesterification reaction to proceed relatively slow. Introduction of catalysts improves the surface contact of the reactants, and consequently increases the reaction rates and biodiesel yield. Without the presence of catalysts, the reaction rate is too slow to produce a considerable yield of biodiesel [117].

Some of the promising alternative processes for biodiesel production are still unprofitable. This is due to limitations such as long reaction times, difficulties in the separation of the products, unaffordable amounts of solvents and generation of large amounts of waste water [122, 123]. To minimize these drawbacks, selection of appropriate oil feedstocks and suitable catalyst is very important. Thus, during selection of a catalysts for transesterification, due consideration should be given to the availability and cost of the catalyst and the quality of the oil feedstock, particularly, the FFA content of the oil [26, 117].

The catalysts commonly used in the transesterification reactions are divided in two general categories: homogenous and heterogeneous catalysts. Homogeneous catalysts act in the same liquid phase as the reactants, while heterogeneous catalysts are usually solids that act in a different phase from the reactants. In addition, both can be either acid or alkaline-based compounds [124].

2.5.3.1. Homogenous catalysts

Homogenous catalysts are categorized as basic and acidic catalysts. The most commonly used basic homogeneous catalysts include sodium hydroxide, sodium methoxide and potassium hydroxide while the mainly preferred homogenous acidic catalysts are sulfuric acid, hydrochloric acid, and sulfonic acid [117].

Homogeneous basic catalysts are commonly used in the industries due to their moderate operation conditions, high conversion within shorter time, high catalytic activity and more availability and low cost. Accordingly, a typical homogeneous base catalyzed reaction occurs at the stoichiometric alcohol to oil molar ratio (or slightly higher), alcohol reflux temperature, atmospheric pressure, low catalyst concentration, and it requires low reaction time [117]. However, homogenous basic catalysts are sensitive to the FFA and moisture contents of the oil. When the oil contains significant amounts of FFA and moisture, an undesired side reaction that produces soap (saponification) occurs. This side reaction reduces the biodiesel yield and causes difficulties to separate biodiesel and glycerin. Saponification also allows emulsions to occur between the obtained biodiesel and the byproduct glycerol, which requires a long settling time for separation [117, 125] .

Homogenous acidic catalysts are not sensitive to the FFA content of the oil used for biodiesel production. This prevents side reactions, like saponification, and consequently results in high-quality glycerol as a byproduct [118]. However, homogenous acid catalyzed reactions require relatively higher catalyst concentration, higher alcohol to oil molar ratio and longer reaction time compared to those catalyzed with homogeneous basic catalysts [117]. Moreover, homogeneous acid catalysts are difficult to recycle and operate at high temperatures, and also they cause serious environmental and corrosion problems, and thus, are not efficient [126-128].

2.5.3.2. Heterogenous catalysts

Heterogeneous catalyst has also been explored extensively for transesterification reaction to produce biodiesel. Heterogeneous catalyst can be recycled, regenerated and reused for subsequent transesterification reaction cycles, thus minimize the cost of biodiesel production. Moreover, the catalysts can be easily separated from the products and therefore, minimizing product contamination and the number of water washing cycles for product purification [120]. Accordingly, using of heterogeneous catalysts offers many advantages over homogeneous catalysts, such as simple catalyst recovery, catalyst reusability, simple product purification, less energy and water consumption, lower costs of purification, and simple glycerol recovery [122, 126, 129]. Thus, to minimize the drawbacks observed in the utilization of homogeneous catalysts, several heterogeneous catalysts such as clays, zeolites, oxides and polymer resins (ion exchange resins) have been evaluated for transesterification of vegetable oils [128, 130]. Metal oxides are the basic heterogeneous catalysts group that have been studied most, and these oxides include calcium oxide, magnesium oxide, strontium oxide, mixed oxides and hydrotalcites [124].

2.5.3.2.1. Using calcium oxide as catalysts

From the heterogeneous catalysts used for transesterification reactions, calcium oxide (CaO) has got attention because of its long catalytic life, high activity, requirement of moderate reaction conditions and low cost. CaO can also be easily prepared from several natural calcium sources such as waste egg shells or mollusk shells [123, 124]. Moreover, CaO has a low solubility in alcohol, tolerance of moisture and FFA, and is non-corrosive and environmentally friendly [131].

In order to have maximum basic sites on the surface of CaO catalyst, pretreatment at high temperatures is required before using it in the transesterification reactions [132]. According to Boey *et al*. [131], CaO requires a thermal activation to remove the adsorbed CO_2 and moisture, and the usual calcination temperature is about 700 ºC. However, in some studies non-calcined (as received) commercial CaO was utilized as catalyst and resulted in higher oil conversion. For instance, in biodiesel production from refined sunflower oil with methanol using non-calcined commercial CaO as catalyst, Reyero et al. [133] obtained an oil conversion of 96% after 91 minutes by employing reaction temperature of 60 ºC, methanol: oil molar ratio of 12 and catalyst amount of 2 % (wt.%) of the oil.

2.5.3.2.2. Ion exchange resins as catalyst

Ion exchange resins are suitable catalysts for etherification, esterification, and transesterification reactions [134-136]. The main advantage of using the resins over other heterogeneous catalysts is the opportunity to prepare tailor-made materials by controlling the polymerization conditions [128]. For instance, ion exchange resins can be prepared with different particle sizes, porosity degrees, and with a wide variety of functional groups [130]. Ion exchange resins can also be easily separated from reaction products as they have relatively larger sizes [136]. Moreover, using these resins is more preferable compared to lipase enzyme and supercritical alcohol from the viewpoint of cost savings [126].

Compared to several reports on the catalytic activities of other heterogenous catalysts in the transesterification of vegetable oils, works on ion exchange resins are very limited. A few investigations have reported that anionic ion exchange resins were more effective than the cationic resins. For instance, Li *et al.* [136] and Shibasaki-Kitakawa *et al.* [126] investigated the transesterification of oil with methanol and ethanol, respectively, using various ion exchange resins as catalysts. From these studies, it was found that in general, the anionic resins were more efficient in their catalytic activities than the cationic ones. Similarly, in the study of the catalytic activities of Amberlyst 15Wet (cationic resin) and Amberlyst A26 (OH) (anionic resin) on the transesterification reactions of Brazilian soybean oil using methanol and ethanol, the anionic resin was found to be more efficient than the cationic resin in biodiesel production [130].

Amberlyst A26 (OH) resin is a macroporous ion-exchange resin with quaternary ammonium functional groups that impart a strongly basic and reactive surface [137]. The quaternary ammonium functional group in the resin is known to ease the removal of FFA from the oil and the process of transesterification reactions [137, 138]. Thus, the resin can carry out both esterification and transesterification reactions consecutively by minimizing the saponification side reactions in cases of biodiesel production from oils containing FFA [137]. Amberlyst A26 (OH) can also be easily recovered from the reaction products and reused for subsequent transesterification reactions similar to other ion exchange resins [136]. However, only a few research reports were found concerning the catalytic activities of Amberlyst A26 (OH) in the transesterification of vegetable oils, and the majority reported very low conversions.

2.5.3.3. Enzymatic and supercritical methods of biodiesel production

The catalytic enzymes such as lipase, have high reaction selectivity and can be immobilized in the support materials. It has been reported that enzymatic reactions are insensitive to FFA and moisture content in oil and hence, they can be used in the transesterification of oils that contain a relatively higher amount of FAA and moisture. However, enzymes are very expensive and have slow reaction kinetics [126, 139]. Moreover, a catalyst-free supercritical method produces quality biodiesel with a very high rate of production, but the method is expensive as it requires higher temperature and pressure conditions [126].

2.5.4. Optimization of conditions for biodiesel production

The most relevant operating variables affecting the transesterification process include reaction temperature, time, pressure, alcohol to oil molar ratio, concentration and type of catalyst, mixing intensity and the type of oil used [117]. Determination of the optimum conditions needed to maximize the conversion of oil and the yield of biodiesel is very important. This can be done by using response surface methodology (RSM). RSM is a collection of statistical and mathematical techniques that are useful for modeling and analysis of problems in which a response of interest is influenced by several variables, and the objective of using RSM is to determine the optimum conditions that maximize this response [140, 141].

3. Materials and methods

This section of the thesis will provide the overview of the materials and methods employed during the experimental works, data analyses and theoretical investigations of the studies presented in **Papers II-VI**. **Paper I** is a review article that has been used as a tool to identify the appropriate oil sources and methods of oil extraction for biodiesel production in this thesis. As **Paper I** was written by investigating the last literature, there is no description of laboratory work for this article.

3.1. Jatropha seed collection and preparation for storage

Thirteen different jatropha seed collections that were collected from different agro-climatic zones of Ethiopia were used for the experiments of the present thesis. From these, seven seed collections (Kurkura, Bira, Salmene$_1$, Salmene$_2$, Salmene$_3$, Shekla and Gerbi) were collected from the north-central part of the country while the rest of the collections (Dimeka, Chali, Kako, Mulato, Dana and Awwaaragamaa) were harvested from the southern part. These collection sites were the areas where large cultivation of jatropha has been practiced by the local farmers relative to other parts of the country. The collected seeds were air and sun dried for storage based on the practices of the local farmers. Then, the dried seeds were transported to the Reaction Engineering and Catalysis Group facilities where the Biodiesel Laboratory is located, at the Faculty of Science and Technology, Norwegian University of Life Sciences (NMBU); and the seeds were stored at room temperature (about 20 ^{o}C) until used for oil extraction. The seed collection names, maturation stages of the seeds, and the coordinates and altitudes of the collection sites are presented blew (Table 3.1).

Table 3.1: Information of seed collection sites, seed maturation stages and time of collection.

Geographical region	Districts	Local name of sampling sites	Code for seed collections	Fruit maturity	Collection year	Location (coordinate)	Altitude (a.s.l.) (m)
North-central	Bati	Kurkura	Kurkura	Yellow	2016	11° 14' 2.86" N, 40° 0' 18.5" E	1412
		Birra	Bira	Unkown[a]	2016	11° 12' 48.14" N, 40° 0' 38.83" E	1720
		Salmene	Salmene$_1$	Yellow	2016	11° 10' 47.74" N, 40° 0' 34.36" E	1668
			Salmene$_2$	Yellow	2016	11° 10' 34.59" N, 40° 0' 33.55" E	1596
			Salmene$_3$	Yellow	2016	11° 10' 35.02" N, 40° 0' 34.18" E	1603
	Dawa Chefa	Shekla	Shekla	Dried dark	2016	10° 47' 59.29" N, 39° 50' 8.62" E	1466
		Gerbi	Gerbi	Dried dark	2016	10° 44'5.42" N, 39° 50'11.38" E	1426
Southern part of Ethiopia	Hammer	Dimeka	Dimeka (dried fruit)[b]	Dried dark	2017	05°10.437'N, 036°32.795'E	1116
		Dimeka	Dimeka (yellow fruit)[c]	Yellow	2017	05°10.437'N, 036°32.795'E	1116
	Benatsemai	Chali	Chali	Yellow	2017 & 2018	05°40.431'N , 036°42.896'E	1340
		Kako	Kako	Yellow	2017	05°39.416'N, 36°39.317'E	1396
	Mi'erab Abaya	Mulato	Mulato	Yellow	2017	06°27.997'N, 037°45.106'E	1210
	Kucha	Dana	Dana	Yellow	2017	06°34.112'N, 037°33.070'E	1270
	Shalla	Awwaaragamaa	Awwaaragamaa	Yellow	2017	07°16.573'N, 038°27.292'E	1687

[a] The maturity stage of Bira seed collection was not known as it was purchased from a farmer after collection. [b] Dimeka (dried fruit) and [c] Dimeka (yellow fruit) were seeds of the same collection but collected at different fruit maturity stages: Dimeka (dried fruit) and Dimeka (yellow fruit) seeds were collected from dried brown fruits and newly matured yellow fruits, respectively.

From the thirteen collections of seeds depicted in Table 3.1, the seven seed collections that were harvested from the north-central part of the country were used for **Paper II**, while all thirteen seed collections were used in the experiments of **Paper IV** and **Paper V**. For the experiments of **Paper III**, only the seed collection named Salmene$_3$ (one of the seven seed collections from the north-central Ethiopia) was utilized. In the experiments of **Paper VI**, the oil extracted from Chali seed collection (a seed collection from the southern Ethiopia) was used.

3.2. Seed drying experiments

3.2.1. Materials used for seed drying experiments

Seven jatropha seed collections: Kurkura, Bira, Salmene$_1$, Salmene$_2$, Salmene$_3$, Shekla and Gerbi were used for the drying experiments. These seeds were at a storage moisture condition as they had already been air and sun dried for storage. For the crushing pretreatment process of jatropha seeds, a bowl-shaped mortar and pestle made from stone were used. After crushing, the particle size of the pulverized seeds was estimated by three different stainless-steel sieves with openings of 500 μm, 1 mm and 2 mm woven cloth (Control Group, 15-D2245/J, 15-D2215/J and 15-D2185/J). All the seed samples were weighed using a digital balance machine having 0.01 mg accuracy (Mettler-Toledo, PG 5002 Delta Range, Switzerland). The seed samples were placed on Petri dishes (100 mm x 15 mm) during drying. The drying experiments were performed using a heating furnace (Narbetherm P300, Germany).

3.2.2. Experimental procedures for seed drying

To determine the effects of temperature and pretreatments on the drying of jatropha seeds, the methodology used in the previously published work by the research group was employed [142]. From the seven seed collections, Salmene$_3$ seed collection was selected and used for the drying experiment as the base line for comparison. This seed collection was selected because it was obtained from the fruits at the physiological maturity stage (yellow fruits), and it has been reported that the maximum oil content of the seeds occurs at this stage [83-85].

In the drying experiment of Salmene$_3$, the non-pretreated whole seeds (WS) and the pretreated crushed seeds (CS) were used. The seeds were cleaned manually by removing all foreign matter such as stones, dirt and broken seeds before the experiment. For all drying experiments, ca. 15 g of jatropha seeds were used. Four 15 g seed samples were weighed separately (two samples for each treatment in order to have duplicate measurements). The first two WS samples were dried without any pretreatment. The second two seed samples were crushed and ground mechanically by hands, using mortar and pestle. The particle sizes of the crushed seeds (PSCS) were estimated using the three different sieves mentioned in the previous section.

Two different dimensional properties (geometric and arithmetic mean diameters) of the whole seeds of the selected seed collection (Salmene$_3$ collection) were determined by measuring the dimensions of 50 whole seeds with measuring calipers, and using equations 3.1 and 3.2, respectively [143, 144].

$$D_g = (L \times W \times T)^{\frac{1}{3}} \tag{3.1}$$

$$D_a = \frac{(L \times W \times T)}{3} \tag{3.2}$$

Where, D_g = geometric mean diameter, Da= arithmetic mean diameter, L=length, W= width and T= thickness of the whole seeds in millimeter.

Five different air temperatures (40, 50, 60, 70 and 80 °C) were adopted for drying the jatropha seed samples, and this variable was selected for the investigation as several studies reported that air temperature is the dominant parameter that affects the drying process of the seeds [90, 142, 145]. All the seed samples were kept in separate Petri dishes (100mm x 15mm), uniformly distributed on it and then, placed in the heating furnace for drying.

The effectiveness of the drying temperatures on the moisture evaporation from jatropha seeds was systematically recorded for 5760 minutes to ensure the achievement of the critical moisture level at which no more moisture loss occurred. To understand the rate of moisture evaporation, the weight loss data were recorded following the methods used in related studies by Perea-Flores *et al.* [90] and Avhad and Marchetti [142]. Accordingly, the seed samples were taken out from the heating furnace and weighed using a digital balance at predetermined time intervals by taking less than 10 seconds to weigh the samples. Thus, the samples were exposed to the room temperature for very short instant during weighing, and then, put back in the hearing furnace. The samples were weighed until no more weight loss occurred in three consecutive weight data. Based on the information obtained for Salmene$_3$ seeds for different temperatures, the WS samples of all the remaining six seed collections from north-central Ethiopia were also dried at the optimal temperature (80 °C) following the same procedures as described above.

All experiments were replicated twice to obtain reproducibility in the experimental findings. Although the results obtained from the replicated experiments did not significantly vary, the average values were used in data analyses and reporting. The weight losses (wt%) of the seed samples (both the WS and CS) were determined relative to the initial weight of the seeds just before drying (wet based). The residual moisture remained in the dried seeds (wt%) at a particular temperature, which could also be referred as the experimental equilibrium moisture content (EMC or M_e) of the dried seeds was calculated using Equation 3.3. The initial moisture contents (M_0) of the seeds were determined by drying 15g of the seed samples at 105 °C for 24 hours [86, 99, 146].

$$M_e = M_0 - M_f \tag{3.3}$$

Where M_0 refers to the initial moisture contents of the seeds, and M_f is the final moisture loss from the seeds at the time when no more moisture (weight) loss occurred.

It is very important to investigate the impacts of drying air temperatures on the physical properties of seeds as these properties greatly affect the drying process [142]. Accordingly, to investigate the physical appearances of the seeds, the drying seed samples were carefully observed and photographed using a digital camera (Canon, DS126061, Japan) every 24 hours (1440 min) during the drying experiment for all drying temperatures.

3.3. Oil extraction experiments

3.3.1. Material used for oil extraction

As it has been already mentioned in Section 3.1 of the thesis, all the thirteen different jatropha seed collections were used for the oil extraction experiments. The seeds were dried just before oil extraction using a heating furnace (Narbetherm P300, Germany) to reduce the moisture content of the seeds. The dried seeds were crushed mechanically by hand using mortar and pestle following the same technique as before.

The crushed seeds were weighed before oil extraction using sensitive electronic balance (AD, GR-202-EC, A&D Instruments, Japan) having 0.0001 mg accuracy. Oil extraction experiments were performed with a Soxhlet extractor using cotton or extraction thimble with single thickness (37x130 mm) as a filter. A heating mantle (LabHeat, SAF, KM-MER 250 ml) was employed during oil extraction to heat the round bottom flask of the Soxhlet extractor at the temperature around the boiling points of the extraction solvents. A rotary evaporator (Rotary Vapo R-3, Butchi Labortechnik AG, CH-9230, Switzerland) with vacuum pump (Shanghai Eyela CO. LTD Aspirator A.1000S, China) was also used to separate the oil and the solvents after oil extraction.

The organic solvents (ethanol, hexane, diethyl ether and heptane) used for oil extraction were standard grades. Diethyl ether, ethanol, phenolphthalein, potassium hydroxide, chloroform, Wijs solution, potassium iodide, sodium thiosulphate ($Na_2SO_3.5H_2O$), potato starch and sulfuric acid used for the determination of the chemical properties of the oils were also analytical reagent grades. Moreover, Plain Jacket bomb calorimeter (Model 1341, Parr Instrument Company, USA) was used to measure the energy contents of the de-oiled seed residues produced after oil extraction.

3.3.2. Oil extraction procedures

The whole seeds were dried at 80 °C for 2 days (2880 minutes) using a heating furnace just before oil extraction based on the results obtained from the drying experiments of **Paper II.** Then, the dried seeds were crushed using mortar and pestle in such a way that the average particle sizes of the pulverized seeds were the same as those of the drying experiments.

The oil extraction experiments involved three round extractions with different purposes. In the first-round oil extraction experiments, $Salmene_3$ seed collection was extracted using four different solvents (diethyl ether, ethanol, heptane and hexane) and cotton as filter to identify the most efficient solvent for oil extraction in terms of the percentage of oil extracted. In second-round oil extractions, all the thirteen seed collections were extracted using the previously selected solvent and cotton. This experiment was carried out to determine the amount of oil (%) that could be extracted from the respective seed collections. After determining the average oil extracted from the seed collections from the north-central and the southern part of the country separately, the seed collections from southern Ethiopia were selected for the third-round oil extraction with thimble as larger amount of oil (%) was obtained from these collections. In all experiments, 50 g of crushed seed was used for the extraction. The energy contents of the selected de-oiled seed residues, produced after oil extraction with hexane using cotton, was also determined by bomb calorimeter. Figure 3.1 shows the schematic diagram of jatropha seed processing for oil extraction, oil extraction procedures and the post extraction process.

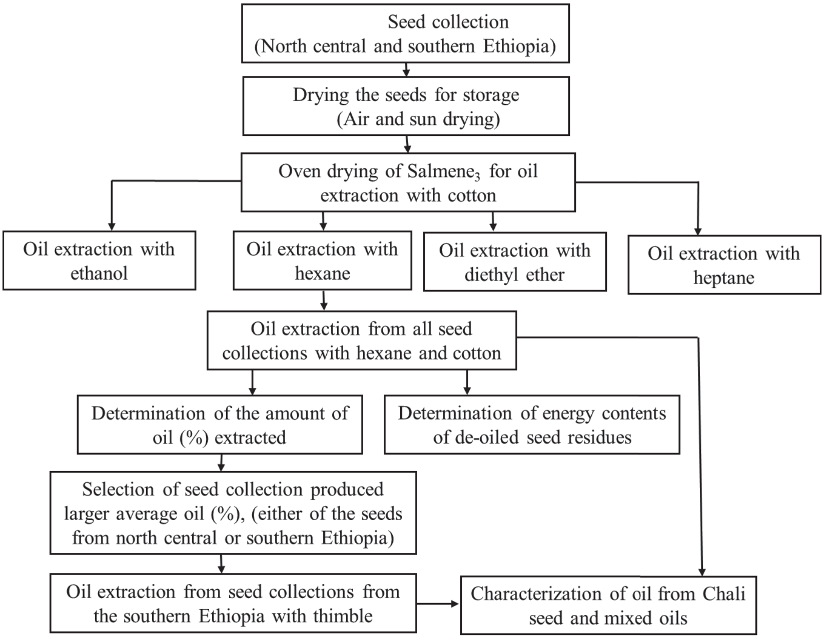

Figure 3.1: Schematic diagram for jatropha seed collection, oil extraction and post extraction processes.

In oil extraction with cotton, the crushed seed samples were placed in Soxhlet extractor column in between two cotton layers. After 240 ml of the respective solvents have been added to the round bottom flask, the flask was placed on the heating mantle and all parts of the Soxhlet extractor were attached to each other to complete the full setup. Then, the solvents were heated to the boiling points of the respective solvents for the oil extraction to occur. The extraction proceeded until five cycles of washes to occur. In the oil extraction experiments presented in this thesis, duration of extraction is expressed in terms of the number of cycles of washes occurred using the Soxhlet extractor. The solvents were recovered from the extract using a rotary evaporator attached to a vacuum, by heating the extract to the temperature around the boiling points of the solvents for 2.5 hours. Finally, the remaining oil was weighed, and its amount was expressed in terms of the percentage of oil (wt%) obtained from the extracted seeds.

Triplicated whole seed samples from southern Ethiopia were dried, crushed and extracted using the selected solvent and thimble with single thickness (37x130 mm) for ten cycles of washes. This experiment was carried out to determine the seed collection that could give the largest percentage of oil from the six seed collections from the southern Ethiopia using the indicated extraction method.

3.3.3. Oil characterization

Two different oil samples: the oil sample from Chali seed collection extracted with a Soxhlet extractor using a thimble (Chali oil) and a sample of mixed oil (the mixture formed by mixing equal volumes of oils extracted from all thirteen seed collections) were characterized for physical and chemical properties. Chali oil was selected for analysis as the amount of oil (%) produced from this seed collection using hexane and thimble was found to be the largest. The properties selected were acid value, percentage of free fatty acids (%FFA), Iodine value, saponification value and oil density.

3.3.3.1. Acidity and percentage of free fatty acids

The acid value (AV) and %FFA of both oil samples were determined following the methods used by Asmare and Gabbiye [147]. Accordingly, 25 ml of diethyl ether and ethanol (1:1) mixture was added to 5 g of oil in a 250ml conical flask and mixed well. After adding 5 drops of phenolphthalein indicator, the solution was titrated with 0.1N ethanolic KOH with consistent shaking until the end point of the titration was confirmed (change from colorless to pink). The volume of 0.1N ethanoic KOH (V) consumed during the titration was recorded. The total acidity of the sample in mg KOH/g was calculated using Equation 3.4.

$$AV = \frac{56.1 * \mathrm{N} * \mathrm{V}}{\mathrm{W}} \tag{3.4}$$

Where 56.1 is the molecular weight of KOH (g/mol), N is the normality of ethanolic KOH used, V is the volume (ml) of ethanolic KOH and W refers to the weight (g) of oil sample.

The %FFA was also calculated from the acid value of the oil with Equation 3.5.

$$\%\mathrm{FFA} = \frac{\mathrm{AV}}{2} \tag{3.5}$$

3.3.3.2. Iodine value

The iodine value (IV) of the oil samples was determined by adopting the procedures used by Amabye and Bezabh [148]. Accordingly, 0.25 g of oil sample was measured and placed in 250 ml flask, and 20 ml of chloroform was added into the flask to dissolve the sample. Then, 20 ml Wijs reagent (the iodine monochloride solution) was added to the mixture. The flask was stoppered and kept in the dark for 1 hour with intermittent shaking. After 1 hour, the mixture was taken out of the dark and 10 ml of 15% potassium iodide solution and 50 ml of distilled water were added and shaken well by inserting the stopper properly to the flask. Then, the liberated iodine was titrated with 0.1 N sodium thiosulphate ($Na_2S_2O_3.5H_2O$ solution) with gently stirring the mixture until the yellow color changed to a light straw. Finally, 5 drops of 1% starch indicator was added to the mixture and the titration was continued until the blue color disappeared. The blank titration was also conducted side by side to use it in the calculation to determine the parameter.

The iodine value of the oil sample was determined using Equation 3.6.

$$IV = \frac{V_b - V_s}{M} * 12.69 * N \qquad (3.6)$$

Where, V_b is the volume (ml) of sodium thiosalphate used for the blank, V_s is the volume (ml) of sodium thiosalphate used for the sample, N is the normality of sodium thiosuphate, and W refers to the mass of the sample used (g).

3.3.3.3. Saponification Value

The saponification value (SV) was determined according to Ogbunugafor *et al*. [149]. 50 ml of 0.5N ethanolic potassium hydroxide (KOH) was added into a conical flask containing 1g of jatropha oil. The flask was connected to a condenser and the mixture was heated to reflux with gentle stirring for 45 minutes. Then, the mixture was cooled to room temperature, after which it was titrated with 0.5N sulfuric acid (H_2SO_4) by adding 5 drops of phenolphthalein indicator until the pink color of the indicator had just disappeared. The blank test was also carried out under the same conditions. The saponification value of the sample was calculated using Equation 3.7.

$$SV = \frac{V_b - V_s}{W} * N * 56.1 \tag{3.7}$$

Where V_b is the volume (ml) of sulfuric acid used for the blank, Vs is the volume (ml) of sulfuric acid used for the sample, N is the normality ethanolic potassium hydroxide (KOH) and W is the mass (g) of the sample.

3.3.3.4. Density

A 50 ml flask was placed on a sensitive electronic balance and the reading of the balance with the flask was adjusted to zero. Then, the oil sample was added to the volumetric flasks using a pipette until the volume of the oil reached 50 ml, and the weight (g) of the oil was recorded. Finally, the density of the oil was determined from the weight and volume readings. The measurement was duplicated, and the average value of the measurements was reported. The densities of the oil samples were determined at an ambient temperature of 293 K.

3.3.4. Determination of the energy content of the de-oiled seed residues

In addition to the biodiesel that is produced from the oil, jatropha seed residues can be used as the source of bioenergy [150]. Accordingly, some selected de-oiled seed residues left after extraction with cotton were dried under fume hood for five days. Then, the upper calorific values (gross calorific values) of the residues were estimated by a bomb calorimeter, using benzoic acid as a standard. The experiment was carried out to determine the energy contents of different de-oiled seed residues and to compare the calorific values obtained with each other and with that of other crop residues from literature.

3.4. Experimental reactions to produce biodiesel

Two different transesterification reactions were carried out to produce biodiesel from jatropha oil using heterogenous catalysts. The reactions were different in the types of oil, alcohol and heterogenous catalysts used, and the reaction conditions employed. In the first reaction, mixed jatropha oil (a mixture formed from equal volumes of oils extracted from all the thirteen seed collections) reacted with ethanol using Amberlyst A26 (OH), an anion exchange resin, and the work was presented in **Paper V**. The second reaction occurred between oil extracted from Chali seed collection (Chali oil) and 1-butanol using glycerol enriched non-calcined commercial CaO as catalyst (**Paper VI)**. The materials used and the experimental procedures for both reactions are described in the following subsections.

3.4.1. Materials used for experimental reactions

As previously mentioned, mixed jatropha oil (a mixture formed from equal volumes of oils extracted from all the thirteen seed collections) and oil of Chali seed collection (Chali oil) were used for the transesterification reactions of **Paper V** and **Paper VI**, respectively. The oils used for both reactions were extracted by a Soxhlet extractor using hexane and thimble with single thickness (37x130mm). Both transesterification reactions were performed in a three-necked glass reactor from Quark Glass and with 500ml volume capacity. The anion exchange resin (Amberlyst A26 (OH)) wet and CaO were purchased from Dow Chemicals and Honeywell Companies, respectively. The absolute ethanol, 1-butanol, tetradecane, pyridine, acetone, methanol, hexane, heptane and glycerol utilized were obtained from Sigma-Aldrich with a purity higher than 99%. The reaction samples were analyzed using the gas chromatography (GC) analyzer (Bruker scion 436 chromatograph).

3.4.2. The experimental setup for the reactions

Both transesterification reactions of mixed jatropha oil and Chali oil were performed in a three-necked glass reactor. A cooling condenser that was connected to tap water was inserted into the middle neck of the reactor to enable the refluxing of evaporated alcohol back into the reactor. The thermostat, attached to the digital heating plate on which the reactor has been placed, was inserted through one of the side necks into the glass reactor to measure the temperature of the reacting mixtures. The other neck of the glass reactor was plugged with a rubber cork through which the samples of the reaction mixture were periodically taken using a syringe. The lower part of the reactor was also connected to a thermostatic water bath that regulated the temperature of the reacting mixtures by circulating the water through the reactor.

For the reactions catalyzed by Amberlyst A26 (OH), 50 g of mixed jatropha oil and the desired amount of ethanol were added to the glass reactor and heated to the reaction temperature by vigorously stirring the mixture at 200 revolutions per minute (rpm). When the temperature of the mixture reached the set value, a measured amount of catalyst was added into the reactor. This was considered as the starting time of the transesterification reaction. The stirring intensity of 200 rpm was maintained for all experiments to overcome the mass-transfer limitation. The aliquots (about 0.5 ml) of the reaction mixture were withdrawn using the syringe at a predetermined time intervals (0, 5, 10,15 20, 30 45, 60, 90, 120, 180, 240, 300, 420, 480 and 540 minutes) to investigate the progress of the reaction. After reacting for 9 hours (540 minutes), the mixture in the reactor was filtrated by putting the filter paper on the separatory funnel to separate the resin from the other constituents of the reaction mixture. Then, the filtrate mixture collected in the separatory funnel was allowed to stand overnight to form different layers of the constituents of the mixture for separation. The resin remaining on the filter paper was washed with acetone and ethanol to be reused [130].

The reaction of Chali oil with 1-butanol using glycerol enriched non-calcined CaO as catalyst was started by dropping about 1.57 g of glycerol (15% by wt% of CaO) on the inner bottom surface of the grass reactor. Then, about 70 g of oil and 10.5 g of CaO (15% by wt% of the oil) were added to the reactor and heated to 60°C by vigorously stirring the mixture at 200 rpm for 60 min to promote the synthesis of glycerol-enriched CaO (glycerol-CaO complex). The amount of the glycerol and the temperature used for the synthesis of glycerol-CaO complex was adapted from the previous related works [151-153]. After the activation of CaO with glycerol, the mixture in the glass reactor was heated to the desired temperature by stirring it as before. When the set temperature was maintained, a measured amount of 1-butanol heated separately to the reaction temperature was added to the mixture. This time was taken as the initial time (t=0). About 0.5 ml samples of the reacting mixture were taken at the predetermine time intervals (0, 10, 20, 30, 60 and 90 minutes) to follow up the progress of the reaction.

3.4.3. Experimental designs for the experimental reactions

For the reactions catalyzed by Amberlyst A26 (OH), the modified central composite design (CCD_m) was applied to determine the effects of three independent factors: temperature (T), ethanol: oil molar ratio (R) and the catalyst present (C) on jatropha oil conversion with ethanol (X_{JOE}) and the yield of fatty acid ethyl esters (Y_{FAEEs}). The reaction time and stirring speed were kept constant at 540 minute (9h) and 200 rpm, respectively.

The selected factors have been chosen based on the previous transesterification reaction studies by Sánchez *et al.*[123] and Ayoola *et al.* [154], where the temperature, methanol: oil molar ratio and catalyst percent were found to be the most significant variables. The values for the factors were also selected based on the information from the product data sheet of the catalyst and a few related previous studies on ion-exchange resins [128, 130, 155]. As it was indicated on the product data sheet of the current catalyst (Amberlyst A26(OH)), its maximum operating temperature is 60 °C and thus, the maximum reaction temperature was kept below 60 °C. The design of the experiment consisted of eight factorial (linear) point and six center point experiments, respectively. Running replicated center points is important to measure the accuracy of the study, and it is also used in checking for the presence of curvature [156]. The values of the selected factors and their associated levels in the CCD_m, are presented in Table 3.2. Response Surface Methodology (RSM) was used for the analysis and modelling of the effects of the selected parameters on the responses.

Table 3.2: Values of the factors at different levels in the modified central composite design.

Factors	Levels		
	-1	0	1
Temperature (°C)	45	50	55
Molar ratio (-)	15	25	35
Catalyst amount (%)	15	20	25

The experiment of the reactions catalyzed by CaO was carried out to determine the effects of two selected independent factors (reaction temperature and butanol: oil molar ratio) with two levels on jatropha oil conversion with butanol (X_{JOB}) and the yield of fatty acid butyl esters (Y_{FABEs}). Accordingly, the central composite design (CCD), that involved two factors and two levels full factorial (2^2), was used to determine the impacts of the factors on the X_{JOB} and Y_{FABEs}, and to optimize the process. The values of the selected factors and their associated levels for the reactions catalyzed with non-calcined CaO are presented in Table 3.3. The catalyst amount was kept constant at 15% (wt%) of the oil while the glycerol used was 15% (wt%) of the catalyst, and these amounts were adopted from the results obtained by Avhad *et al*. [152]. A reaction time and stirring speed of 90 minutes and 200 rpm, respectively, were used.

Table 3.3: Values of the factors at different levels of the design for the reaction catalyzed with CaO.

Factors	Levels				
	-α	-1	0	1	α
Temperature (°C)	65.9	70	80	90	94.10
Molar ratio (-)	4.77	6	9	12	13.23

3.4.4. Analysis of reaction samples

The reaction samples were analyzed with a gas chromatography (GC) using GCMS analyzer (Bruker scion 436 chromatograph) equipped with an autosampler (CP-8400), a flame ionization detector (FID) and using a 5-phenyl-methylpolysiloxane capillary column (DB-5HT column, Agilent Technologies). The GC column has 15 m length, 0.32 mm diameter and 0.10 µm thickness. The injection system was split-splitless, and helium was used as carrier gas with flow rate of 1ml per min. The temperature of the injector was set at 320 °C while that of the detector was adjusted at 350 °C. The initial temperature in the oven was 80 °C and it was programmed to raise with 10 °C/min until it reached a final temperature of 360 °C. The GC samples were prepared following the American Oil Chemists' Society (AOCS) Official Method Cd 11b-91 [157]. Accordingly, tetradecane and pyridine were used as the internal standard and solvent for GC samples, respectively. The GC analysis was performed by injecting 1µl of the prepared samples into the equipment.

Using the area obtained for a given weight of the sample and internal standard from the chromatogram, the weight was converted to molar values with the help of the standards and the response factors using equations 3.8 and 3.9 [152].

$$Grams\ of esters\ = \frac{Grams\ of\ internal\ standard\ \times\ Area\ of\ esters}{Response\ factor\ \ of esters\ \times\ Area\ of\ internal\ standard} \tag{3.8}$$

$$Moles\ of\ esters = \frac{Grams\ of\ esters}{Molar\ mass\ of\ esters} \tag{3.9}$$

The equation used to calculate jatropha oil conversion (X_{JO}) from the initial and final moles of the oil is expressed as:

$$X_{JO} = \frac{Initial\ moles\ of\ oil - Final\ moles\ of\ oil}{Initial\ moles\ of\ oil} \tag{3.10}$$

Moreover, the yield of fatty acid esters (Y_{FAEs}) obtained was calculated using the Equation 3.11 below following the study by Wang *et al.* [158].

$$Y_{FAEs} = \frac{FAEs\ (\%)}{TG(\%) +\ DG(\%) + MG\ (\%) + FAEs(\%) + FAA(\%)}\ x\ 100 \qquad (3.11)$$

3.5. Mathematical modelling and statistical analyses

3.5.1. Mathematical modeling of the drying kinetics of the seeds

The drying data of the WS and CS of Salmene_3 seed collection were also utilized for the mathematical modeling for the drying kinetics of the jatropha seeds. The data obtained from the weight measurements of the drying seed samples at different temperatures and drying time were changed to moisture content in order to use it to determine the drying kinetics. Accordingly, the recorded weight loss data of seed samples at different time intervals were changed to moisture loss. From the initial moisture content of the seed (M_0), the moisture content data at different time intervals (M_t) and equilibrium moisture content of the seeds for different temperatures (M_e), the dimensionless moisture ratio (MR) was calculated. Then, the MR as a function of time was used for fitting the mathematical models. Equation 3.12 is used to calculate the MR of the seed samples.

$$MR = \frac{M_t - M_e}{M_0 - M_e} \qquad (3.12)$$

The equilibrium moisture content (M_e) of jatropha seeds at each temperature was obtained experimentally by drying the seed samples in the heating furnace until no change in weight occurred for three successive weight measurements [99].

In the present thesis, the drying data from five different drying temperatures were fitted to the three most commonly used semi-theoretical mathematical models: Lewis, Henderson and Pabis, and Page models [159-161]. The experimental data were also fitted to the Avhad and Marchetti model, which is a combination of Page model and Henderson and Pabis model and was found to be best fitted to the drying kinetics of Hass avocado seeds [162]. The expression of Lewis, Henderson and Pabis, Page, and Avhad and Marchetti models are given in Equations 3.13, 3.14, 3.15 and 3.16, respectively.

$$MR = exp(-k * t) \quad (3.13)$$

$$MR = a * exp(-k * t) \quad (3.14)$$

$$MR = exp(-k * t^N) \quad (3.15)$$

$$MR = a * exp(-k * t^N) \quad (3.16)$$

where, a, k and N are the constants of the models, and k follows an Arrhenius expression.

The drying rate constant “k” and the drying activation energies (Ea) were used to analyze the change of moisture content at different temperatures. Activation energies (Ea) for the crushed and whole seeds of jatropha were obtained from the slopes of the plots of ln(k) versus T^{-1} that were predicted using the experimental data for the tested models using Arrhenius equation. Then, the k values calculated from the activation energy for the respective drying temperatures were inserted into the expression of all drying mathematical models. Similarly, the rate constant k was used in the studies of drying kinetics of *Cuminum cyminum* grains (Zomorodian and Moradi, 2010), jatropha seeds (Siqueira *et al*., 2012), plantain sample (Oforkansi and Oduola, 2016), and pumpkin fruit slices (Onwude *et al*., 2016). Arrhenius equation is presented in Equation 3.17 below.

$$k = A * exp^{\left(\frac{-E_a}{RT}\right)} \quad (3.17)$$

where, k refers to rate constant, A is the pre-exponential factor, E_a is the activation energy (KJ mol-^{1}), R is the universal gas constant (8.314 J mol^{-1}K), and T is the absolute air temperature (K).

3.5.2. Fitness of the seed drying mathematical models

The values of five statistical parameters were used to compare the fitness of the data predicted by the drying mathematical models to the drying curves of the experimental data. The parameters utilized include coefficient of determination (R^2), chi-square test (X^2), root mean square error (R_{MSE}), mean bias error (MBE), and mean absolute error (MAE). In the comparison of the fitness of the models to the experimental drying curves, the most fitted model must have the largest values of R^2, and conversely, it should have the smallest values of X^2, R_{MSE}, MBE and MAE [163, 164].

The statistical parameter R^2 was calculated according to the expressions by Oforkansi and Oduola [165]. The other statistical parameters were calculated using the equations used by Gunhan *et al* [166], Zomorodian and Moradi [167], Sridhar and Madhu [168], Naderinezhad *et al.* [169], Oforkansi and Oduola [165], Avhad and Marchetti [162], and Mazandarani *et a*l. [170]. The expression for these statistical parameters were presented in Equations 3.18 to 3.22 as:

$$R^2 = 1 - \left(\frac{\sum_{i=1}^{N} \left(MR_{pre,i} - MR_{exp,i} \right)^2}{\sum_{i=1}^{N} \left(MR_{exp,i} - \overline{MR}_{exp} \right)^2} \right) \qquad (3.18)$$

$$X^2 = \frac{\sum_{i,=1}^{N} \left(MR_{ex,i} - MR_{pr,i} \right)^2}{N - z} \qquad (3.19)$$

$$E_{RMS} = \left[\frac{1}{N} \sum_{I,=1}^{N} \left(MR_{ex,i} - MR_{pr,i} \right)^2 \right]^{\frac{1}{2}} \qquad (3.20)$$

$$MBE = \frac{1}{N} \sum_{i=1}^{N} \left(MR_{ex,i} - MR_{pr,i} \right) \qquad (3.21)$$

$$MAE = \frac{1}{N} \sum_{i=1}^{N} \left| MR_{ex,i} - MR_{pr,i} \right| \qquad (3.22)$$

where, $MR_{exp,i}$ is the i^{th} experimental moisture ratio; $MR_{pre,i}$ is the i^{th} predicted moisture ratio; $\overline{MR}_{exp}$ is the mean of the experimental moisture ratio; N refers to the number of observations; z represents the number of constants in the models.

3.5.3. Comparison of the amount of oil extracted

The data of oil content of six jatropha seed collections from southern Ethiopia that were extracted by thimble with single thickness and that of Salmene$_2$ stored at three different temperatures were subjected to the analysis of variance (ANOVA test). Significant difference among the amount of oil produced (%) from the six different seed collections from southern Ethiopia and those of Salmene$_2$ stored at three different temperatures, respectively, were analyzed at $p \leq 0.05$. Duncan's post hoc test ($p \leq 0.05$) was used to determine the homogeneity subsets whenever significant differences existed among the treatments. The statistical software used was SPSS for windows, version 20.

3.5.4. Statistical analyses using Statgraphics

The statistical analyses of the effects of reaction parameters on the responses and the optimization of the reaction process were performed using the Statgraphics Centurion 17 (Statgraphics Technologies, Inc USA). The analyses enabled the determination of the influences of the main factors and their interactions on the conversion of jatropha oil and yield of the fatty acid esters. The equations of the regression models were used to interpret the effects of the main factors and their interactions on the selected responses and predict the optimum conditions needed to maximize the responses.

The presence of curvature was tested statistically using the responses of the factorial points and that of the replicated center points, by employing the statistical Equations 23-25 [156, 171]. Then, the p value associated with the calculated F value was determined to test the significance of the curvature ($p \leq 0.05$).

$$SS_{pure\ quadratic} = \frac{n_F n_C(\bar{y}_F - \bar{y}_C)^2}{n_F + n_C} \tag{3.23}$$

$$\mathrm{MS_E} = \left(\sum\nolimits_{\text{Center points}} (\mathrm{y}_i - \bar{\mathrm{y}})\right)^2 / (\mathrm{n_C} - 1) \tag{3.24}$$

$$F = \frac{SS_{pure\ quadiratic}}{MS_E} \tag{3.25}$$

Where $SS_{pure\ quadiratic}$ refers to a sum of square for pure quadratic curvature and $\mathrm{MS_E}$ is mean square error of center points. $\bar{\mathrm{y}}_\mathrm{F}$ and $\bar{\mathrm{y}}_\mathrm{C}$ are the average of responses of factorial and center points, respectively. n_F and n_C are the number of factorial and center points, respectively. y_i refers to the responses of the center points and $n_C - 1$ is the degree of freedom for center points. F is F-statistic, the test statistic for F-tests.

4. Main results and discussion

The research activities of the present thesis focused on oil extraction from thirteen different collections of jatropha seeds from Ethiopia and biodiesel production from the extracted non-edible oils using renewable alcohols and reusable and low cost heterogenous catalysts. A selected jatropha seed collection at storage was dried at different temperatures to determine the appropriate temperature that reduced the seed moisture to its minimum for oil extraction. From the dried seeds, oil was extracted with different solvents to identify the most efficient solvent in terms of the percentage of oil extracted. Then, the selected solvent was used for extraction to determine the oil contents of all the thirteen seed collections. After characterizing the selected oil samples, transesterification of the mixed oil with ethanol using Amberlyst A26 (OH), anion ion exchange resin as catalyst was performed to systematically investigate the influences of the reaction temperature, ethanol: oil molar ratio and the catalyst percent on oil conversion and biodiesel yield, and to optimize the process. In addition to the transesterification of mixed oil with ethanol using ion-exchange resin, butanolysis of Chali oil (oil of Chali seed collection) was carried out using glycerol enriched non-calcined CaO as catalyst by modifying the biodiesel production method used by Avhad *et al*. [152]. Accordingly, in the latter reaction, the influences of reaction temperature and butanol to oil molar ratio on oil conversion and biodiesel yield were investigated by keeping the amount of CaO and glycerol constant (15% wt. % of the oil and the catalyst, respectively).

4.1. Drying jatropha seeds

4.1.1. Characteristics of seeds used for drying

The dimensional properties of the WS of Salmene$_3$ collection, the seed collection used for the seed drying experiments, was determined as these parameters could affect the drying process of the seeds [144]. Table 4.1 presents the dimensional properties of the WS of Salmene$_3$ collection. As it can be seen from Table 4.1, the mean value for the seed length, width, thickness, geometric mean diameter, and arithmetic mean diameter were found to be 15.46±0.74, 10.24±0.54, 7.28±0.57, 10.47± 0.501 and 10.99±0.48 mm, respectively. All the seed mean dimensions obtained in the current study were in the range of the values determined for jatropha seeds collected from Egypt [172].

Table 4.1: Dimensional properties of jatropha seeds (Salmene$_3$ collection)

Type of dimension	Seed dimensions (mm)	
	Range	Mean
Length	13.5–17.0	15.46±0.74
Width	9.0–11.50	10.24±0.54
Thickness	6.5– 9.0	7.28±0.57
Geometric mean diameter	9.3 –11.83	10.47±0.501
Arithmetic mean diameter	9.83–12.16	10.99±0.48

The initial moisture content of Salmene$_3$ collection before drying was also found to be 6.81 %, and this result showed that the moisture content of the selected seed collection was in the range of the safe seed storage moisture content (6-10%) for jatropha seeds [69]. Moreover, the particle sizes of the crushed seeds (PSCS) used for the drying experiments were estimated using sieves with openings of 500 µm, 1 mm and 2 mm woven cloth, and thus, the pulverized seed used for the experiment was a mixture of four different particles sizes. Accordingly, it was found that the average proportions (%) of different PSCS: PSCS >2 mm, 2 mm > PSCS >1 mm, 1 mm > PSCS >500 µm and PSCS<500 µm were 14.95±8.2, 29.96±4.38, 35.32±10.5 and 19.77±4.74, respectively.

4.1.2. Effects of temperatures on the physical appearances of the seeds

The experiment on the effects of drying temperatures on the physical appearance of jatropha seed samples was conducted to investigate if charring of the surface of the seeds would occur. Charring of the seed surface could reduce the moisture loss from the seeds, particularly during drying the seeds at higher temperatures [142]. Accordingly, a close observation and evaluation of photographs that were taken during the drying process was made. However, with the exception of a slight blackening of the seed coat of WS and the upper surface of the CS, and the sticking together of the upper surface of crushed seed particles, no other major changes occurred to the seeds after drying (**Figure 1** of **Paper II**). The results obtained for the current study were in contrast to the physical appearance that occurred to the Hass avocado seeds dried at 40, 50, 60, 70 and 80 °C, where rupturing of the seeds into two pieces, and hardening and charring of the outer surface of the seeds occurred at 60 °C and higher temperatures [142]. The authors also reported that rupturing of the seeds promoted moisture evaporation; however, charring occurred to the seeds due to a higher temperature resulted in incomplete evaporation of water from the seeds at the end of drying.

4.1.3. Moisture loss of crushed and whole seeds

In **Paper II**, the drying experiment of WS and CS of Salmene_3 collection was carried out to investigate the effects of five drying temperatures (40, 50, 60, 70 and 80 ºC) on the degree of moisture loss from jatropha seeds at storage, and the suitability of the drying processes to reduce the moisture of the seeds to its minimum for oil extraction and/ or in situ transesterification. The weight loss data recorded for 5760 minutes were changed to weight loss percentage which is assumed to be equal to seed moisture loss percentage. Then, the effect of different drying temperatures on the moisture evaporation from the WS and CS of jatropha were compared.

From the result of the drying experiment, it was found that weight loss by the CS was faster than that of the WS around the beginning of seed drying and then slowed down after some hours, depending on the drying temperatures. Accordingly, the weight losses (wt. %) by the CS were larger than that of the WS before the drying times of around 1440, 480, 330, 270 and 240 minutes for the drying temperatures of 40, 50, 60, 70 and 80 ºC, respectively. However, after the indicated drying times, the weight losses (wt. %) by the CS was found to be lower than that of the WS for all respective temperatures. The time at which the weight losses of WS and CS became about equal for the same drying temperature, and the respective weight loss recorded are presented in Table 4.2.

Table 4.2: Weight loss (wt. %) and the approximate time for the weight losses of WS and CS to be about equal.

Temperature (ºC)	Treatments	Weight loss (wt. %)	Time (min) for weight loss to be about equal
40	WS	4.28	1440
	CS	4.21	
50	WS	4.42	480
	CS	4.47	
60	WS	4.88	330
	CS	4.80	
70	WS	5.23	270
	CS	5.23	
80	WS	6.01	240
	CS	5.99	

As it can be seen from Table 4.2, the time taken for the weight losses (wt.%) by CS and WS to be about equal was the longest at the lowest drying temperature (around 1440 min for 313 K) and the shortest at the highest temperature (around 240 min for 353 K). This shows that the time that is needed for the weight losses (wt.%) of CS and WS dried at 353 K to be roughly equal to each other was 6 times shorter compared to that of the same samples dried at 313 K. The reason for this is that due to a faster seed moisture evaporation rate at a higher temperature [99], the process rapidly reached at the falling drying rate period compared to the drying process at a lower temperature.

4.1.4. Effects of temperatures and seed pretreatment on seed drying

The influences of different drying temperatures on the extent of moisture evaporation from the WS and CS are graphically represented in Figure 4.1 and Figure 4.2, respectively. The results showed that the rise in operative air temperature accelerated the drying process of the seeds. Drying temperature of 80 °C resulted in 6.15% weight reduction in the WS after 360 min, and this was about twice the weight reduced using 40 °C at the same drying time. Weight loss of CS at the drying temperature of 80 °C was also much higher than that of 40 °C. This behavior was in line with the findings in which fresh jatropha seeds were dried at 40 and 60 °C, and found that evaporation of water from the seeds at 60 °C was 2 times faster than those dried at 40 °C [86]. In other drying experiment using freshly collected jatropha seeds, the evaporation of water from the seeds was found to be 8 times faster when the temperature was increased from 36 °C to 105 °C to reduce the moisture of the seeds from 61% to 11 % (d.b) [173]. Thus, the rise in operating temperature minimizes the time required for the drying process. The larger weight reduction at higher temperature in the latter investigation compared to the present study might be due to larger initial moisture contents of the fresh seeds.

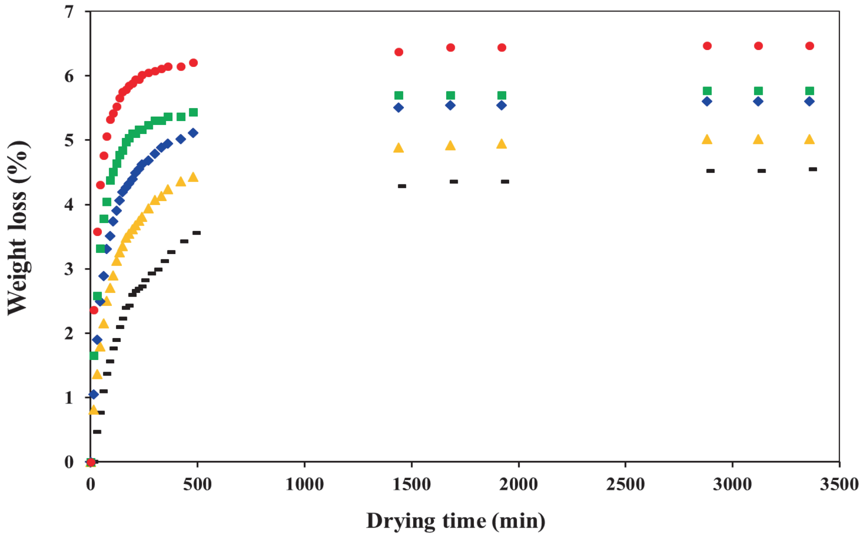

Fig. 4.1: Weight loss profile of the whole jatropha seeds at drying temperatures of (—) 40 °C, (▲) 50 °C , (♦) 60 °C, (■) 70 °C and (●) 80 °C [174].

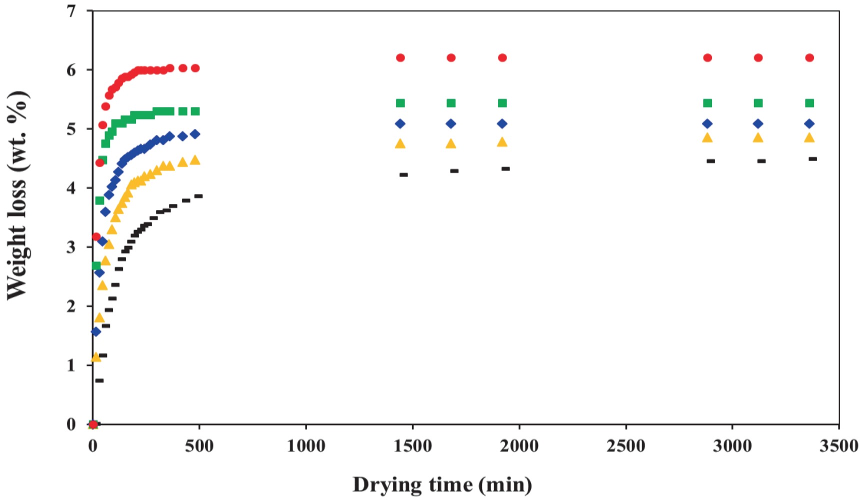

Fig. 4.2: Weight loss profile of crushed jatropha seeds at drying temperatures of (—) 40 °C, (▲) 50 °C, (♦) 60 °C, (■) 70 °C and (●) 80 °C [174].

As it could be seen from Figure 4.1 and Figure 4.2, for all temperatures, the weight losses of the CS and WS were found to increase with time until it reached a critical value above which there was no further increase of the weight loss. With an increase of drying time, the rate of weight loss decreased gradually, and finally, no more weight loss was observed. This happened when the moisture content of a seed becomes in equilibrium with the relative humidity of the surrounding air [175]. The residual moisture remained in the seed at this time, for a drying temperature, is termed as the equilibrium moisture content (M_e) of the dried seed. Table 4.3 shows the final weight loss by WS and CS, the M_e for different temperatures and the time taken to reach the M_e.

Table 4.3: Final weight loss of the whole seeds (WS) and crushed seeds (CS), M_e for different temperatures and the approximate time to reach at M_e.

Temp. (°C)	Treatments	Final weight loss (wt. %)	M_e (wt. %)	Time to reach M_e (min)
40	WS	4.61	2.19	4320
	CS	4.51	2.29	4320
50	WS	5.01	1.79	2880
	CS	4.85	1.95	2880
60	WS	5.60	1.21	2880
	CS	5.09	1.71	1440
70	WS	5.76	1.04	2880
	CS	5.44	1.36	1440
80	WS	6.47	0.34	2880
	CS	6.21	0.60	1440

From Figure 4.1, Figure 4.2 and Table 4.3, it can be seen that the weight losses (wt. %) by CS were faster than that of WS for higher temperatures, particularly for the drying temperatures of 60, 70 and 80 °C. The total time required to reach at the equilibrium moisture content for the WS is 2 times longer than that of CS. The result of the present study was in line with the findings reported for the drying experiments of crushed kernels (paste), kernel with particles size of 4 and 8 mm, and the whole kernels of *Buccholzia coriacea* and *Butyrospermum parkii* using drying temperatures of 45 and 60 °C [176]. From this investigation, it was found that the decrease in weight of the paste was very fast compared to those of other treatments, and the highest drying rate was recorded for the paste compared to samples with larger particle sizes. The faster moisture loss from the crushed seeds could be due to the fact that the grinding of the seeds provoked rupture of the cell membranes, thus, providing a larger surface area for rapid moisture loss to occur [176].

In the current study, although weight loss (wt. %) of the CS was faster than that of the WS, the final weight losses (wt. %) of the WS were larger than that of the CS, for all respective temperatures (Table 4.3). The maximum final weight loss (6.47%) from the WS was obtained for the seeds dried at 80 °C, and this value was greater than the maximum weight loss from the CS (6.21%) dried at the same temperature. The lowest residual moisture content (0.34%) was also found in the WS dried at 80 °C. The smaller final weight loss (wt.%) of the CS compared to the WS might be due to the hardening of crushed seed particles due to larger surface area that could be exposed to the drying temperatures. Some amount of moisture might also be lost by adhering to the surface of mortar and pestle during crushing the seeds [142], and to the surface of sieves during the estimation of CS particle size. There were also larger air spaces for drying air circulation between individual whole seeds than that of the particles of crushed seeds. These might also result in a smaller final weight loss of the crushed seeds.

As it is evident from Table 4.3, the drying temperature of 80 °C could reduce the moisture content of both WS and CS to below 1% while other drying temperatures could not do so. It was reported that reducing the moisture content of jatropha seeds to 0.912% allows the production of quality oil with FFA content of 0.9% [94], which could be directly used in alkaline catalyzed transesterification for biodiesel production [94, 177]. Dried seeds with a moisture content less than 1% could also be used in alkaline catalyzed in situ transesterification for biodiesel production [97, 178]. Moreover, although the drying temperature of 80 °C could reduce the moisture content of WS and CS to less than 1%, the moisture loss by WS (6.47%) was larger than that of CS (6.21%). Drying of the seed samples at a temperature higher than 80 °C has not been tested based on the work done by Subroto *et al.* [86], where it has been shown that temperatures higher than 60 °C could increase oil peroxidation in shell unprotected jatropha seeds. Oil peroxidation reduces the quality of oil as jatropha seed has high unsaturated oil content [86]. Therefore, drying the whole jatropha seeds at 80 °C for 2880 min drying time was considered as optimal for satisfactory drying of jatropha seeds for oil extraction and in situ biodiesel production.

4.1.5. Drying different collections of the whole seeds

Based on the seed drying results obtained for Salmene$_3$ seed collection, the WS samples of all the remaining six seed collections from north-central Ethiopia were dried at 80 °C. Table 4.4 shows the initial moisture content (wt. %) and the results obtained after drying the WS of different seed collections from north-central Ethiopia. As it can be seen from Table 4.4, all the seven seed collections had different initial moisture contents. The initial moisture contents of the seed collections named Gerbi, $Salmene_1$, Shekla, $Salmene_3$, Kurkura, Bira and $Salmene_2$ were found to be 8.72, 7.44, 7.12, 6.81, 6.80, 6.71 and 6.51% (wt.%), respectively. The differences in moisture content of the seed collections might be due to differences in the climatic conditions of the area from where the seeds were collected, stage of seed maturity [179] and differences of postharvest processing of the seeds [89]. Moreover, the moisture contents of all the seven seed collections were in the range of safe storage moisture content (6-10%) recommended for jatropha seed [69].

Table 4.4: Seed collections and their initial, final and equilibrium moisture contents (Me) and time to reach at M_e.

Seed collection	Initial moisture content (wt. %)	Final moisture loss (wt. %)	Residual moisture (M_e)	Time to reach M_e (min)
Gerbi	8.72	8.58	0.14	2880
$Salmene_1$	7.44	6.80	0.64	1440
Shekla	7.12	6.77	0.35	2880
$Salmene_3$	6.81	6.47	0.34	2880
Kurkura	6.80	6.17	0.63	1440
Bira	6.71	5.97	0.74	2880
$Salmene_2$	6.51	5.36	1.15	1440

The trends of weight loss in the seven seed collections was almost similar as it can be seen from **Figure 4** of **Paper II**. However, the amount of moisture losses by different seed collections were different. As it is evident from Table 4.4, the final moisture loss by Gerbi collection was the largest (8.58%) and that of $Salmene_2$ (5.36%) was the smallest. The differences in the amount of moisture loss (%) for different collection of jatropha seeds might be due to the differences of the initial moisture contents, seed sizes and other physical traits for various seed collections. It was also reported that seed grain size [180], porosity, shape and surface area [181] are some of the important seed physical properties that affect the drying profile of the seeds. Factors such as the climatic conditions of the seed collection sites, stage of seed maturity and the differences in postharvest processing of the seeds could also influence the moisture loss (%) of the seed collections [89, 179].

4.1.6. Mathematical modelling of the drying kinetics of jatropha seeds

In **Paper III,** simulation of the experimental results of the drying process of Salmene$_3$ seed collection presented in **Paper II** was performed. In this study, the systematically recorded moisture loss from the WS and CS of jatropha were converted to moisture ratio and fitted to the data predicted by four semi-theoretical drying mathematical models: Lewis, Henderson and Pabis, Page and Avhad and Marchetti models [159-162] to select a model that best describe the drying process of the seeds. Accordingly, the data predicted by the models were fitted to the drying curves of the experimental data of the seeds. **Figures 3a–c** and **Figures 4a–c** of **Paper III** show the comparison of the fitness of data predicted by the four models to experimental data of the WS and CS of jatropha, respectively, at 40 °C (the lowest), 60 °C (medium) and 80 °C (the highest) drying temperatures.

The graphical representations suggested that all the employed models are suitable to describe the drying kinetics of the jatropha seeds. However, the selection of best fit mathematical model was based on the values of R^2, X^2, R_{MSE}, MBE and MAE, and the values of R^2 were taken as the primary criteria for selecting the best-fit model to the drying kinetics of the seeds [182]. Among the four tested models, the Avhad and Marchetti model showed the best fitting to the experimental data with R^2 varied from 0.9914 to 0.9969 and 0.9908 to 0.9917 for all tested temperatures for the whole seeds and crushed seeds of jatropha, respectively. Moreover, the values of X^2, R_{MSE}, MBE and MAE were lower when Avhad and Marchetti model was used for both the WS and CS. The calculated statistical parameters for the WS and CS of jatropha for all the four models and the drying air temperatures (40–80 °C) are presented in **Table 2** of **Paper III.**

The maximum value of R^2 (0.9969) and the smallest values of X^2 (2.37×10^{-4}), R_{MSE} (0.01454), MBE (1.95×10^{-3}) and MAE (0.01171) were obtained when the WS were dried at 40 °C and the Avhad and Marchetti mode [162] was employed. Moreover, in the drying of CS of jatropha, the maximum R^2 value (0.9917) was obtained when the seeds were dried at 60 °C and Avhad and Marchetti model was used. The smallest values of E_{RMS} (0.02039) and MBE (3.64×10^{-3}) for CS were also found when the Avhad and Marchetti model was used. Thus, the results of this experiment suggested that the Avhad and Marchetti model showed superior fit to the experimental data at the drying temperature of 40 °C for the WS and at 60 °C in the case of CS. Figure 4.3a and

4.3b show the fitness of Avhad and Marchetti model with the experimental data for temperatures varying from 40 ºC to 80 ºC for the WS and CS of jatropha, respectively.

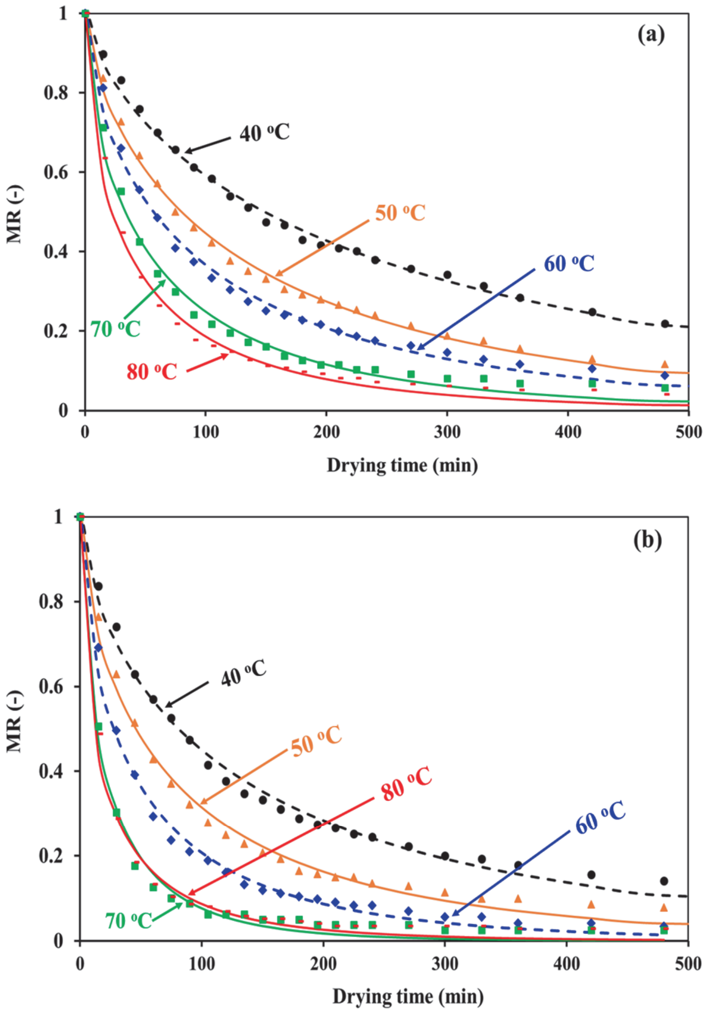

Figure 4.3: (a) Comparison of the experimental and predicted moisture ratios using the Avhad and Marchetti drying mathematical model at 40–80 ºC air temperatures for whole seeds of jatropha: (●) Experimental data, (—) model; (▲) Experimental data, (–) model; (♦) Experimental data, (–)model; (■) Experimental data, (–) model; (–) Experimental data, (—) model. (b) Comparison of the experimental and predicted moisture ratios using the Avhad and Marchetti drying mathematical model at 40–80 ºC air temperatures for crushed seeds of Jatropha: (●) Experimental data, (—) model; (▲) Experimental data, (–) model; (♦) Experimental data, (–)model; (■) Experimental data, (–) model; (–) Experimental data, (—) model [183].

The activation energy values for the WS and CS of jatropha were found to vary from 23.67 to 36.06 and 32.88 to 45.75 KJ mol^{-1}, respectively, for all mathematical models used (**Table 1** of **Paper III**). The activation energies obtained for the WS and CS of jatropha were in line with those reported for other agricultural products such as sorghum [184], grape seeds [185], sliced, and crushed Hass avocado seeds [162] and castor oil seeds [90]. Moreover, the activation energy of the CS was greater than that of the WS and this was unexpected as the rate of water evaporation in the CS was faster than that of the WS. From the study of activation energy of water release rate from corn kernel, Voća, *et al.* [186] reported that if the activation energy is higher, the moisture release from the kernels became slower. The present result was also in contrast to the findings of Avhad and Marchetti [162] in which the activation energy of the crushed Hass avocado seeds (24-32 KJ mol^{-1}) was found to be less than that of the sliced (34-36 KJ mol^{-1}) and non-pretreated (43-129 KJ mol^{-1}) seeds.

4.2. Oil extraction from jatropha seeds and utilization of seed residues

Oil extraction from different jatropha seed collections from Ethiopia was performed using Soxhlet extractor, and the heat contents of the selected de-oiled seed residues were also determined and presented in **Paper IV.** In this study, firstly, the most efficient organic solvent in terms of the percentage of oil extracted was determined. Then, in the second-round oil extraction, the previously selected solvent and cotton were used to extract the oils from all the thirteen jatropha seed collections to determine the seed collection that gave the largest amount of oil (%). In the third-round extraction, extraction thimble was used to extract the oil from jatropha seed collections from southern Ethiopia as presented below.

4.2.1. Extraction of oil using different solvents

To select the most efficient solvent in terms of the amount of oil (%) that could be extracted, Salmene$_3$ seed collection was extracted with different organic solvents (ethanol, hexane, diethyl ether and heptane) using cotton as a filter by applying five cycles of washes. The percentage of oil extracted from Salmene$_3$ using different organic solvents is shown in **Table 2** of **Paper IV**. Among the four solvents, hexane was found to extract the largest amount of oil (41.24%) from the seeds. This is in line with the reports in the comprehensive reviews on oil extraction techniques and biodiesel production technologies by Atabani, *et al.* [27] and Bhuiya, *et al.* [32] in which they indicated that oil extraction using n-hexane method results in the highest oil yield, and this made it the most commonly used solvent. Based on the result of the current experiment, hexane was selected as the best solvent in terms of the amount of oil (%) extracted and thus, it was used to determine the oil contents of all jatropha seed collections used in this study. However, using ethanol as solvent is more preferable in terms of environmental health and being renewable [107].

4.2.2. Extraction of oil from different seed collections

In the second-round oil extraction, the previously selected solvent (hexane) and cotton were used to extract the oil from all the thirteen jatropha seed collections. Table 4.5 shows the amounts of oil (%) extracted from jatropha seed collections from north-central and southern Ethiopia, using hexane and cotton by applying five cycles of washes. As it is evident from Table 4.5, the amounts of oil (%) extracted from the seed collections from north-central Ethiopia varied from 26.05 to 41.51% and with an average of 34%. The percentages of oil obtained from the seed collections from southern Ethiopia were also found to range from 30.66 to 48.29%, and with an average of 40.43%. By using this extraction method, the largest oil yield (48.29%) was obtained from the Dana seed collection (a seed collection from southern Ethiopia) whereas the smallest oil yield (26.05 %) was found from Salmene$_1$ (a seed collection from north-central Ethiopia). The amounts of oil (%) extracted from different seed collections also differed, and this could be due to the climatic differences of the collection sites and the genetic variation of the seeds [187].

Table 4.5: Oil extracted (%) from jatropha seeds collections from north-central and southern Ethiopia, using hexane and cotton.

	Seed collections from north-central Ethiopia			Seed collections from southern Ethiopia	
No.	Seed collection	Oil extracted (%)	No.	Seed collection	Oil extracted (%)
1	Kurkura	31.59	1	Dimeka (dried fruit)	44.18
2	Bira	31.92	2	Dimeka (yellow fruit)	36.29
3	Salmene$_1$	26.05	3	Chali	43.48
4	Salmene$_2$	41.51	4	Kako	30.66
5	Salmene$_3$	41.24	5	Mulato	43.86
6	Shekla	34.75	6	Dana	48.29
7	Gerbi	30.94	7	Awwaaragamaa	36.31
	Average	**34.00**		**Average**	**40.43**

When the amounts of oil (%) extracted from the seed collections from north-central and southern Ethiopia were compared (Table 4.5), generally, the average oil extracted from the seed collections from southern Ethiopia (40.43%) was greater than that of the seed collections from north-central Ethiopia (34%). The maximum (48.29%) and minimum (30.66%) amounts of oils extracted from the seed collections of southern Ethiopia were also greater than the maximum (41.51%) and minimum (26.05 %) oil yields obtained from those of the north-central part of the country, respectively. The difference in the amounts of oil extracted from the seed collections from the southern and north-central parts of the country might be due to the differences of the growing conditions (altitude, climatic and soil conditions) and some genetic differences of the jatropha plants growing in the southern and north-central parts of the country [68, 187-189].

Based on the average oil extracted (%) from the seed collections of the two geographical regions (north-central and southern parts) of Ethiopia, the seed collections from the southern part of the country, which gave larger average oil (40.43%) (Table 4.5), were selected to be extracted with extraction thimble. These seed collections were selected to be extracted with an extraction thimble for further investigations.

4.2.3. Oil extraction from seed collections from southern Ethiopia

In the third-round oil extraction, six seed collections from southern Ethiopia were extracted using thimble to identify a seed collection that gave the largest oil yield in order to use the oil of the selected seed collection for biodiesel production using basic heterogenous catalyst. Figure 4.4 presents the mean oil extracted (%) from jatropha seeds collected from southern Ethiopia using hexane and thimble with single thickness. Among the mean oil yields of the six seed collections, the largest oil yield (45.79±0.54%) was obtained from Chali seed collection. The mean oil extracted from Chali seed collection was also significantly larger ($p \leq 0.05$) than those extracted from of Kako (37.14±0.46%), Awwaaragamaa (38.04±1.24), Mulato (41.61±0.21) and Dana (43.29±0.12) seed collections. However, it was not significantly different ($p \leq 0.05$) from the mean oil extracted from Dimeka seed collection obtained from dried fruit (43.91±0.71%). The mean oil extracted from Kako (37.14±0.46%) and Awwaaragamaa (38.04±1.24%) were significantly lower ($p \leq 0.05$) than those of the other seed collections presented in Figure 4.4. Moreover, the overall average oil extracted (%) from these six jatropha seed collection was calculated to be 41.63±0.54%.

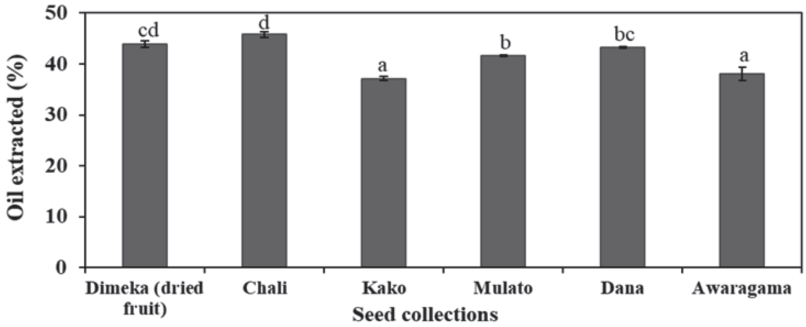

Figure 4.4: Mean oil extracted (%) from jatropha seed collections from southern part of Ethiopia using hexane and thimble by employing ten cycles of washes. Bars show means ± SE (standard errors) and different letters indicate significant differences among the mean oil extracted from the seed collections (Duncan's post hoc test at $p \leq 0.05$).

The overall average oil yield (41.63±0.54%) obtained in the present study was larger than the average oil yield (34.34%) that was found by Beemnet, *et al.* [68] by extracting different jatropha seed collections from the Southern Nation Nationalities and Peoples Regional State (from southern Ethiopia) with Soxhlet extractor using hexane and thimble. The higher average oil yield obtained in the current study compared to the previously reported value might be due to the difference in the pretreatment of the seeds for oil extraction, the thickness of thimbles used, and the particle sizes of the CS used for the experiments. In the present study, the whole jatropha seeds were dried before crushing at 80 °C until no more moisture loss occurred, and the filter used was thimble with single thickness (37x130 mm). However, in the oil extraction by Beemnet*, et al.* [68], neither a seed drying procedure nor the thickness of the extraction thimble used was reported.

4.2.4. Physico-chemical analysis of the oils

The values for acid value, %FFA, iodine value, saponification value and density of Chali oil and mixed oil samples, and values reported in literature for the same parameters for oils from different origin (countries) are presented in **Table 7** of **Paper IV**. The detailed discussion of the values obtained from the current experiment for the indicted parameters, in comparison to values from literature, can be seen from **Paper IV**.

As it can be seen from **Table 7** of **Paper IV**, the acid value and %FFA for Chali oil and mixed oil samples were found to be 1.32±0.14 and 2.12±0.15 mg KOH/g and 0.66±0.07 and 1.06±0.07%, respectively. Acid value indicates the amount of FFA found in oil, and it also provides information about how much FFA generation has taken place. The age of oil sample and oil exposure to atmospheric oxygen could increase acid value and %FFA of the oil [190, 191]. In the present study, the higher acid value and %FFA for the mixed oil compared to that of Chali oil could be due to the age of the seeds as mixed oil contained oils from thirteen different jatropha seed collections that were collected in 2016, 2017 and 2018 while Chali oil was extracted from the seed that was collected in 2018. Moreover, as larger %FFA of the oil results in saponification side reaction in alkaline catalyzed transesterification, Chali oil is more preferable for such biodiesel production method than the mixed oil [190, 192].

The Iodine value of Chali oil and mixed oil samples were found to be 116.02±3.50 and 109.24±0.05 g/100 g, respectively. Iodine value is a measure of the degree of unsaturation of the oil. The larger the iodine value of the oil, the greater the degree of its unsaturation [86, 193]. According to the EN 14214 specification [80], the maximum limit of iodine value for biodiesel is 120 g/100 g. Heating higher unsaturated fatty acid results in polymerization of glycerides and could lead to the formation of deposits and deterioration of the lubricating properties [78]. Higher unsaturated fatty acids have also a negative impact on oil stability [194]. Vegetable oil with an iodine value between 100 and 130 g/100 g belongs to the groups of semi-drying oil, and this group of oil absorbs atmospheric oxygen slowly, partially hardens and forms a soft film after prolonged exposure to air [86, 191]. Accordingly, the iodine values obtained for Chali oil and mixed oil samples suggested that both oils could be classified under semi-drying oil group. Furthermore, both oils can also be used for biodiesel production as their iodine value do not exceed the maximum values for biodiesel in the European EN 14214 specification [80].

Saponification value of oil is the number of mg of potassium hydroxide required to saponify 1 gram of the oil. It indicates the nature of fatty acids available in triacylglycerol. For instance, if the carbon chains of the fat hydrolyzed is longer, the quantity of the acid liberated per gram of sample will be reduced and hence, the saponification value of such oil sample will be less [190]. In the present study, the saponification value of Chali oil and mixed oil were found to be 191.40±3.11 and 205.77±3.81 mg KOH/g, respectively. These results show that the saponification value for the mixed oil was larger than that of Chali oil. Moreover, the saponification values of both oil samples were high and in the range of the values for jatropha oils from different origin [194-196]. According to Rania *et al.* [197], jatropha oil is usually associated with high saponification value due to the fact that the oil contains normal triglycerides [78]. From the present experiment, it was also found that the densities of Chali oil (0.906±0.001 g/ml) and that of the mixed oil (0.9104±0.001 g/ml) were about equal. These values were in line with the values of the densities of jatropha oil reported in literature [94, 191, 194].

4.2.5. Energy contents of de-oiled seed residues

The experimentally determined gross calorific values of the selected de-oiled jatropha seed residues were compared with each other and with the values reported in literature and discussed in detail in **Paper IV**. Accordingly, the gross calorific values obtained from the seed residues left after oil extraction are shown in **Table 8** of **Paper IV**. The upper calorific values (gross calorific values) of the analyzed samples were found to range from 18.57- 24.03 MJ kg^{-1}, and with an average of 19.64 MJ kg^{-1}. The gross calorific values of all the de-oiled seed residues analyzed in the present study, and their average, were in the range of the gross calorific values (14.3-25.4 MJ·kg^{-1}) determined by Gravalos *et al.* [198] for different agroforestry species and bio-based industry residues.

As it can be seen from **Table 8** of **Paper IV**, the largest gross calorific value (24.03 MJ kg^{-1}) was obtained from the residue of Kako WS that was dried, crushed and extracted by thicker thimble (40x150 mm) and ethanol, by employing five cycles of washes (KWDCS/TEth5). By applying the indicated extraction method, only 11.99% of oil (the smallest amount of oil for the overall study) was obtained from Kako seed collection. The smallest gross calorific value (18.57 MJ kg^{-1}) was recorded in the case of the residue of Salmene$_2$ WS that was stored at 4 °C, dried, crushed and extracted with hexane (S$_2$WS(4°C)DCS/Hex). The de-oiled seed residue that produced the second smallest gross calorific value (18.77 MJ kg^{-1}) was also the residue of Dana seed collection that was extracted by hexane and cotton by applying five cycles of washes (DnWSDCS/Hex). The amount of oil obtained from Dana seed collection by this extraction method was 48.29% (the largest amount of oil for the extractions with cotton). These results showed that the de-oiled seed residues, that were produced after the extraction of the smallest amount of oil (%), gave the largest gross calorific value and vice versa. This suggested that the residual oil in de-oiled seed residues could impact their gross calorific values. Elemental composition (particularly, carbon content), ash (non-combustible material) and moisture contents are the main factors that determine the gross calorific values of crop residues [198]. Accordingly, seeds and kernels have higher gross calorific values than the seed shell, husks, and de-oiled seed residues as the seeds and kernels have a higher unit mass and higher lipid content compared to the residues [198].

The average gross calorific value of jatropha seed residues found from the present experiment (19.64 MJ kg^{-1}) was in agreement with the value reported for the cake of jatropha seed by Kavalek *et al.* [199], which was 19.11 MJ kg^{-1}. As the cake of jatropha seed has a very low moisture content and its residual oil content does not tend to take in water, it is suitable for direct combustion [199]. Moreover, using de-oiled jatropha seeds residues, seed shell, fruit husk and other residues of the plant as a source of energy, could contribute to the profitability of investments on jatropha cultivation for biodiesel production [200].

4.3. Anion-exchange resin catalyzed biodiesel production

The study of an anion-exchange resin (Amberlyst A26 (OH)) catalyzed transesterification of jatropha oil with ethanol was conducted to determine the effects of three variables: reaction temperature, ethanol: oil molar ratio and catalyst amount, on jatropha oil conversion with ethanol (X_{JOE}) and fatty acid ethyl esters yield (Y_{FAEEs}) and presented in **Paper V.** The CCD_m involving three independent factors with two levels, but not including the non-linear stage, was employed to optimize the process as it is discussed in the subsections below.

4.3.1. Experiment design and the responses

As already mentioned, in study of the reaction catalyzed with Amberlyst A26 (OH), the influences of the three selected factors and their interaction on the conversion of jatropha oil to biodiesel and the biodiesel yield were investigated. The CCD_m that involved three reaction factors (reaction temperature, ethanol: oil molar ratio and catalyst amount) and two levels factorial (2^3) that consisted of only two stages (eight factorial or linear points and six center points). Accordingly, the experiments of the eight linear stage and the six center points were carried out randomly, and the obtained X_{JOE} and Y_{FAEEs} were recorded. The natural and coded factors and the resulting X_{JOE} and Y_{FAEEs} for the experiments are presented in **Table 2** of **Paper V**. As it could be seen from **Table 2** of **Paper V,** the largest experimental X_{JOE} (38.12%) and Y_{FAEEs} (36.81%) were found when the reaction was carried out at temperature of 55 ^{o}C and using ethanol: oil molar ratio of 35:1 and 15% catalyst.

4.3.2. Effects of reaction variables and optimization of the responses

4.3.2.1. Effects of the reaction variables

Using Amberlyst A26 (OH) as a catalyst, four reactions were carried out by varying the temperature, ethanol: oil molar ratio and catalyst amount at a time, and keeping the other reaction conditions constant (at the value of the center points), to investigate the effects of the respective factors on the responses. Figures 4.5a-c show the effects of temperature, ethanol: oil molar ratio and catalyst amount on the X_{JOE} and Y_{FAEEs} by keeping two of the three factors constant (at center point conditions) at a time. As it can be seen from Figure 4.5a, the raising of reaction temperature from 41.6 to 55 °C resulted in the increase of X_{JOE} and Y_{FAEEs} from 26.89% to 32.28 % and 25.81 to 31.08%, respectively. The raising of the ethanol: oil molar ratio from 8.18:1 to 35:1 found to increase the X_{JOE} and Y_{FAEEs} from 11.53 to 45.24% and 10.98 to 43.86%, respectively (Figure 4.5b). Furthermore, increasing the catalyst amount from 11.6 to 25% resulted in the increase of X_{JOE} and Y_{FAEEs} from 33.01 to 35.43% and 31.79 to 34.16%, respectively (Figure 4.5c). Thus, the results of these experiments showed that among the influences of the three investigated reaction factors, the effects of ethanol: oil molar ratio on both responses were found to be the largest.

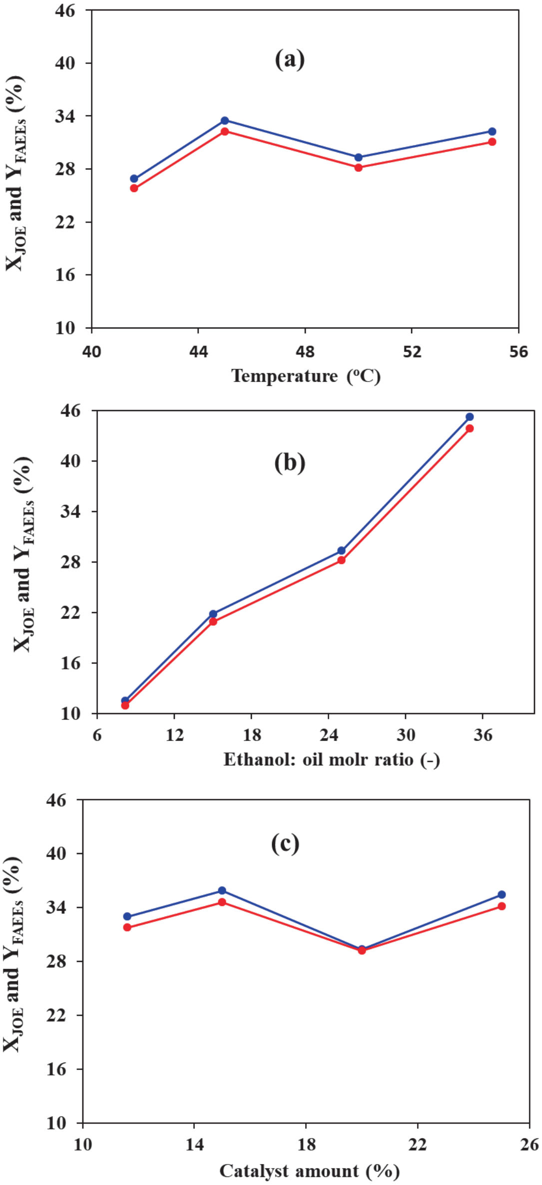

Figure 4.5: (a) Effect of reaction temperature (●) on X_{JOE} and (●) Y_{FAEEs} at ethanol: oil molar ratio of 25:1, catalyst amount: 20 wt%. (b) Effect of ethanol: oil molar ratio (●) on X_{JOE} and (●) Y_{FAEEs} at reaction temperature of 50°C and catalyst amount of 20 wt%. (c) Effect of catalyst amount (●) on X_{JOE} and (●) Y_{FAEEs} at reaction temperature of 50°C and ethanol: oil molar ratio of 25:1. The stirring intensity of 200 rpm and reaction time of 540 min were common for all the three cases [201].

4.3.3. Statistical analysis of the influences of the reaction variables

The statistical analyses were performed by considering the reaction temperature, ethanol: oil molar ratio and the catalyst amount. The effects of the main factors and their interactions on X_{JOE} and Y_{FAEEs} were determined using Statgraphics Centurion 17. The presence (significance) of curvatures ($p \leq 0.05$) in the response surface plots was also tested by calculating $SS_{pure\ quadratic}$, MS_E and the values of F statistics using Equations 3.23-3.25 [156, 171]. The results obtained from the statistical analyses of the experimental responses are presented in Table 4.6. As it can be seen from Table 4.6, among the three reaction variables, ethanol: oil molar ratio was the factor with the highest positive impact. The reaction temperature and the catalyst percent were found to have a very small positive impact on the transesterification process compared to that of ethanol: oil molar ratio. Moreover, the effects of all the binary interactions on the transesterification process were found to be small and negative.

Table 4.6: Results from the statistical analysis for the transesterification catalyzed with Amberlyst A26 (OH)

Parameters	Responses	
	Oil conversion	Biodiesel yield
Main effects and interactions	$\bar{y}$ =27.63	$\bar{y}$=26.55
	I_T = 2.32	I_T = 2.26
	I_R= 16.48	I_R= 16.06
	I_C= 0.95	I_C= 0.92
	I_{TR}= -0.24	I_{TR}= -0.22
	I_{TC}= -2.31	I_{TC}= -2.26
	I_{RC}= -0.092	T_{RC}= -0.08
Significance of curvature (at $p \leq 0.05$)		
Mean response (factorial points, $\bar{y}_F$)	27.053	26.00
Mean response (center points, $\bar{y}_C$)	28.415	27.29
Curvature	-1.36	-1.29
$SS_{pure\ quadratic}$	6.35	5.76
MS_E	4.56	4.35
F calculated	1.39	1.32
p value	0.291	0.301
Significance of curvature ($p \leq 0.05$)	Not significant	Not significant

Where: T is temperature, R is ethanol: oil molar ratio, C refers to catalyst percent, I_{TR} is interaction of temperature and molar ratio, I_{TC} is interaction of temperature and catalyst percent and I_{RC} refers to interaction of molar ratio and catalyst percent.

The results from Figure 4.5b and Table 4.6 showed that ethanol: oil molar ratio has the highest positive impact on the transesterification of jatropha oil. This is in line with literature reports for transesterification of different vegetable oils using ion-exchange resins as catalyst, in which an increase in alcohol to oil molar ratio highly influenced the oil conversion. For example, in the transesterification of soybean oil with ethanol, Oliveira, *et al.* [130] found an increase of oil conversion from 50% to 100% when the alcohol to oil molar ratio increased from 50:1 to 150:1. Moreover, in the study of the influence of methanol: oil molar ratio on the conversion of babaçu coconut oil by using Amberlyst 15 wet as catalyst, Reis *et al.*[155] found the oil conversion of around 70% by using an alcohol to oil molar ratio of 300:1, which is very high. According to Balat and Balat [202], the commonly accepted alcohol: oil molar ratios for transesterification reactions are 6:1-30:1. From the industrial perspective, higher amount of alcohol has several disadvantages such as requirement of bigger sized reaction equipment and larger investment cost, consumption of more energy for heating the reactors and longer time for separation of the alcohol from the products [203].

In the present study, compared to the influence of ethanol: oil molar ratio, the impacts of the reaction temperature and catalyst amount on the oil conversion and biodiesel yield is very low (Figure 4.5a-c and Table 4.6). According to Yatish *et al.* [204], generally, temperature has a positive impact on the transesterification of different vegetable oils although this depends on the type of catalyst and the experimental range studied.

The natural values of the experimental variables were used to predict the suitable mathematical regression models for the transesterification of jatropha oil using Amberlyst A26 (OH) as catalyst. The curvature for both responses are not significant ($p \leq 0.05$) as it can be seen from Table 4.6, and thus, the first order mathematical model (linear model) was found to be more suitable to be used for the optimization of the transesterification process [156, 171]. Accordingly, the linear regression models that express the X_{JOE} and Y_{FAEEs} under the current experimental ranges were presented in Equation 4.1 and 4.2, respectively.

$$X_{JOE} = -56.20 + 1.21T + 0.96R + 2.42C - 0.0024TR - 0.046TC - 0.00092RC \quad (4.1)$$

$$Y_{FAEE} = -55.14 + 1.18T + 0.93R + 2.37C - 0.0022TR - 0.045TC - 0.00085RC \quad (4.2)$$

Based on the regression models, three-dimensional (3D) response surface plots were produced to illustrate the effects of binary interactions of the reaction temperature, ethanol: oil molar ratio and catalyst percent (Figure 4.6-4.8). From the binary interactions of the reaction factors (I_{TC}, I_{TR} and I_{RC}), the effect of the interactions of temperature and catalyst percent on the responses was relatively larger and negative while that of the interaction of ethanol: oil molar ratio with catalyst amount was the smallest (Table 4.6). As previously indicated, generally, the effects of the binary interactions of the factors on the X_{JOE} and Y_{FAEEs} were low. The negative impact of the interaction of the temperature and catalyst amount on the responses might be due mass-transfer limitation at higher concentration of the catalyst (Table 4.6 and Fig. 4.8 a and b).

In the interaction of temperature and ethanol: oil molar ratio (at catalyst amount of 20%) and those of the catalyst percent and ethanol: oil molar ratio (at constant temperature, 50 ^{o}C), the impacts of the interacted factors on both responses were dominated by the alcohol to oil molar ratio (Figure 4.6a and b and Figure 4.7a and b). As the alcohol molar ratio increased from its minimum (15:1) to the experimental maximum (35:1), the X_{JOE} and Y_{FAEEs} increased linearly whereas the effects of the temperature and catalyst amount, respectively, were relatively lower. When ethanol: oil molar ratio raised to 35:1, both responses were predicted to reach above 33% even at the minimum temperature (45 ^{o}C) and catalyst amount (15%), respectively. Moreover, the linearity and continuous increasing of both X_{JOE} and Y_{FAEEs} with the raising of the alcohol molar ratio up to the maximum value of the experiment suggested that further increasing of ethanol: oil molar ratio above the experimental maximum could result in higher X_{JOE} and Y_{FAEEs} compared to those obtained in the current experiments.

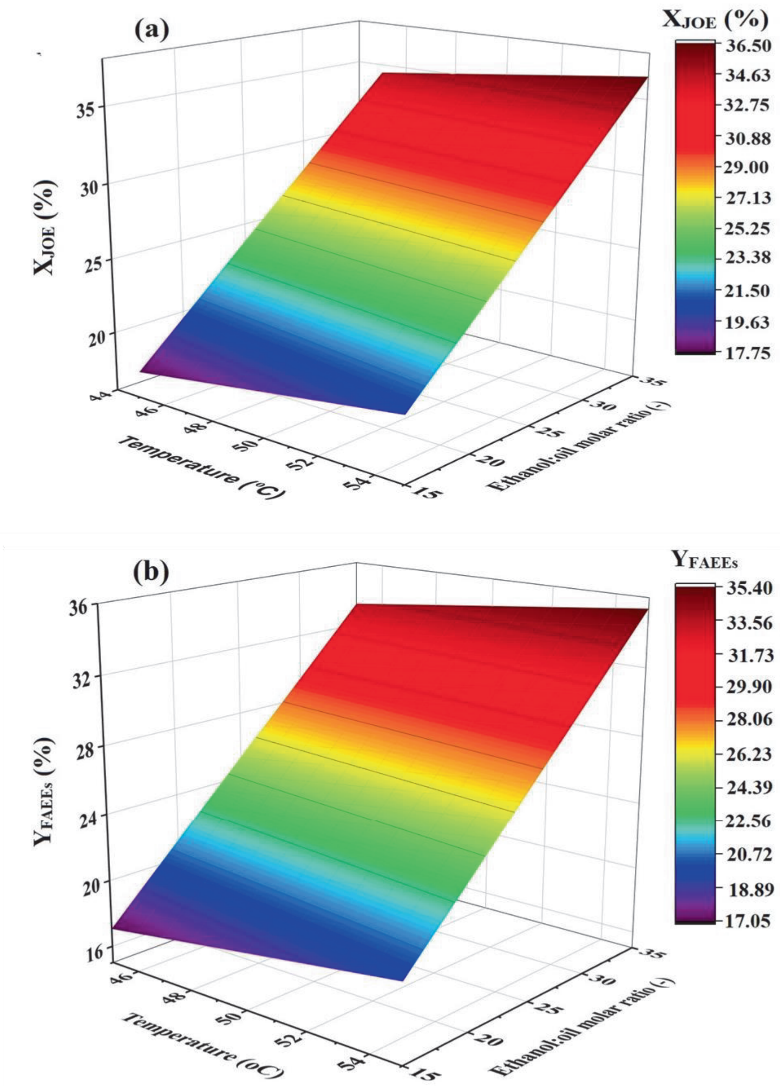

Figure 4.6: Response surface 3D plot indicating the influence of temperature and ethanol: oil molar ratio on (a) the X_{JOE} and (b) Y_{FAEEs}. Catalyst amount =20% (temperature and ethanol: oil molar ratio refer to the actual values) [201].

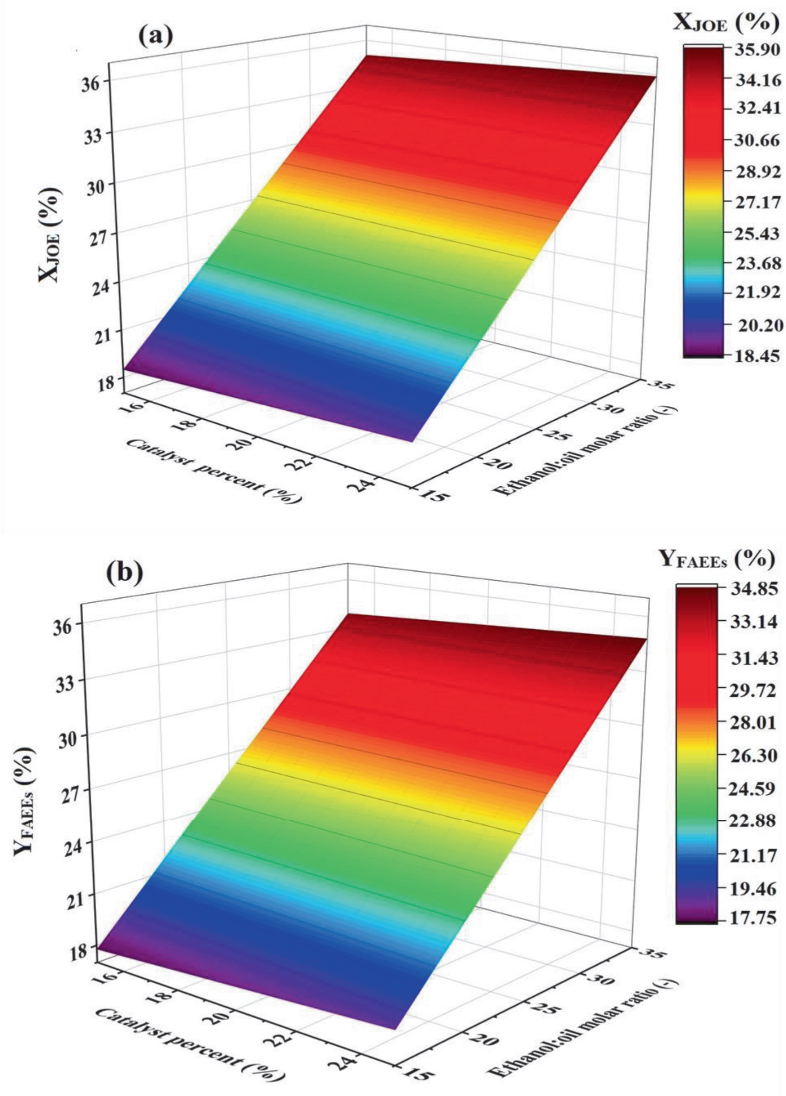

Figure 4.7: Response surface 3D plot indicating the of influence of catalyst percent and ethanol: oil molar ratio on (a) the X_{JOE} and (b) Y_{FAEEs}. Temperature=50 ºC (catalyst percent and ethanol: oil molar ratio refer to the actual values) [201].

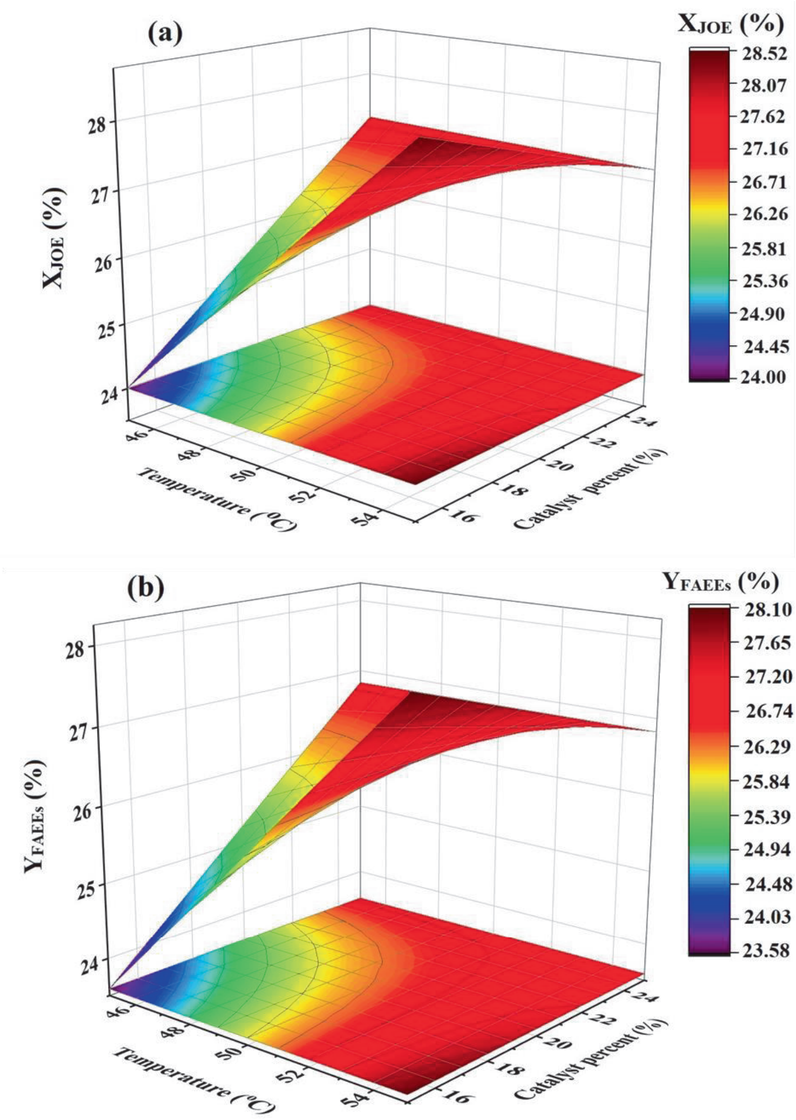

Figure 4.8: Response surface 3D plot indicating the influence of temperature and catalyst percent on the X_{JOE} and (b) Y_{FAEEs}. Ethanol: oil molar ratio= 25 (temperature and catalyst percent refer to the actual values) [201] .

For the binary interactions of reaction temperature and catalyst amount (Figure 4.8a and b), the maximum X_{JOE} and Y_{FAEEs} were predicted to be obtained when the reaction temperature raised to the experimental maximum (55 °C) but at the minimum catalyst amount (15%). Although the catalyst amount, generally, has a slight positive impact on the transesterification process of the oil

(Table 4.6), its interaction with temperature at the average ethanol: oil molar ratio (25:1) had a negative impact on both responses. As it can be seen from Figure 4.8a and b, when the catalyst amount raised from the minimum (15%) to the maximum (25%) range of the experiment, both the X_{JOE} and Y_{FAEEs} slowly decreased. The decreasing of the X_{JOE} and Y_{FAEEs} with the raising of the catalyst amount and temperature at the average alcohol molar ratio (25%) might be due to the lower ethanol: oil molar ratio than the optimum value predicted (35:1) (**Table 4** of **Paper V**) and the mass-transfer limitation that could be occurred as the catalyst amount increased.

Using the Statgraphics software, linear model equations and the response surface plots, the optimum X_{JOE} and Y_{FAEEs} of 37.63% and 36.31%, respectively, were predicted to be found at the optimum temperature of 55 °C, ethanol: oil molar ratio of 35:1 and catalyst amount of 15% (**Table 4** of **Paper V**). The experimentally obtained X_{JOE} and Y_{FAEEs} at the same reaction variables (reaction temperature of 55 °C, ethanol: oil molar ratio of 35:1 and catalyst amount of 15%) were 38.12% and 36.81%, respectively (**Table 2** of **Paper V**), and thus, the experimentally obtained values were in agreement with those predicted.

The maximum oil conversion experimentally obtained in the current study (38.12%) at the optimum conditions was larger compared to the conversion reported by Vicente *et al.* [205] for the transesterification of sunflower oil with methanol using ion-exchange resins (anionic Amberlyst A26 (OH) and A27 (OH) and cationic Amberlyst 15) which was less than 1% for each resin. However, upgrading of the current transesterification process is needed by employing the integrating reaction factors in order to enhance the oil conversion and biodiesel yield as well as reducing the alcohol to oil molar ratio.

4.4. Calcium oxide catalyzed butanolysis and optimization of the process

In addition to the transesterification of mixed oil with ethanol using recyclable ion exchange resin, butanolysis of Chali oil was performed as an alternative method of biodiesel production by employing butanol, a rarely used renewable alcohol, using glycerol enriched non-calcined CaO as catalyst and presented in **Paper VI**. In the current butanolysis reaction, unlike several reports in literature, the non-calcined commercial CaO was used as catalyst in order to minimize the cost that is needed to calcinate it. The results obtained from the butanolysis of Chali oil using glycerol enriched non-calcined commercial CaO are presented and discussed in the subsequent subsections

4.4.1. Experimental design and the responses

As previously mentioned, butanolysis of jatropha oil was performed using glycerol enriched non-calcined CaO as catalyst to investigate the influences of reaction temperature and butanol: oil molar ratio and their interaction on X_{JOB} and the Y_{FABEs}. The central composite design (CCD) with two factors and two levels factorial (2^2) that consisted of three stages (each with four experiments) was used to optimize the process. Accordingly, four experiments for the factorial, center points and non-linear stage, respectively, were carried out randomly and the obtained X_{JOB} and Y_{FABEs} were recorded.

The natural and coded factors and the resulting X_{JOB} and Y_{FABEs} for the experiments were presented in **Table 2** of **Paper VI**. As it is evident from **Table 2** of **Paper VI**, the maximum experimental X_{JOB} (96.39%) and Y_{FABEs} (93.131%) were obtained when the reaction run at the reaction temperature of 90 °C and butanol: oil molar ratio of 6. The lowest X_{JOB} (22.80%) and Y_{FAEEs} (9.46%) were obtained when the reaction was performed at the reaction temperature of 70 °C and butanol: oil molar ratio of 12. When the reactions were performed at 65.9 and 70 °C, the oil conversions and ester yields were found to be less than 50% in spite of the variation of alcohol to oil molar ratio. However, for the reactions that occurred at 80 °C and above, the oil conversion and biodiesel yields obtained were more than 80% regardless of the differences in the butanol: oil molar ratio. Hence, these results suggested that the effect of reaction temperature on both responses was higher than that of the alcohol: oil molar ratio. Moreover, for all experiments, the values of X_{JOB} were larger than that of the Y_{FAEEs}, and this might be due to some unreacted diglycerides and monoglycerides remaining in the reacting mixture at the end of the reaction.

4.4.2. Influences of the reaction variables on the responses

The statistical analysis was performed by considering the reaction temperature and alcohol to oil molar ratio to determine the effects of the main reaction factors and their interactions on the responses of the butanolysis process. The influences of the main factors and their interactions on X_{JOB} and Y_{FABEs} were determined using Statgraphics Centurion 17, and the presence (significance) of curvatures ($p \leq 0.05$) in the response surface plots were also tested [156, 171]. Table 4.7 shows the results obtained from the statistical analysis of the experimental responses. As is can be seen from Table 4.7, reaction temperature was found to be the factor with the highest positive impact whereas butanol: oil molar ratio had a medium negative effect on the butanolysis process. The impact of butanol: oil molar ratio on both responses was negative, however, the interaction of both factors was found to have a positive influence on the responses. The effects of the main factors and their binary interactions on the Y_{FABEs} were relatively larger than their impacts on the X_{JOB}. Moreover, based on ANOVA test, it was understood that the reaction temperature and its interaction with itself (T^2) had a significant impact ($p \leq 0.05$) on the current butanolysis process (Table 4.7).

Table 4.7: Results from the statistical analysis for the transesterification reaction catalyzed with calcium oxide.

Parameters and types of tests	Responses	
	X_{JOB} (%)	Y_{FABEs}(%)
Main effects and interactions	$\bar{y}$ =89.55	$\bar{y}$=82.71
	$I_T = 47.23$	$I_T = 56.96$
	$I_R = -6.39$	$I_R = -9.12$
	$I_{T^2} = -32.40$	$I_{T^2} = -37.23$
	$I_{TR} = 9.19$	$I_{TR} = 14.91$
	$I_{R^2} = -4.29$	$I_{R^2} = -0.92$
Test for significance of variables (ANOVA test, $p \leq 0.05$)		
Significant variables	T and T^2	T and T^2
R^2 and R^2 adjusted (%)		
R^2 (%)	88.37	93.54
R^2 adjusted (%)	78.68	88.16
Test for significance of curvature		
Mean response (factorial points, $\bar{y}_F$)	64.19	58.75
Mean response (center points, $\bar{y}_C$)	89.55	82.71
Curvature	-25.35	-23.96
$SS_{pure\ quadratic}$	1286.19	1148.22
MS_E	12.87	28.53
F calculated	99.89	40.24
p value	0.0021	0.00094
Significance of curvature ($p \leq 0.05$)	Significant	Significant

Where: T refers to temperature, R is butanol: oil molar ratio, and I_{TR} represents interaction of temperature and alcohol: oil molar ratio and R^2 refers to R-squared.

The natural values of the experimental factors were used to predict the suitable regression models to describe the butanolysis of jatropha oil using glycerol enriched CaO as catalyst. From the statistical analysis, it was found that curvature is significant ($p \leq 0.05$) for both X_{JOB} and Y_{FAEEs} (Table 4.7). Thus, the second order mathematical model (quadratic model) was found to be suitable to be used for the optimization of the butanolysis process [156, 171]. Hence, quadratic regression models for X_{JOB} and Y_{FABEs} under the present experimental ranges are expressed in equations 4.3 and 4.4, respectively.

$$X_{JOB} = -1035.61 + 26.90T - 9.03R - 0.16T^2 + 0.15TR - 0.23R^2 \quad (4.3)$$

$$Y_{FABE} = -1148.06 + 30.39T - 20.48R - 0.18T^2 + 0.24TR - 0.051R^2 \quad (4.4)$$

To show the effects of the binary interaction of the reaction temperature and butanol: oil molar ratio on the X_{JOB} and Y_{FABEs}, the three-dimensional (3D) response surface plots were produced (Figure 4.9a and b) based on the regression models expressed above. As it is depicted in Table 4.7, the effects of the binary interactions of temperature and butanol: oil molar ratio (I_{TR}) on both responses were found to be positive and lower than that of the main factors.

The response surface plot for the effects of the interaction of reaction temperature and butanol: oil molar ratio on the X_{JOB} and Y_{FABEs} are shown in Figure 4.9a and b, respectively. As it can be seen from Figure 4.9a and b, generally, raising in the reaction temperature increased both the X_{JOB} and Y_{FABEs} until the optimum values (the temperature at which the maximum responses obtained) would be reached regardless of the amount of butanol: molar ratio. However, at the lower temperature, the increase of butanol: oil molar ratio highly reduced both the X_{JOB} and Y_{FABEs}. As the reaction temperature raised from its experimental minimum (65.9 °C) to around the optimum values for both X_{JOB} and Y_{FABEs} (**Table 4** of **Paper VI**), the negative impacts of butanol: oil molar ratio on both responses rapidly decreased, and then, started to positively contribute to maximize the responses as the optimum amount of butanol: oil molar ratio would be approached.

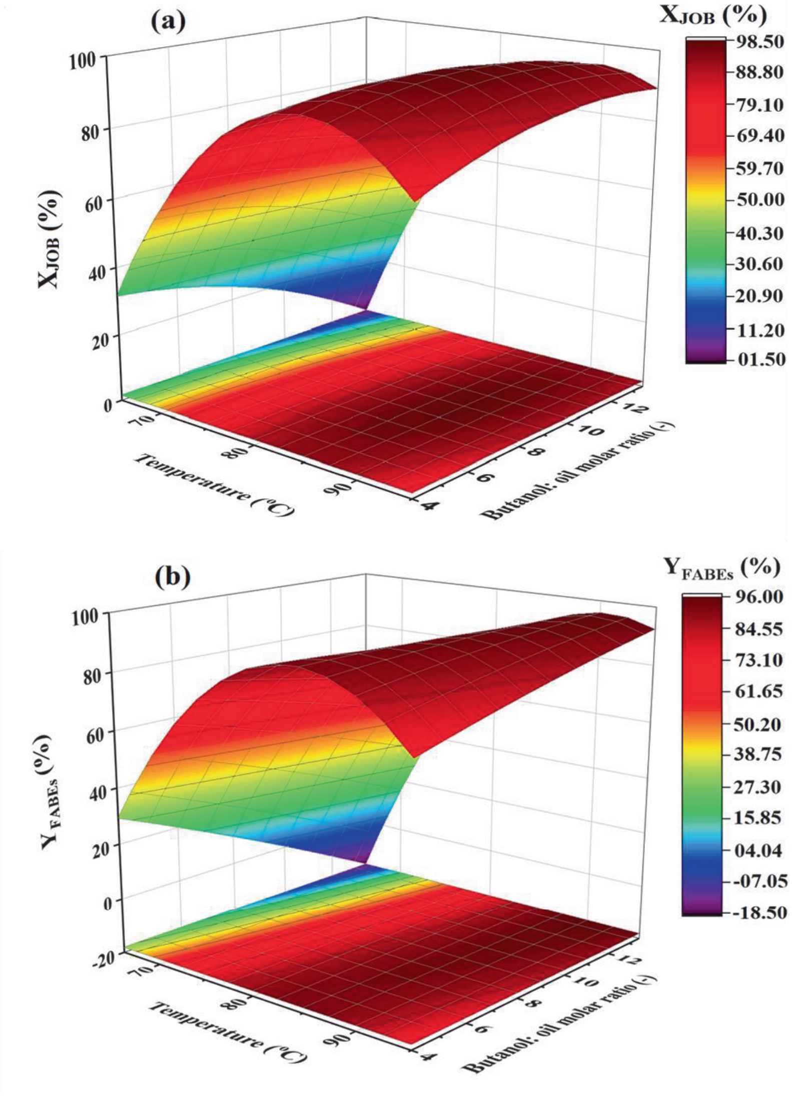

Figure 4.9: Response surface 3D plot indicating the influence of temperature and butanol: oil molar ratio on (a) the X_{JOB} and (b) Y_{FABEs}. The catalyst used was 15% (wt%) of oil while the amount of glycerol was 15% (wt %) of the catalyst (temperature and butanol: oil molar ratio refer to the actual values).

By using the quadratic model equations produced and the response surface plots, the maximum X_{JOB} of 98.16% was predicted to be obtained at the optimum temperature and butanol: oil molar ratio of 87.35 °C and 9.13:1, respectively. The maximum Y_{FABEs} of 95.79 % was also estimated to be found at the optimum temperature of 90.48 °C and butanol: oil molar ratio of 13.24:1 (**Table 4** of **Paper VI**). Moreover, after the prediction of the optimum conditions, duplicated experiments were carried out at the optimum conditions estimated for Y_{FABEs} (at temperature of 90.48 °C and butanol: oil molar ratio of 13.24:1) to compare the average of experimental result with the predicted optimum Y_{FABEs}. The optimum conditions predicted for Y_{FABEs} were selected to perform the experiments as the R^2 and R^2-adjusted for Y_{FABEs} were larger than those of X_{JOB} (Table 4.7). Accordingly, the average experimental Y_{FABEs} of 95.64% was obtained, and this is in excellent agreement with the predicted optimum Y_{FABEs} (95.79 %).

5. Conclusion

The present study attempted to identify the most appropriate oil crops for biodiesel production and a suitable oil extraction method based on the previous works, extraction of oils from the selected oil crop and production of biodiesel from the oil using renewable alcohols and reusable heterogenous catalysts. Accordingly, the results presented in the thesis include the following interrelated works: i) determining an appropriate oil crop for biodiesel production and suitable method of oil extraction from the seeds, ii) identification of suitable pretreatments of the oilseeds for oil extraction, iii) selection of the seed collection that produced the highest percentage of oil, and iv) production of biodiesel from the extracted oils through transesterification using renewable alcohols and recyclable heterogenous catalysts and optimization of the process. The findings obtained from these stepwise works were presented in six papers.

Paper I discussed different potential biodiesel feedstocks which include edible and non-edible oils, animal fats, waste oils and algal biomass. For the satisfactory replacement of fossil fuel with biodiesel, the biodiesel feedstocks should be easily available, environmentally acceptable and having relatively a low cost. However, as nowadays the major sources of biodiesel are edible oils such as rapeseed, sunflower, palm and soybean oils, this resulted in food versus fuel debates, the rising in the price of oil and some environmental problems. To overcome these problems, researches identified different relatively cheaper feedstocks such as non-edible oils, waste animal fats and waste oils which would not compete with human consumption. Based on the information from several literature and by comparing the advantages and disadvantages of using various biodiesel resources, oil of non-edible crops in general and that of jatropha in particular, was identified as one of the most suitable feedstocks for biodiesel production. This paper also investigated the merits and demerits of using the three major conventional oil extraction methods, namely mechanical, chemical or solvent and enzymatic methods. From these oil extraction methods, the chemical oil extraction method, particularly, Soxhlet extraction using hexane as solvent was identified as the most widely used method due to its efficiency of oil extraction. The paper also discussed some newly developed oil extraction methods such as accelerated solvent extraction, supercritical fluid extraction and microwave-assisted extraction to overcome some limitations of the conventional oil extraction methods, however, these methods require higher cost compared to the conventional ones.

Biodiesel production from edible vegetable oils makes the process costly as the feedstock alone account up to 75% of the total price of the biodiesel. Thus, the production of biodiesel from low cost non-edible oil feedstock such as jatropha has considered as a potential solution. It was reported that the oil contents of jatropha seeds and kernels ranged from 30–50% and 45– 60% (wt%), respectively. As moisture content of a seed is one of the main factors that determine the quantity of its oil, due consideration should be given to it during seed handling, storage, milling and oil extraction. Accordingly, drying jatropha seed to an appropriate moisture content prior to oil extraction and/ or in situ biodiesel production may be needed as the moisture in the seed can reduce the yield and quality of the oil. In **Paper II**, the effects of five different drying temperatures (40, 50, 60, 70 and 80 ^{o}C) on the degree of moisture evaporation and the physical appearances of the non-pretreated (whole seeds) and pretreated (crushed seeds) of Salmene$_3$ seed collection was systematically studied. From this study, it was concluded that drying the whole seeds of jatropha at 80 ^{o}C for 2880 minutes could provide the dried seeds with suitable moisture content for oil extraction and /or in situ biodiesel production. Because, the largest weight loss (6.47%) and the smallest seed residual moisture content (0.34%) were obtained when the whole seeds dried at 80 ^{o}C. Moreover, the drying temperatures did not cause any significant damage to the surface of both the whole and crushed seed samples. In addition to the measurement of moisture loss from the drying seeds, mathematical modeling of the drying process of the seeds could help to predict the behavior of moisture removal from the seeds, reduce the time and costs of seed drying, and helps in the invention of appropriate drying equipment. Thus, mathematical modelling of the drying kinetics of the whole and crushed dried jatropha seeds was performed and presented in **Paper III.** The moisture loss data from the seeds was systematically recorded, converted to moisture ratio, and fitted to four semi-theoretical drying mathematical models: Lewis, Henderson and Pabis, Page and Avhad and Marchetti models. From the current simulation, it was concluded that Avhad and Marchetti model with R^2 ranged from 0.9914 to 0.9969 and 0.9908 to 0.9917 for the whole seeds and crushed seeds, respectively, best fitted to the drying kinetics of the seeds. This model showed superior fit to the experimental data at the drying temperature of 40 ^{o}C with R^2 of 0.9969 for the whole seed, and at 60 ^{o}C in case of crushed seeds for which the R^2 value was 0.9917.

One of the important steps in biodiesel production from plant seeds is oil extraction. From the three most commonly employed conventional oil extraction methods (mechanical, solvent and enzymatic extraction methods), the most commonly used at commercial level are solvent extraction and mechanical pressing. However, oil extraction using n-hexane as solvent results in the largest oil yield compared to mechanical and enzymatic methods although using hexane has some negative environment impacts. In **Paper IV**, oil extraction from thirteen different jatropha seed collections from Ethiopia was carried out with Soxhlet extractor using hexane as solvent and cotton or thimble as filter to determine the seed collection that gave the largest percentage of oil. This study also determined the energy contents of some selected de-oiled seed residues. The study concluded that in the extraction with cotton and thimble, the largest amount of oils was obtained from Dana seed (48.29%) and Chali seed (45.79±0.54%) collections, respectively. Oil of Chali seed collection (Chali oil) was found to be more suitable for alkaline catalyzed biodiesel production than the mixed oil (mixture of oil of all seed collections) as the %FFA of the former oil (0.66±0.07%) is lower than that of the latter one (1.06±0.07%). Moreover, since the iodine values of Chali oil (116.02±3.50 g/100 g) and mixed oil (109.24±0.05 g/100 g) did not exceed the maximum standard for biodiesel according to the European EN 14214 specification, both oils could be used for biodiesel production. The de-oiled jatropha seed residues left after oil extraction can be used as the source of heat because the gross calorific values of the residues were found to range from 18.57- 24.03 MJ kg^{-1}, and with an average value of 19.64 MJ kg^{-1}.

Ion exchange resins are suitable catalysts for etherification, esterification and transesterification reactions. They can be prepared with different particle sizes, porosity degrees, and with a wide variety of functional groups, and they can also be easily separated from the biodiesel as they have larger sizes. Amberlyst A26 (OH), anionic ion-exchange resin, can carry out both esterification and transesterification reactions consecutively. Thus, it can minimize the saponification side reactions in cases of biodiesel production from oils containing free fatty acids. In **Paper V**, Amberlyst A26 (OH) catalyzed transesterification of mixed jatropha oil (mixture of oils extracted from thirteen jatropha seed collections) with ethanol was carried out to determine the effects of reaction temperature, ethanol: oil molar ratio and catalyst amount on oil conversion and ester (biodiesel) yield. This study concluded that from the main factors and their interactions, ethanol: oil molar ratio highly affected the oil conversion and biodiesel yield. As curvature is not significant ($p \leq 0.05$), linear regression model was found to be more suitable to optimize the responses. Moreover, it was concluded that the reaction temperature of 55 ^{o}C, ethanol: oil molar ratio of 35:1, and catalyst amount of 15% were the optimum reaction conditions as the maximum oil conversion (38.12%) and ester yield (36.81%) were experimentally obtained at these predicted optimum conditions. Applying larger amount of catalyst reduced both responses, particularly, when the variable interacted with the reaction temperature.

In **Paper VI**, butanolysis of oil of Chali seed collection was performed using glycerol enriched non-calcined CaO as catalyst to investigate the effects of reaction temperature and butanol: oil ratio on oil conversion and the yield of fatty acid butyl ester. From the results of this study, it was suggested that reaction temperature caused a significant positive effect ($p \leq 0.05$) on the butanolysis process. Raising the reaction temperature from the experimental minimum to the optimum value resulted in the increasing of both oil conversion and ester yield regardless of the alcohol molar ratios whereas increasing of butanol: oil molar ratio had a negative impact on both responses, particularly at the lower temperatures. Moreover, in this study, the maximum X_{JOB} of 98.16% was predicted to be obtained at the optimum temperature of 87.35 ºC and butanol: oil molar ratio of 9.13:1. The maximum Y_{FABEs} of 95.79 % was also estimated to be found at the optimum temperature of 90.48 ºC and butanol: oil molar ratio of 13.24:1. Furthermore, the Y_{FABE} of 95.64% was experimentally obtained at the indicated optimum conditions predicted for Y_{FABEs}. Based on the results obtained for the experimental ranges used in this study, it was suggested that glycerol enriched non-calcined commercial calcium oxide can be used as good alternative catalyst for biodiesel production using butanol. More future studies are also suggested for upscaling the reaction process of the current experiments by using more integrated reaction factors.

6. Future prospective

The two main focuses of the present thesis were to identify jatropha seed collections of Ethiopia that provide better oil yield, and to search for reusable and relatively low cost heterogenous catalysts that resulted in satisfactory and/ or better jatropha oil conversion and biodiesel yield using renewable alcohols. Accordingly, the study attempted to identify two jatropha seed collections, Chali and Dana seed collections, that could provide the largest oil yield with the extraction methods described in this thesis. However, the reasons for such larger differences of the oil contents of different jatropha seed collections are not addressed by the current study. Amberlyst A26 (OH), an anion ion exchange resin that has been very rarely used as catalyst for the transesterification of vegetable oils, and the glycerol enriched non-calcined CaO were also used as catalyst for biodiesel production using ethanol and butanol, respectively. In the reaction catalyzed with Amberlyst A26 (OH), lower oil conversion and biodiesel yield were obtained within the range of the reaction conditions used, thus, this reaction needs upscaling by integrating several reaction factors to improve both the oil conversion and biodiesel yield. The reusability of the resin was also not tested. In reaction catalyzed with glycerol enriched non-calcined CaO, larger oil conversion and biodiesel yield were obtained within relatively shorter reaction time, but the reusability of the catalyst was not tested. Moreover, the reaction kinetics of the reactions catalyzed with both catalysts have not been determined. Hence, the future research works that are suggested to cover the limitations observed in the present study are:

i) detailed study of the genetic and climatic factors that resulted in differences of the oil contents of jatropha seed collections,

ii) upscaling the catalytic activities of Amberlyst A26(OH) to catalyze transesterification of jatropha oil with higher FFA and optimization of the reaction using integrated reaction factors,

iii) studies on the reusability of Amberlyst A26(OH) and glycerol enriched non-calcined CaO as catalyst to reduce biodiesel production cost, and

iv) investigation of the reaction kinetics of the reactions catalyzed with Amberlyst A26 (OH) and glycerol enriched non-calcined CaO.

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8. Papers

Paper I: Keneni YG, Marchetti JM . Oil extraction from plant seeds for biodiesel production. *AIMS Energy*. 2017; 5: 316-340. https://doi.org/10.3934/energy.2017.2.316.

Paper II: Keneni YG, Marchetti JM. Temperature and pretreatment effects on the drying of different collections of *Jatropha curcas* L. seeds. *SN Applied Sciences*. 2019; 1:943 | https://doi.org/10.1007/s42452-019-0969-3.

Paper III: Keneni YG, Hvoslef-Eide T, Marchetti JM. Mathematical modelling of the drying kinetics of *Jatropha curcas* L. seeds. *Industrial Crops and Products*. 2019; 132:12-20. https://doi.org/10.1016/j.indcrop.2019.02.012.

Paper IV: Keneni YG, Bahiru LA, Marchetti JM. Effects of different extraction solvents on the amount of oil extracted from Jatropha seeds from Ethiopia and the potential of de-oiled seed residues as a heat provider. Submitted to *BioEnergy Research*.

Paper V: Keneni YG, Hvoslef-Eide T, Marchetti JM. Optimization of the production of biofuel from Jatropha oil using a recyclable anion-exchange resin. *Fuel*. 2020;278:118253. https://doi.org/10.1016/j.fuel.2020.118253.

Paper VI: Keneni YG, Marchetti JM. Butanolysis of Jatropha oil using glycerol enriched non-calcined calcium oxide: optimization of the process. Submitted to *Fuel*.

Paper I

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Review

Oil extraction from plant seeds for biodiesel production

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Abstract: Energy is basic for development and its demand increases due to rapid population growth, urbanization and improved living standards. Fossil fuels will continue to dominate other sources of energy although it is non-renewable and harm global climate. Problems associated with fossil fuels have driven the search for alternative energy sources of which biodiesel is one option. Biodiesel is renewable, non-toxic, environmental-friendly and an economically feasible options to tackle the depleting fossil fuels and its negative environmental impact. It can be produced from vegetable oils, animal fats, waste oils and algae. However, nowadays, the major feedstocks of biodiesel are edible oils and this has created food vs fuel debate. Therefore, the future prospect is to use non-edible oils, animal fats, waste oils and algae as feedstock for biodiesel. Selection of non-expensive feedstock and the extraction and preparation of oil for biodiesel production is a crucial step due to its relevance on the overall technology. There are three main conventional oil extraction methods: mechanical, chemical/solvent and enzymatic extraction methods. There are also some newly developed oil extraction methods that can be used separately or in combination with the conventional ones, to overcome some disadvantages of the conventional oil extraction methods. This review paper presents, compare and discusses different potential biofuel feedstocks, various oil extraction methods, advantages and disadvantages of different oil extraction methods, and propose future prospective for the improvement of oil extraction methods and sustainability of biodiesel production and utilization.

Keywords: biodiesel; biodiesel feedstock; edible oil; fatty acid; non-edible oil; oil extraction; renewable energy

Abbreviation List

AEOE	Aqueous enzymatic oil extraction
ASE	Accelerated solvent extraction

BP	British petroleum
FAME	Fatty acid methyl esters
FFA	Free fatty acid
IRAR	Infrared radiation assisted reactor
L.	Linnaeus
MAAEE	Microwave-assisted aqueous enzymatic extraction
MAE	Microwave-assisted extraction
PSE	Pressurized solvent extraction
SFE	Supercritical fluid extraction
TAG	Triacylglycerol
UAE	Ultrasound-assisted extraction

1. Introduction

Energy demand is expected to increase due to rapid population growth, expanding urbanization and better living standards [1]. Fossil fuels remain the dominant source of energy [2] though it is non-renewable and has negative impact on global climate [3]. According to BP's Energy Outlook to 2035 [2], world energy consumption is projected to increases by 34% between 2014 and 2035, and fossil fuels remain the dominant source of energy (accounting for almost 80%) powering the global economy in 2035 (down from 86% in 2014). The transport sector, which heavily depends on oil-derived liquid products such as gasoline and diesel, globally occupies the third place when total energy consumption and greenhouse gas (GHG) emissions are considered (after the industry and the building sectors). This consumption level is predicted to increase by 60% by 2030 [4].

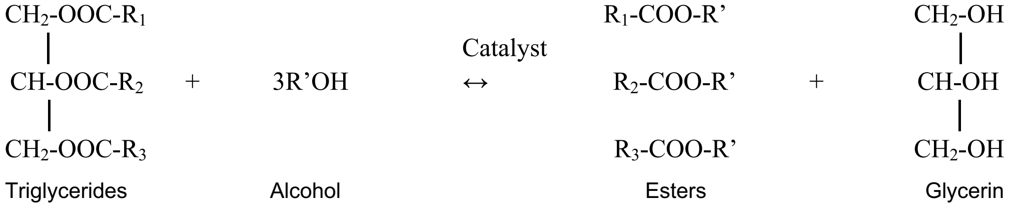
Rapid growth in both global energy demand and carbon dioxide emissions associated with the use of fossil fuels has driven the search for alternative energy sources which are renewable and have a lower environmental impact [5,6]. Thus, it has become apparent that biodiesel is destined to make a substantial contribution to the future energy demands of domestic and industrial economies [6]. Biodiesel is produced from vegetable oil or animal fat reacts in the presence of a catalyst (usually a base) with an alcohol (usually methanol) to give the corresponding alkyl esters (for methanol, fatty acid methyl esters) [7]. Biodiesel is non-toxic, biodegradable and a portable fuel produced from renewable sources [3,8] and it is one of the technically and economically feasible options to tackle the fast depletion of fossil fuels and environmental pollution [1]. The other benefit of biodiesel fuel is that it can be used in any mixture with petro diesel fuel, as it has very similar characteristics [3].

The potential feedstocks for biodiesel production are edible (first generation feedstocks) and non-edible vegetable oils (second generation feedstocks), wasted oils and animal fats [9] First-generation biofuels are directly related to a biomass that is generally edible, and are usually produced from edible oils, such as soybeans, palm oil, sunflower, safflower ,rapeseed, coconut and peanut [4,10]. Second-generation biofuels are fuels that are produced from a wide array of different feedstock, ranging from lignocellulosic feedstocks to municipal solid wastes. Third-generation biofuels are related to algae which have been considered as emerging non-edible oil sources of growing interest because of their high oil content and rapid biomass production [10,11,12] but could also to a certain extent be linked to utilization of CO_2 as feedstock [10]. However, the first generation biofuels seems to create some skepticism to scientists. There are concerns about environmental impacts and carbon balances, which sets limits in the increasing production of biofuels of first generation. The main disadvantage of first generation biofuels is the food-versus-fuel debate, one of the reasons for rising food prices is due to the increase in the production of these fuels [9,13,14]. Therefore, non-edible biodiesels feedstocks get great attention to overcome the problem that occurs due to continuous utilization of edible oils for biodiesel [13].

In the different literature, various biodiesel feedstocks: edible oils, non-edible oils, animal fats, waste oils and algal biomass and methods of biodiesel production from these feedstocks were well described and reviewed. However, the preparation of different feedstocks for oil extraction, oil extraction methods from different feedstocks, advantages and disadvantages of the extraction methods and ways to improve them are, to our knowledge, not yet well reviewed. Thus, the aim of this review is to identify the major biodiesel feedstocks, oil extraction and separation methods, the advantages and disadvantages of various oil extraction methods, particularly that of non-edible oils, and suggest how to optimize the appropriate method(s) to enhance the sustainability of biodiesel production and utilization.

2. Biodiesel and Its Feedstock

Biodiesel is defined as the mono-alkyl ester of long chain fatty acids derived from renewable lipid feedstock such as vegetable oils or animal fats [15]. Biodiesel is a non-toxic, biodegradable and renewable fuel that can be produced from a range of organic feedstock including fresh or waste vegetable oils, animal fats, and oilseed plants [16] (the reaction for biodiesel formation is shown in Figure 1).



$$\begin{array}{ccccccc} CH_2\text{-}OOC\text{-}R_1 & & & & R_1\text{-}COO\text{-}R' & & CH_2\text{-}OH \\ | & & & \text{Catalyst} & & & | \\ CH\text{-}OOC\text{-}R_2 & + & 3R'OH & \leftrightarrow & R_2\text{-}COO\text{-}R' & + & CH\text{-}OH \\ | & & & & & & | \\ CH_2\text{-}OOC\text{-}R_3 & & & & R_3\text{-}COO\text{-}R' & & CH_2\text{-}OH \\ \text{Triglycerides} & & \text{Alcohol} & & \text{Esters} & & \text{Glycerin} \end{array}$$

Figure 1. Transesterification reaction for biodiesel production [17,18].

The major components of plant oils and animal fats are triacylglycerol (TAGs); the esters of fatty acids and glycerol. The TAGs, also known as triglycerides, consists of different fatty acid composition which influences both physical and chemical properties of plant oils and animal fats [15,18,19]. There are two kinds of fatty acids: saturated fatty acids containing carbon-carbon single bond, and unsaturated fatty acids which include one or more carbon-carbon double bond. The major components of biodiesel are straight fatty acid chain and the common fatty acids are palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3). The other fatty acids which are also present in several plant oils include myristic acid (C14:0), palmitoleic acid (C16:1), arachidic acid (C20:0), and erucic acid (C22:1) [11,18,19]. According to Sajjadi et al. [17], physico-chemical properties of oils from different sources differ, and it is noteworthy that although some oils may be extracted from a unique root, their compositions are significantly dependent on the main parts from which the oil is extracted.

2.1. Different types of oils

Globally, there are more than 350 oil-bearing crops identified as potential sources for biodiesel production [13,17]. The availability of wide range of biodiesel feedstocks is one of the most significant factors that enables the sustainable production of biodiesel [20,21,22]. According to Avhad and Marchetti [18], satisfactory replacement of petroleum diesel with biodiesel depends on two basic requirements: first is its easy availability and environmentally acceptability, and the second is being economically reasonable. Availability of feedstock for producing biodiesel depends on the regional climate, geographical locations, local soil conditions and agricultural practices of any country [13].

From the literature, it has been found that feedstock alone represents about 75% of the overall biodiesel production cost [13,23,24] as presented in Figure 2. Therefore, minimizing the cost of biodiesel production has been the main agenda for biodiesel producers in order to be competitive with petroleum-derived diesel [25]. Hence, it is crucial to employ inexpensive feedstocks to replace expensive refined oils [4,13]. Using low-cost triglyceride sources such as waste cooking oil and animal fats is also important to minimizing the total cost as these wastes are three times cheaper than refined oils, and are abundantly available [25].

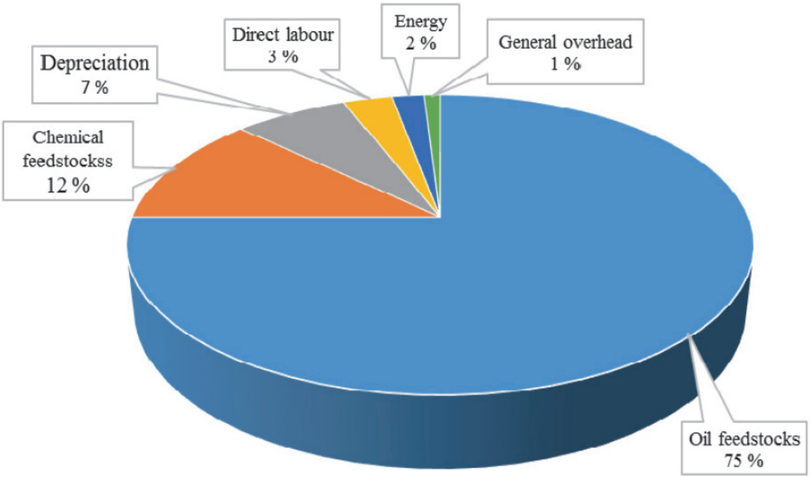


Figure 2. General cost breakdown for production of biodiesel [13,23,24].

Feedstocks of biodiesel can be divided into four main categories: edible vegetable oil, non-edible oils, waste or recycled oils, and animal fats [13,18,23,26,27,28]. Accordingly, some forms of plant oils, animal fats, and other feedstocks that are used for producing biodiesel are listed in Table 1.

Table 1. Main feedstocks of biodiesel [18,20,29–36].

Edible oils	**Non-edible oils**	**Animal fats**	**Other sources**
Barley	*Abutilon muticum*	Beef tallow	Cyanobacteria
Canola	*Aleurites moluccana*	Chicken fat	Bacteria
Coconut	Camelina (*Camelina Sativa*)	Fish oil	Cooking oil
Corn	Coffee ground (*Coffea arabica*)	Pork lard	Fungi
Groundnut	Cotton seed (*Gossypium hirsutum*)	Poultry fat	Latexes
Palm and palm kernel (*Elaeis* guineensis)	*Croton megalocarpus*	Waste salmon	Microalgae (Chlorellavulgaris)
Peanut	*Cynara cardunculus*		Miscanthus
Pumpkin seed	*Jatropha curcas*		Pomace oil
Rapeseed (*Brassica napus L.*)	Jojoba (*Simmondsia chinensis*)		Poplar
Rice bran oil (*Oryza sativum*)	Karanja or honge (*Pongamia pinnata*)		Soapstocks
Safflower(*Carthamus tinctorius*)	Mahua (*Madhuca indica*)		Switchgrass
Sesame (*Sesamum indicum L.*)	Moringa (*Moringa oleifera*)		Tall oil
Sorghum	Nagchampa (*Calophyllum inophyllum)*		Tarpenes
Soybeans (*Glycine max*)	Neem (*Azadirachta indica*)		
Sunflower (Helianthus annuus)	*Pachira glabra*		
Wheat	Passion seed (*Passiflora edulis*)		
	Pongamia (*Pongamia pinnata*)		
	Rubber seed tree (*Hevca brasiliensis)*		
	Terminalia belerica		
	Tobacco seed		

2.1.1. Edible plant oils

Edible oils resources such as soybeans, palm oil, sunflower, safflower, rapeseed, coconut and peanut are considered as the first generation biodiesel feedstocks because they were the first crops to be used for biodiesel production [13]. Edible oil contents of seeds and kernels of some plants are shown in Table 2. Currently, more than 95% of the world biodiesel is produced from edible oils such as rapeseed (84%), sunflower oil (13%), palm oil (1%), soybean oil and others (2%) [4,13]. Plantations of these feedstock plants have been also well established in many countries around the world such as Malaysia, USA and Germany [13]. However, continuous large-scale usage of edible plant oils for biodiesel production raises many concerns such as food versus fuel crisis and major environmental problems such as deforestation and destruction of vital soil resources, conversion of much available farm lands to oil bearing plants [13,14].

The prices of vegetable oil have also increased dramatically in the last few decades and this will affect the economic viability of biodiesel industry [13,14,51]. Furthermore, the use of such edible oils to produce biodiesel is not feasible in the long term due to the growing gap between demand and supply [13]. Thus, the current use of the food-grade plant oils as a feedstock for producing biodiesel are considered to be not worthy and stipulates search for relatively less expensive resources [13,18].

Table 2. Species name and oil content of edible and non-edible plant [6,11,12,13,30,37–50].

Type of oil	Common name	Species name	Oil content of seed/kernel (wt%)		Reference
			Seed	Kernel	
Edible	Coconut	*Cocos Nucifera L.*	63–65	63.1 (± 2.8)	[6,38]
	Corn	*Zea mays*	24.44	-	[39]
	Hemp seed	*Cannabis Sativa L.*	22–38	-	[40]
	Mustard seed	*Brassica nigra*	33	-	[41]
	Olive	*Olea europaea*	45–70	-	[37]
	Palm	*Elaeis guineensis*	30–60	-	[6]
	Peanut	*Arachis hypogea L.*	45–55	47–61	[6,37]
	Pumpkin seed	*Cucurbita maxima*	31.5	43.69 (± 3.92)	[42,43]
	Rapeseed	*Brassica napus*	38–46	-	[6]
	Rice bran	*Oryza sativa*	15–23	-	[37]
	Safflower seed	*Carthamus tinctorius*	35	-	[44]
	Sesame seed	*Sesamum indicum*	58	-	[45]
	Soybean	*Glycine max*	18–20	-	[46]
	Sunflower	*Helianthus annuus*	25–35	50	[37,47]
Non-edible	Castor	*Ricinus* communis *L.*	45–50	-	[30]
	Cottonseed	*Gossypium hirsutum L.*	18–25	31.42	[37,48]
	Desert date	*Balanites aegyptiaca*	45–50	36–47	[12]
	Jatropha	*Jatropha curcas L.*	20–60	40–60	[12,30,49]
	Jojoba	*Simmondisa chincnsis*	45–50	-	[37]
	Karanja	*Pongamia pinnata*	30–40	30–50	[30]
	Linseed	*Linum usitatissimum*	35–45	-	[30]
	Mahua	*Madhuca indica*	35–40	50	[30]
	Neem	*Azadirachta indica*	20–30	25–45	[30]
	Polanga	*Calophyllum inophyllum*	65	22	[12]
	Caster	*Ricinus communis*	45–50	-	[11]
	Rubber seed	*Hevea brasiliensis*	40–60	40–50	[12]
	Tobacco	*Nicotiana tabacum L.*	30–43	-	[37]
		Nicotiana tabacum	36–41	17	[11,12]
		Zanthoxylum bungeanum	24–28	25	[12]
	Tung	*Vernicia montana*	16–18	-	[37]
	Ethiopian mustard	*Brassica carinata*	42	2.2–10.8	[12]
	Sea mango	*Cerbera odollam*	54	6.4	[12]
	Croton oil plant	*Croton tiglium*	30–45	50–60	[50]

The average fatty acid composition of different edible vegetable oils are shown in Table 3. The dominant fatty acids of edible oils are oleic acid (C18:1), linoleic acid (C18:2), palmitic acid (C16:0) and staeric acid (C18:0). The fatty acid composition of edible oils from different plants seeds differ. For example, caprylic acid, which is the lightest compound is only available in wheat grain (11.4 wt%) and coconut oils (8.45 wt%) [17]. According to Sajjadi et al. [17], generally is assumed that the compositions of fatty acids compositional profiles do not change during the conversion of the feedstocks to fuel via transesterification and thus, greatly affect the quality of biodiesel to be produced.

Table 3. Comparison of the fatty acid composition of the selected edible oils.

Source	Fatty Acids Composition													Reference
	C14:0 Myristic acid	**C16:0 Palmitic acid**	**C16:1 Palmitoleic acid**	**C18:0 Stearic acid**	**C18:1 Oleic acid**	**C18:2 Linoleic acid**	**C18:3 Linolenic acid**	**C20:0 Arachidic acid**	**C22:0 Behenic acid**	**C20:1 Gadoleic acid**	**C22:1 Erucic acid**	**C24:0 Lignoceric acid**	**C8:0 Capryli acid**	
Waste coconut oil	0.50	21.40	0.20	3.00	27.50	47.40	-	-	-	-	-	-	8.45	[52]
Corn	-	-	11.67	1.85	25.16	60.60	0.48	0.24	-	-	-	-	-	[15]
Hempseed	-	6.0–8.5	-	2.5–3.0	12.0–15.0	52.0–56.0	-	0.5–0.8	-	-	-	-	-	[53]
Mustard seed	0.05	5.54	0.21	1.51	8.83	10.79	20.98	1.21	1.09	5.27	37.71	1.68	-	[41]
Olive	-	11.60	1.00	3.10	75.00	7.80	0.60	0.30	0.10	-	-	0.50	-	[54]
Palm	0.70	36.70	0.10	6.60	46.10	8.60	0.30	0.40	0.10	0.20	-	0.10	-	[54]
Peanut	0.20	8.0	-	1.80	53.30	28.40	0.30	0.90	3.00	2.40	-	1.80	-	[54]
Pumpkin seed	-	13.80	-	11.20	29.50	45.5	-	-	-	-	-	-	-	[42]
Rapeseed	-	-	3.49	0.85	64.40	22.30	8.23	-	-	-	-	-	-	[15]
Rice bran	-	22.00	-	3.00	38.00	35.00	-	-	-	-	-	-	-	[55]
Safflower seed	-	11.07 (± 0.10)	-	4.37 (± 0.10)	12.76 (± 0.22)	69.65 (± 0.24)	0.49 (± 1.15)	0.78 (± 0.05)	0.59 (± 0.09)	-	-	0.29 (± 0.13)		[56]
Sesame	-	9.80 (± 0.21)	-	6.3 (± 0.15)	41.82 (± 0.91)	40.50 (± 1.01)	0.32 (± 0.01)	0.67 (± 0.03)	-	-	-	-	-	[57]
Sunflower	-	16.29 (± 0.54)	-	6.66	22.70 (± 0.07)	44.13 (± 0.60)	8.97 (± 0.52)	0.62 (± 70.11)	0.63 (± 70.02)	-	-	-	-	[55]
Soybean	-	6.14	0.09	4.11	34.30	51.17	2.23	0.17	0.41	-	0.53	-	-	[58]
Wheat grain	0.13	17.71	0.2	0.78	16.5	56	2.9	-	-	-	-	-	11.4	[17]

One of the possible solutions to reduce the utilization of the edible oil for biodiesel production is by exploiting non-edible oils. They got great attention as the plants from which these oils obtained are easily available in many parts of the world [6,13,59]. These plants can grow on wastelands that are not suitable for food crops, eliminate competition for food, reduce deforestation rate, and their oils are very economical compared to edible oils [13].

2.1.2. Non-edible plant oils

Non-edible plant oils which are known as the second generation feedstocks can be considered as promising substitutions for traditional edible food crops for the production of biodiesel [6]. Recently, these oils have gained enormous attention as a new generation feedstock because of their high oil content, easy availability, and having the advantage that it could be grown on lands which are not suitable for agriculture [6,13]. Non-edible oil bearing plants could also be grown with less intensive attention; thus, reducing the cost of cultivation [6,12,13,18]. Therefore, production of biodiesel from non-edible oils is an effective way to overcome the associated problems with edible oils [6]. Some of the main and most investigated non-edible plant oils for biodiesel production include jatropha seed oil [32,36], karanja oil [33], jojoba oil [34], linseed oil [35], cottonseed oil [60], amongst others (Table 1).

During selection of any feedstock as a biodiesel source, the amount of oil that can be obtained from the seeds or kernel is an important parameter. Estimated oil contents of seed and kernel of some non-edible vegetable oil were shown in Table 2 [6,12]. Moreover, fatty acid composition is an important characteristic of biodiesel feedstock as it determines the efficiency of process to produce biodiesel. It has been observed that the percentage and type of fatty acid compositions depends mainly on the plant species as well as their growth conditions [6].

The fatty acid composition and distribution of non-edible oils are generally aliphatic compounds with a carboxyl group at the end of a straight chain [4]. Ong et al. [19] reported that the presence of fatty acid compositions has interfered fuel properties and quality of biodiesel. It has also been found that the biodiesel with a high level of methyl oleate (mono unsaturated fatty acid) might have excellent characteristics in ignition quality, fuel stability and flow properties at low temperature [19,61].

Generally, non-edible oil is composed of a high number of double carbon chain (polyunsaturated acid) which indicate that the these oil group has a greater degree of unsaturated fatty acid than saturated carbon chain [19,62]. Moreover, it was reported that cetane number, heat of combustion, melting point, and viscosity of neat fatty compounds increase with increasing chain length and decrease with increasing unsaturation [62,63] of the fatty acid methyl esters (FAME) molecule. Therefore, structural fatty acid composition will affect the physico-chemical properties of biodiesel such as cetane number, cold flow properties, heat of combustion and viscosity [6,61,62]. Fatty acid compositions of various non-edible oils that were found to be suitable for production of biodiesel are shown in Table 4.

Table 4. Comparison of the fatty acid composition of the selected non-edible plant oils [4,17,30,32,34,37,64–70].

Feed stocks	Fatty Acids												Reference
	C14:0 Myristic acid	C16:0 Palmitic acid	C16:1 Palmitoleic acid	C18:0 Stearic acid	C18:1 Oleic acid	C18:2 Linoleic acid	18:3 Linolenic acid	C20:0 Arachidic acid	C22:0 Behenic acid	C20:1 Gondoic acid	C22:1 Erucic acid	C18:1 Riconoleic acid	
Caster seed	-	1.00	-	-	3.00	5.00	1.00	-	-	-	-	89.00	[64]
Cottonseed	1.00	25.80	0.60	2.5	16.4 (± 0.8)	51.50	0.20	0.20	0.20	-	-	-	[65]
Desertdate kernel	-	15.40 (± 0.26)	-	19.01 (± 0.29)	25.74 (± 0.35)	39.85 (± 0.48)	-	-	-	-	-	-	[66]
Jatropha	-	15.20	0.70	6.80	44.60	32.20	-	0.40	-	-	-	-	[32,34]
Jojoba	-	1.20	-	-	10.70	-	-	9.10	-	59.50	12.30	-	[67]
Karanja	-	11.65	-	2.4–8.9	51.59	16.46	2.65	-	-	-	-	-	[68]
Linseed	-	5.10	0.30	2.5	18.90	18.10	55.10	-	-	-	-	-	[69]
Mahua	-	17.80	-	14.00	46.30	17.90	-	-	-	1.7	-	-	[70]
Moringa	-	7.60	1.40	5.5	66.60	8.10	0.20	5.80	-	-	-	-	[71]
Neem	0.2–0.26	14.9	0.1	20.6	43.9	17.9	0.4	1.6	0.3	-	-	-	[72]
Polonga	-	12.01	-	12.95	34.09	38.26	0.30			-	-	-	[68]
Rubber seed	2.2	10.2	-	8.7	24.6	39.6	16.3	-	-	-	-	-	[73]
Tobaco	0.14	8.46	-	3.38	11.24	75.58	1.14	-	-	-	-	-	[74]
Tung	-	4.00	-	1.00	8.00	4.00	3.00	-	-	-	-	-	[37]

2.1.3. Waste oils and animal fats

The residual obtained after using oil for the cooking purposes is generally discarded with no further application [18]. Over the last few years, waste cooking oil has been considered as a possible feedstock for biodiesel production due its low cost, and as its biofuel was found to fulfill the requirements specified by European standard for biodiesel (EN) and American Society for Testing and Materials (ASTM) standards [75]. However, waste oil is highly impure consisting mainly of high free fatty acid (FFA), and thus, could be categorized in two groups based on its FFA content: the yellow grease (FFA < 15%), and the brown grease (FFA > 15%). These oils after the filtration and purification processes could be used for biodiesel production [18].

Animal fats such as tallow [76], chicken fat [77], lard [78] and yellow grease [79] are also considered as feedstocks. According to Adewale et al. [80], animal fat wastes are low cost, mitigate environmental damage and increase the quality of the resultant biodiesel fuel. However, it has been reported that these may not be plentiful enough to satisfy the global energy demand. Moreover, biodiesel derived from animal fats has a relatively poor performance in cold weather. Furthermore, the transesterification process is difficult for some types of fats due to the presence of a high amount of saturated fatty acids. [4,13].

2.1.4. Algae as biodiesel feedstocks

The amounts of oily crops, both edible and non-edible, animal fats and waste cooking oils are limited, so it is unlikely to provide worldwide biodiesel production demand. The search for other renewable sources is needed to provide the required amount of oily feedstocks. In recent years a high interest towards producing biodiesel from microalgae has been developed. The advantages of using microalgae for biodiesel production are: much higher biomass productivities than land plants, some species can accumulate up to 20–50% triacylglycerol, no agricultural land is required to grow the biomass and they required only sunlight and a few simple and cheap nutrients [81].

3. Oil Extraction Methods

One of the important steps in the production of biodiesel is oil extraction, and different methods and techniques of oil extraction are in use [4,12,13]. Preparation of feedstocks and various oil extraction methods are discussed in the following parts.

3.1. Feedstock preparation

The pre-requisite for oil extraction is seed preparation [4,13,82]. The preparation of seeds involves removal of outer layers of the fruit to expose the kernels or seeds, and its drying to reduce moisture content [82]. The seeds are separated from fruits, and the fruits that do not dehisce are cracked open manually. The separated seeds or kernels are sieved, cleaned and stored at room temperature [13].

According to Atabani et al. [13,82] seeds can be either dried in the oven or sun dried to appropriate moisture. The kernels or seeds have to be prepared in such a way that they contain optimum moisture content for high oil extraction. For instance, Jahirul et al. [82] has found that seed kernel of beauty leaf (*C. inophyllum*) prepared to 15% moisture content provided the highest oil yields in both mechanical and solvent extraction methods. The drying process should be checked very carefully by weighing the trays several times in a day whenever possible and after reaching the desired dryness; the trays are stored in a refrigerated room [4]. Mechanical expellers or presses can be fed with either whole seeds or kernels or a mix of both, but common practice is to use seeds only. However, for chemical extraction only kernels are employed [83].

3.2. Extraction methods

After preparation, the raw material is ready for oil extraction. There are three main methods that have been identified for oil extraction: (i) mechanical extraction, (ii) chemical or solvent extraction, and (iii) enzymatic extraction [4,6,13]. Moreover, accelerated solvent extraction (ASE), supercritical fluid extraction (SFE) as well as microwave-assisted extraction (MAE) methods are frequently used [4]; however, they are not as common or well known as the first three mentioned alternatives

It has been observed that mechanical pressing and solvent extraction are the most commonly used methods for commercial oil extraction [6]. According to Atabani et al. [13], the main products during oil extraction are the crude oil, and the important by-products are such as seeds or kernel cakes. Seed cakes can be used as fertilizers for soil enrichment [6], feed for poultry, fish and swine, and some oil cakes have also application in fermentation and biotechnological processes [84].

3.2.1. Mechanical oil extraction

Mechanical press oil extraction is the most conventional technique. A manual ram press or an engine driven screw press can be used [4]. Jahirul et al. [82] and Bhuiya et al. [85] used a Mini 40 screw press to extract oil from beauty leaf kernels (*C. inophyllum*). It has been found that engine driven screw press can extract 68–80% of the available oil while the ram presses only achieved 60–65%. Oil extraction efficiencies calculated from data reported in more recent studies are found to generally correspond to these ranges, although the efficiency range of engine driven screw presses can be broadened to 70–80% [4,6,13]. This broader difference is due to the fact that seeds can be subjected to a different number of extractions through the expeller [82,85]. Calculated oil yields (% of contained oil) of mechanical extraction method is presented in Table 5.

Table 5. Calculated oil yields (% of contained oil) of mechanical extraction methods [6,82,83,86].

Press type	Oil yield (%)	Necessary treatment
Engine driven screw press	68.0	Filtration and degumming
	80.0	
	79.0	
Ram press	62.5	

The oil extracted by mechanical presses needs further treatment of filtration and degumming in order to produce a more pure raw material [6,87]. Another problem associated with conventional mechanical presses is that the design of mechanical extractor is suited for some seeds, and therefore, the oil yield is affected if that mechanical extractor is used for other seeds [4,6,13,87]. It has been also found that pretreatment of seeds before applying mechanical extractor increases the amount of oil recovery [6,83]. For instance, by cooking jatropha seeds in water for one hour at 70 °C and using screw pressing, Beerens [88] obtained oil yield of 89% after single pass and 91% after dual pass compared to 79% and 87% oil yield recovery of untreated seeds, respectively. Therefore, several other methods have been proposed recently for oil extraction such as solvent extraction, enzymatic extraction and microwave assisted techniques in order to improve the oil extraction yield.

3.2.2. Solvent oil extraction (chemical extraction)

Solvent extraction is the process in which the oil is removed from a solid by means of a liquid solvent, it is also known as leaching [4]. The chemical extraction using n-hexane method results in the highest oil yield which makes it the most commonly used solvent [4,13]. Jahirul et al. [82] has used n-hexane to extract the oil from Australian native beauty leaf seeds (*Calophyllum inophyllum*), although the cost of oil extraction technique by mechanical screw press is low it is ineffective due to relatively lower oil yields. On the contrary, the chemical oil extraction method was found to be very effective because of high oil yield and for its consistent performance.

Table 6. Advantages and disadvantages of mechanical and chemical oil extraction methods for beauty leaf seeds [82].

Mechanical Extraction		**Chemical Extraction**	
Advantages	**Disadvantages**	**Advantages**	**Disadvantages**
✓ Virgin oil is more sought after ✓ No potential for solvent contamination ✓ Relatively inexpensive after initial capital costs ✓ Minor consumables cost	• Generally ineffective for processing Beauty Leaf seed • Time and labor intensive • Relatively low oil yields • Operators require experience to achieve best results • High dependence on kernel moisture content	✓ Repeatable and reproducible results and process ✓ High oil yields ✓ Relatively simple and quick ✓ Hexane can be recovered and reused, reducing cost significantly	• Less sought after than virgin oil • Potential for solvent contamination • Safety issues and environmental concerns regarding the use of hexane • Very costly if the hexane cannot be recovered

It has been observed that there are many factors affecting the rate of solvent extraction such as particle size, the type of solvent used, temperature and agitation speed [6,13]. The solvent has to be selected in such a way that it would be a good selective solvent and its viscosity would be sufficiently low to circulate freely. Sayyar et al. [89] extracted J. curcas oil by n-hexane and petroleum ether and found that the extraction yield with n-hexane to be about 1.3% more than that of petroleum ether (47.3% and 46.0% wt, respectively) under similar conditions. The authors recognized n-hexane as a more preferable solvent for extraction of jatropha oil as compared to petroleum ether. In the extraction of olive oil using organic solvents like hexane, ethanol, petroleum ether, isopropyl alcohol and carbon tetrachloride by a Soxhlet extractor, Banat et al. [90] did also obtain the highest oil yield (12.7%) by n-hexane. However, it has been observed that this method consumes much more time compared to other techniques. The solvent extraction is only economical attractive at a large-scale of production (more than 50 ton biodiesel per day) as reported [13]. In addition, n-hexane solvent extraction has a negative environmental impact because of the wastewater generation, higher specific energy consumption and higher emissions of volatile organic compounds and human health impacts [6]. According to Achten et al. [83] and Mahanta and Shrivastava [91], there are three other types of solvent extraction technique: hot water extraction, soxhlet extraction and ultrasonication technique that could be use instead of hexane solvent extraction.

Jahirul et al. [82] reported that in oil extraction from beauty leaf seeds *(Calophyllum inophyllum)* by mechanical method (using the screw press) and chemical extraction (using hexane as a solvent), each method has advantages and disadvantages. The advantages and disadvantages of oil extraction by mechanical extraction and chemical extraction from beauty leaf seeds is presented in Table 6.

3.2.3. Accelerated solvent extraction (ASE)

Accelerated solvent extraction (ASE) is also referred to as pressurized solvent extraction (PSE) is another modern oil extraction technique which uses organic and/or aqueous solvents at elevated temperatures and pressures [4]. It has been observed that high temperature accelerates the extraction rate, while elevated pressure prevents boiling at temperatures above the normal boiling point of the solvent.

Khattab and Zeitoun [92] have extracted oil of flaxseed by different methods by supercritical fluid extraction (SFE), accelerated solvent extraction (ASE) and conventional solvent extraction (SE) and found the highest oil yield (42.40%) by SE using n-hexane which did not differ significantly from the one obtained by accelerated solvent extraction ASE in terms of oil quantity (41.90%) and their physicochemical properties and fatty acid profiles. The supercritical fluid extraction (SFE), however, showed significantly lower oil yield (36.49%) in this particular oil extraction from flaxseed. Sarip et al. [93] have also extracted crude palm oil from palm mesocarp by using hot compressed water extraction method and obtained 70 ± 0.5% of the oil with averaged free fatty acid of 0.81 ± 0.08%. Moreover, it was also reported that ASE has been used for the extraction of different materials including wheat germ [94] and flaxseed hulls [95]. In ASE, time as well as solvent consumption is significantly reduced compared to the other solvent extraction techniques [92,94].

3.2.4. Enzymatic oil extraction

Aqueous enzymatic oil extraction (AEOE) method is a promising technique for extraction of oil from plant materials [96,97]. In this method, enzymes should be used to extract oil from crushed seeds [91]. Aqueous enzymatic oil extraction can also be used in combination with other methods of oil extraction. For instance, Shah et al. [97] used a combination of ultrasonication and aqueous enzymatic oil extraction (using an alkaline protease at pH = 9.0) method to extract oil from *J. curcas* seeds and obtained 74% of the seed oil which is very large compared to the 17–20% oil extracted by aqueous oil extraction alone. Moreover, using of ultrasonication also resulted in reducing the process time from 18 to 6 h. The main advantages of using enzymatic oil extraction are that it is environmental-friendly and does not produce volatile organic compounds. However, the long process time is the main disadvantage associated with this technique [91].

Table 7 shows the reaction temperature, reaction pH, time consumption and oil yield of different chemical and enzymatic extraction methods tested on *J. curcas*. It has been found that the chemical extraction using n-hexane method results in the highest oil yield which makes it the most commonly used method. Moreover, the negative environmental impacts associated with solvent extraction can be reduced significantly by using AEOE technique although the later method takes long time to complete the process [83,91].

Table 7. Reported oil yields percentage for different chemical and enzymatic extraction methods and different reaction parameters for *J. curcas*.

Extraction technique	Reaction temperature (°C)	Reaction pH	Time consumption (h)	Oil yield (%)	Reference
n-Hexane oil extraction (Soxhlet) apparatus	-	-	24	95–99	[86]
First acetone, second n-hexane	-	-	48	-	[98]
AOE	50	9	6	38	[83,97]
AOE with 10 min of ultrasonication as pre-treatment	50	9	6	67	[83,97]
AEOE (hemicellulase or cellulase)	60	4.5	2	73	[6,13,83]
AEOE (alkaline protease)	60	7	2	86	[6,13,83]
	50	9	6	64	[83]
AEOE (alkaline protease) with 5 min of ultrasonication as pre-treatment	50	9	6	74	[83,97]
Three-phase partitioning	25	9	2	97	[83,99]

3.2.5. Supercritical fluid extraction (SFE)

Supercritical fluid extraction (SFE) technique is used to avoid the use of organic solvents and to increase the speed of extraction [4]. SFE using CO_2 has numerous advantages over the solvent extraction [92,100]. It uses CO_2 as a solvent which is a nontoxic, inexpensive, nonflammable, and nonpolluting supercritical fluid solvent for the extraction of natural products, and also almost 100% oil can be extracted by this method [100].

Maran and Priya [101] have used a supercritical fluid extraction (at 44 MPa, 49.8 °C, and 0.64 g/min of CO_2 flow rate and within 81 min) method for extraction of oil from muskmelon seed (*Cucumis melo*) and produced slightly higher oil yield (48.11 ± 0.04%) than that of Soxhlet extraction method (46.83 ± 0.29%). Moreover, these authors reported that the fatty acids composition of muskmelon seed oil extracted by SFE was similar to that of Soxhlet extraction. However, the main limitation of the SFE is the high cost at production scale, not only due to the use of high pressure equipment but also because of the raw material should be freeze dried to reduce its moisture to values below 20%, as high water concentration in fluid phase negatively affects the oil yield [102,103].

3.2.6. Microwave-assisted extraction (MAE)

Microwave-assisted extraction (MAE) also called microwave extraction, is a new extraction technique, which combines microwave and traditional solvent extraction [104]. MAE has been recognized as a technique with several advantages over other extraction processes, such as reduction of costs, shorter time, less solvent, higher extraction rate, better products with lower cost, reduce energy consumption and CO_2 emissions [104,105]. In microwave-assisted aqueous enzymatic extraction (MAAEE) of pumpkin seed oil by using mixtures of cellulose, pectinase and proteinase (w/w/w), Jiao et al. [106] obtained the highest oil recovery of 64.17%. The authors also reported that there were no significant variations in physicochemical properties of MAAEE and soxhlet extracted oils, and thus, MAAEE is a promising and environmental-friendly technique for pumpkin seed oil extraction. Moreover, it has been found that the MAE method needs a few minutes compared to SFE and the apparatus of MAE extraction is simpler and cheaper, and can be used with a variety of materials with less limit of the polarity of extractants [104]. Therefore, MAE extraction is an interesting alternative to conventional liquid solvent extraction methods, especially in the case of plant material [4,104]. In microwave-assisted solvent extraction of oil from soybeans and rice bran by using solvent (ethanol) to feedstock ratio of 3:1, the maximum oil yields of 17.3% and 17.2% at 20 min and 120 ^{o}C were achieved as compared to 11.3% and 12.4% using control extraction for soybeans and rice bran, respectively [107].

4. Advantages and Disadvantages of Main Oil Extraction Methods

From the above discussions, it is possible to observe that each method of oil extraction has its own advantages and disadvantages. The advantages and disadvantages of the main three oil extraction methods: mechanical, chemical or solvent and ASE are summarized in Table 8.

Table 8. Advantages and disadvantages of main three oil extraction methods [4,82,108].

Methods	Advantages	Disadvantages
Oil press	✓ Virgin oil is more sought after	• Generally ineffective in beauty leaf oil extraction
	✓ No potential for solvent contamination	• Time and labor intensive
	✓ Relatively inexpensive after initial capital costs	• Relatively low oil yields
	✓ Minor consumable costs	• Operators require experience to achieve best results
	✓ Whole seeds or kernels can be processed	• High dependence on kernel moisture content
	✓ No environmental problem regarding the use of screw press	• Relatively dirty process
		• Filtration or degumming process pf oil is required
		• Low and inconsistent oil production
		• High oil loss
n-Hexane	✓ Repeatable and reproducible results and process	• Less sought after than virgin oil
	✓ High oil yields	• High potential for solvent contamination
	✓ Relatively simple and quick	• Safety issues and environmental concerns
	✓ Suitable for bulk oil extraction	• Very costly if the hexane cannot be recovered
	✓ Low capital investment	• High hexane requirement
	✓ No especial equipment required	• Only kernel can be processed
	✓ Hexane can be recovered and reused, reducing cost significantly	
ASE	✓ Automatic technique	• Very high initial cost
	✓ Condition can be optimized	• High preparation required
	✓ More efficient	• Special equipment and skill required
	✓ Clean process	• Potential for solvent contamination
	✓ Relatively less solvent consumption	• Only kernel can be processed
	✓ Less time and labor incentives	
	✓ High oil yield	

5. Single and Combined Oil Extraction Methods to Reduces Problems of Extraction

Traditional oil extraction methods have their own advantages and disadvantages. To overcome the disadvantages and improve the strong sides, different oil extraction methods are combined. Moreover, to decrease the environmental impacts of solvents of chemical extraction, different methods of oil extraction have been developed. For instance, Conte, et al. [109] have extracted safflower oil by Soxhlet extraction, ultrasound-assisted extraction (UAE) and pressurized liquid extraction (PLE) techniques (using pressurized ethanol). Soxhlet and ultrasound-assisted extractions gave maximum global oil yield of 36.53% and 30.41%, respectively (70 ^oC and 240 min) while a maximum global yield for pressurized liquid extraction would be 25.62% [109]. According to the authors, although traditional extraction methods (Soxhlet and UAE) showed maximum global oil yields, the advantages derived from PLE make it a promising alternative for the extraction of essential oil from vegetable matrices due to the reduction of solvent consumption and extraction time.

At optimal conditions of sonication, ultrasonic-assisted extraction (UAE) of raspberry seed oil was able to provide a higher content of beneficial unsaturated fatty acids, whereas conventional Soxhlet extraction resulted in a higher amount of saturated fatty acids [110]. Ultrasound-assisted extraction gave grape seed oil yield (14% w/w) similar to Soxhlet extraction in 6 hours, and no significant differences for the major fatty acids was observed in oils extracted by both methods. The advantage of using ultrasound is that it's lower solvent consumption and a shorter extraction time [111].

6. Future Prospective of Oil Extraction Methods

Biodiesel production from non-edible feedstocks is increasingly attractive alternative to both fossil diesels and renewable fuels derived from food crops. Thus, one of the current research focus in biodiesel production is optimization of oil extraction methods from non-edible oils sources, characterization the oils and suitability test for biodiesel [112], and searching for appropriate methods of biodiesel production from these oils [4,17]. Non-edible biodiesel feedstocks include non-edible oils, animal fats and waste oils [4, 13] and algal biomass [10,11,12]. Some of the recently optimized non-edible seed oil extraction methods include extraction from seeds of waste date pits (*Phoenix dactylifera L.*) [112], Sesame (*Sesamum indicum L.*) [113], jatropha seed kernels [114], beauty leaf seed *(Calophyllum inophyllum)* [85], *Moringa oleifera* [115] and karanja (*Pongamia pinnata*) [116].

According to Sajjadi et al. [17], animal fats are important feedstocks for biodiesel production as their cost is substantially lower than the cost of vegetable oil. However, many types of animal fats contain high amount of saturated fatty acids, which make the transesterification process difficult. To overcome such problems, various biodiesel production methods have been optimized by different investigators. For instance, Kumar and Math [117] investigated the combined effects of catalyst (NaOH) concentration, reaction time and methanol quantity on biodiesel yield from waste animal fat at 55 ^oC to 60 ^oC, and obtained the maximum animal fat methyl ester yield of 91% v/v, at 35% v/v methanol and 0.46% w/v catalyst within 90 minutes. Chakraborty and Sahu [118] have also carried out a study on the impacts of methanol to goat tallow molar ratio, infrared radiation assisted reactor (IRAR) temperature and H_2SO_4 concentration on the tallow conversion to biodiesel. Under optimal conditions, 96.7% FFA conversion was achieved within 2.5 h at 59.93 wt.% H_2SO_4, 69.97 °C IRAR temperature and 31.88:1 methanol to tallow molar ratio. According to the authors, infrared radiation strategy could significantly reduce the reaction time compared to conventionally heated reactor while providing appreciably high biodiesel yield. Nuhu and Kovo [119] used a two-step transesterification to produce biodiesel from chicken fat due to the presence of high FFA (4.16%) in the feedstock, and the first esterification step was a pretreatment process that could reduce the FFA to 0.43%. The second step, the transesterification reaction, yielded 93.4% fat methyl ester from 50g of chicken fat at 60 °C reaction temperature and within 2 hours corresponding to 6:1 molar ratio of oil-to-methanol and 1% wt catalyst concentration.

From various types of biomass, microalgae have the potential of becoming a significant energy source for biofuel production in the coming years. Currently, researches are mainly focusing on optimization of cultivation methods and the conversion of microalgae to biodiesel (lipids for biodiesel production) [120]. Martinez-Guerra and Gude [121] has also wrote that algal biodiesel production will play a significant role in sustaining future transportation fuel supplies, and a large number of researchers around the world are investigating into making this process sustainable by increasing the energy gains and by optimizing resource-utilization efficiencies. Some of the studies that focus on optimization of biodiesel production from microalgae include the investigations by Misau et al. [122], Gülyurt et al. [123], Barreiro, et al. [120] and Rajendran et al. [124].

7. Conclusions

The increasing demand of energy, where the major part of that energy is derived from fossil sources and the problem associated with petroleum fuels have led to search for renewable alternative energy sources of which biodiesel is a promising alternative. The potential feedstock of biodiesel include, edible and non-edible oils, animal fats, waste oils and algal biomass. However, nowadays, more than 95% of the world biodiesel is produced from edible oils and this resulted in food versus fuel debates, rising in the price of oil and environmental problems. To overcome these problems, it is important to use relatively cheaper and non-edible biodiesel feedstock such as non-edible oils, waste animal fats and waste oils.

Many non-edible plat oils have fatty acid composition and other physico-chemical properties that enable them to be suitable for biodiesel production as that of edible oils. Moreover, many potential non-edible plant oil for biodiesel have been identified, and the oil extraction and biodiesel production methods have also been optimized. Methods to extract oil from waste animal fats and refining animal oils and waste oils, and converting them to biodiesel were also optimized by different scholars.

The major oil extraction methods are mechanical extraction, chemical or solvent extraction, and enzymatic extraction. From these methods, chemical or solvent oil extraction method, particularly, Soxhlet extraction by using hexane as solvent, is the most widely used method due to its efficiency of oil extraction. However, chemical oil extraction method has a negative environmental impact. There are also other oil extraction method such as accelerated solvent extraction, supercritical fluid extraction, microwave-assisted extraction and ultrasonic-assisted extraction.

All oil extraction methods have their own advantages and disadvantages. Therefore, by combining the appropriate oil extraction methods, it is possible to reduce the disadvantages and improve the oil extraction efficiency and reduce the negative environmental impacts. Furthermore, for non-edible and low-cost biodiesel feedstocks gradually gain acceptance and well establish and continue to settle in the biodiesel market, various aspects must be scrutinized and studied. Researches that focus on the study of low-cost biodiesel feedstocks, various efficient and environmental-friendly oil extraction techniques, and study of oil yield and fatty acid profiles of non-edible oils, animal fats and waste oils and efficient and cost effective biodiesel conversion technologies are crucial. It can also be concluded that the emphasis must be given to those feedstocks which are neither compete with food crops nor lead to land clearing, and provide significant greenhouse-gas reductions.

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Conflict of Interest

All authors declare no conflicts of interest in this paper.

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Paper II

Research Article

Temperature and pretreatment effects on the drying of different collections of *Jatropha curcas* L. seeds

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Abstract

Drying oilseeds to reduce their moisture content is crucial in order to preserve the seeds and their contents. However, due to the nature of conventional storage facilities, it is ideal to dry seeds just before using them for oil extraction and/or in situ biodiesel production as the seeds dried in advance might recover the equilibrium moisture content due to the humidity from the air. Thus, drying the seeds immediately before oil extraction is vital to reduce the moisture content to its minimum. In the present study, the effects of five drying temperatures (313, 323, 333, 343 and 353 K) on the degree of moisture loss from Jatropha seeds at storage and the suitability of the drying processes to reduce the seed moisture to its minimum were investigated. The drying experiments of non-pretreated (whole seeds) and pretreated (crushed seeds) seeds were performed in a heating furnace. It was found that increasing in drying temperature promoted the rate of moisture loss, and the evaporation of moisture from the crushed seeds was faster than that of the whole seeds. However, the largest weight loss (6.47%) and the smallest seed residual moisture content (0.34%) were obtained when the whole seeds dried at 353 K. The findings of the present experiments suggested that drying the whole seeds of Jatropha at 353 K could provide dried seeds with suitable moisture content for oil extraction and/or in situ biodiesel production.

Keywords Crushed seed · Drying temperature · Jatropha (*Jatropha curcas* L.) seed · Moisture content · Seed collection · Whole seed

1 Introduction

Biodiesel is an alternative to petroleum-based fuels and can be produced from a variety of feedstock, including vegetable oils, animal fats, and waste cooking oils [1]. Currently, more than 95% of the biodiesel is being produced from edible vegetable oils such as rapeseed, sunflower, palm and soybean [2–4]. The price of edible oils has significantly increased [3, 5] as a result of the increasing of vegetable oil demands caused by the ever-increasing global population [5]. Using expensive edible vegetable oils for biodiesel production makes the process costly as the feedstock alone account up to 75% of the total price [4, 6]. Thus, the cost of the biodiesel feedstock becomes the main obstacle for the commercialization of the product [7]. Moreover, extensive conversion of edible oils to biodiesel may lead to food crisis [1] and causes major environmental problems such as serious destruction of vital soil resources, deforestation and usage of much of the available arable land [4]. Therefore, production of biodiesel from low cost non-edible oil feedstock such as *Jatropha curcas* L. seeds and waste cooking oils would be a potential solution [1, 8].

The oil content of Jatropha seed is reported to be ranged from 30 to 50% by weight of the seed and 45–60% by weight of the kernel [9]. Due to the presence of major toxic compound (the phorbol esters) in Jatropha seed oil, biodiesel production from the seeds does not compete with human consumption [10, 11]. Production of biodiesel from non-edible feedstock such as Jatropha could be a good alternative to overcome the food versus fuel crisis

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that could occur due to continuous conversion of edible oils to biodiesel [3, 4].

Jatropha seeds are storable and its further processing can be delayed, and this makes the production of the crop suitable to remote areas [12]. However, the moisture of contents of the seeds should be reduced just after harvest to minimize loss of quality [13]. According to Almeida et al. [14], due consideration should be given to the seed moisture content during storage as this parameter affects seed chemical composition and the speed of seed metabolic activities. Moisture content of oilseeds is also one of the important parameters that determine the quantity of oil which can be obtained from the seeds [15]. Thus, its measurement is an inevitable operation during postharvest processing such as handling, storage, milling and oil extraction [16]. Moisture contents of oilseed may depend on the conditions of collections, stages of seed maturation [17], postharvest processing [16] and storage conditions [15].

It has been reported that Jatropha seeds that were harvested from green, yellow and brown fruits differed in their moisture content, but the moisture contents of the seeds reach values between 7.6 and 8.3% after natural drying at room conditions, independent of the harvest stages [17]. The seeds should be shade dried for sowing but dried in the sun for oil production, and its moisture content should be reduced to around 6–10% for storage. If kept dry and stored at optimum conditions, the seeds may be stored for up to 12 months without loss of oil content [12].

The drying of seeds is a required step to achieve the desired moisture content. Knowing the drying characteristics of Jatropha seeds is very essential in its handling and as a preventive protection approach to preserve the material in its current form [18]. Drying processes are also very important for easy extraction of oil from the seeds [19]; and dried seeds with low moisture content give higher percentage of oil than the wet seeds [18]. For instance, in the study of oil extraction from soybean, using hexane as solvent, Lawson et al. [20] obtained the oil yield of 15% and 11.81% from seeds with moisture content of 10% and 20%, respectively. According to the authors, non-polar solvents such as hexane are immiscible in water and oil extraction efficiency of these solvent from seeds with high moisture contents would be reduced, and thus, resulted in lower oil yield.

Drying oilseeds to a lower moisture content, particularly to the moisture content for oil extraction and/or in situ biodiesel production, and keeping it up at this moisture content in storage is impractical. During seed storage, drying oilseeds to very low moisture content is not of such use as the seeds return back to the equilibrium moisture content in relation to the relative humidity of storage environment [21]. Thus, drying the seeds at storage prior to oil extraction and/or in situ biodiesel production may be needed.

There were several research reports on the optimum moisture contents of Jatropha seeds for various oil extraction methods. It was found that the rate of Jatropha oil extraction by screw press increased with increase in temperature and decreased with increasing of seed moisture content [22]. Oil extraction by this method also demonstrated that Jatropha seeds with low moisture content provide higher oil yield than seeds with high moisture content [23]. In the extraction of oil by mechanical press, drying of fresh Jatropha seeds to moisture content of about 5.9% and deshelling the seeds to kernels with moisture content of 3.8% and pressing the kernels gave a maximum oil yield of 87.4% (at applied pressure of 19 MPa, 90 °C pressing temperature and 10 min of pressing) [24]. This moisture content was also reported as the optimum moisture level for the extraction method used. Moreover, in the mechanical extraction of oil from Nyamplung (*Calophyllum inophyllum* L.) by screw press, the larger oil yield (33.39%) was obtained from seeds with moisture content of 1.2% (dry based, d.b) compared to 15.56% oil yield from seeds with moisture contents of 20% [25].

Higher moisture content of the oilseeds is also one of the important factors that could cause oil hydrolysis and the formation free fatty acids (FFA) in the seeds, which reduces the oil quality. The post extraction pre-treatment of the oil to reduce its FFA gives lower oil yield; and this does also make the oil production process more costly [26]. Oil with lower FFA content is often preferred for direct utilization in alkaline catalyzed transesterification of biodiesel production [27], and the above limit of FFA in the oil should be 1% for satisfactory base catalyzed transesterification [28]. Higher moisture and FFA contents (15% FFA) of Jatropha oil have resulted in the current commercial alkaline catalyst based transesterification not being suitable to be employed [29]. The acid-catalyzed transesterification of Jatropha oil is an alternative, but it is much slower than the base catalyzed one, and thus, not efficient [30]. The complicity of multistage processing involved (extraction, drying, degumming and deacidification) would also add to the production cost and thus contribute negatively to the biodiesel cost effectiveness [31].

In the extraction of Jatropha oil from ground kernel with moisture content of 0.912%, using Soxhlet extractor and hexane as solvent, a maximum of 45% oil that contained 0.9% FFA was obtained [32]. It was also reported that the oil obtained by this method did not need pretreatment with acid for basic catalyzed biodiesel productions [32], as its free fatty acid content is less than 1% [33].

In basic catalyzed in situ biodiesel production, tolerance to moisture content of the feedstock depends on the in situ technology to be adopted and the amount of alcohol being used [34]. However, reports from several investigations showed that seeds with moisture content less than 1% is suitable for in situ transesterification of biodiesel production. For instance, in an integrated extraction and transesterification process from Jatropha seeds using hexane and methanol via base catalyzed transesterification, seeds with moisture content less than 1% was used, and the highest yield obtained was of 90.8% at optimum conditions [35]. Kartika et al. [36] reported that in a solvent extraction and in situ transesterification by alkaline catalyst, seeds with moisture content less than 1% was used as increase in water content of the oilseeds can cause ester saponification [36, 37].

In the study on direct in situ alkaline-catalyzed transesterification of cottonseeds, Qian et al. [37] found that decreasing in seed moisture content had increased the amount of oil dissolved in methanol. Moreover, in reactive extraction technologies using hexane as co-solvent, it was found that seeds with moisture content of 1% gave the maximum biodiesel yield (68.3%) compared to seeds with 3 and 5% moisture contents [38]. It was also reported that reducing moisture content of the seeds did lower the amount of chemicals requirements during in situ transesterification process. Accordingly, a reduction of 60% methanol and 56% sodium hydroxide was found when soybean flakes with moisture contents of 7.4% were dried in a convection oven until the water content reached 0% prior to in situ transesterification [39].

Research papers that deal with drying process of oilseeds in general and that of Jatropha in particular, mainly deal with drying of freshly collected seeds for storage and/or for oil extraction. However, to our knowledge, no research investigation has been found on the influence of different temperatures on the degree of moisture removal from Jatropha seeds at a storage moisture level.

In the present study, we investigated the impact of five different drying air temperatures (313, 323, 333, 343, and 353 K) on the moisture removal process of Jatropha seeds under different pretreatment conditions in order to produce the dried seeds with minimum moisture content. In addition, the physical appearance of the seeds during drying was investigated.

2 Materials and method

2.1 Materials

Seven Jatropha seed collections at storage: Kurkura, Bira, Salmene$_1$, Salmene$_2$, Salmene$_3$, Shekla and Gerbi were used for the experiments. For the crushing pretreatment process of Jatropha seeds, a bowl-shaped mortar and pestle made from stone were used. After crushing, the particle sizes of the pulverized seeds were estimated by three different stainless steel sieves with openings of 500 µm, 1 mm and 2 mm woven cloth (Control Group, 15-D2245/J, 15-D2215/J and 15-D2185/J). All the seed samples were weighed on a digital balance machine having 0.01 mg accuracy (Mettler-Toledo, PG 5002 Delta Range, Switzerland). The seed samples were placed on Petri dishes (100 mm × 15 mm) during drying. The drying experiments and determination of initial and residual moisture contents of the seed samples were performed using a heating furnace (Narbetherm P300, Germany).

2.2 Experimental procedures

To determine the effects of temperature and pretreatments on the drying of Jatropha seeds at the storage moisture content, the methodology employed previously in the group has been followed [40]. From the seven seed collections, Salmene$_3$ seed collection was selected and used for the drying experiment as base line for comparison. This collection was selected based on the information recorded during seed collection, and it was chosen as the best one since it was obtained from the fruits at the physiological maturity stage. It has been reported that maximum physiological quality and lipid content of Jatropha seeds occur at physiological seed maturity, which corresponds to seeds obtained from yellow fruits [41, 42].

In the drying experiment, the non-pretreated whole seeds (WS) and the pretreated crushed seeds (CS) of Salmene$_3$ collection were used. The seeds were cleaned manually by removing all foreign matter such as stones, dirt and broken seeds before the experiment. For all drying experiments, ca. 15 g of Jatropha seeds were used. Four 15 g seed samples were weighed separately for the drying at a particular drying temperature (two samples for each treatment in order to have duplicate measurements). The first two WS samples were dried without any pretreatment with its seed coat. The second two seed samples were crushed and grinded mechanically by hands, using mortar and pestle. The particle sizes of the crushed seeds (PSCS) were estimated using three different sieve sizes as it was described in the previous study published elsewhere [43]. Thus, the crushed seeds used in this experiment was a mixture of four particles sizes. The average proportions (%) of the PSCS: PSCS > 2 mm, 2 mm > PSCS > 1 mm, 1 mm > PSCS > 500 µm and PSCS < 500 µm were 14.95 ± 8.2, 29.96 ± 4.38, 35.32 ± 10.5 and 19.77 ± 4.74, respectively.

Two different dimensional properties (geometric and arithmetic mean diameters) of the whole seeds of the selected seed collection (Salmene$_3$ collection) were determined as these properties could affect the drying process of the seeds. The geometric and arithmetic mean diameters (mm) of the selected seed collection were calculated by measuring the length, width and thickness of 50 whole seeds with measuring calipers, and using Eqs. 1 and 2, respectively [44, 45].

$$D_g = (L \times W \times T)^{\frac{1}{3}} \tag{1}$$

$$D_a = \frac{(L \times W \times T)}{3} \tag{2}$$

where D_g = geometric mean diameter, Da = arithmetic mean diameter, L = length, W = width and T = thickness of the whole seeds in millimeter.

Five different air temperatures (313, 323, 333, 343, and 353 K) that were used to dry Hass avocado seeds were adopted for drying the Jatropha seed samples [40]. The influence of these five air temperatures was selected for the investigation as several studies reported that air temperature is the dominant parameter that affecting the drying process of the seeds [40, 46, 47]. All the seed samples were kept in separate Petri dishes (100 mm × 15 mm), uniformly distributed on it and then placed in the heating furnace for drying.

The effectiveness of the drying temperatures on the moisture evaporation from Jatropha seeds was systematically recorded for 5760 min to ensure the achievement of the critical moisture level at which no more moisture loss occurred. To understand the rate of moisture evaporation, the weight loss data were recorded following the methods used in related studies by Perea-Flores et al. [46] and Avhad and Marchetti [40]. Accordingly, the seeds samples were taken out from the heating furnace and weighed on a digital balance at a predetermined time intervals by taking less than 15 s to weigh the samples. Thus, the samples were exposed to the room temperature for very short instant during weighing, and then, put back in the hearing furnace. The samples were weighed until no more weight loss occurred in three consecutive weight data. Based on the information obtained for Salmene$_3$ seeds for the different temperatures, the WS samples of all the remaining six seed collections were also dried at 353 K following the aforementioned procedures. This was done to compare the methodology for different seed collections.

All experiments were replicated twice to obtain reproducibility in the experimental findings. Although the result obtained from the replicated experiments did not significantly vary, the average values were used in data analysis and reporting. The weight losses (wt%) of the seed samples (both the WS and CS) were determined relative to the initial weight of the seeds just before drying (wet based). The residual moisture remained in the dried seeds (wt%), which could also be referred as the experimental equilibrium moisture content (EMC) of the dried seeds was calculated using Eq. 3 below. The initial moisture contents (M_0) of the seeds were determined by drying 15 g of the seed samples at 105 °C for 24 h [48, 49].

$$EMC = M_0 - M_f \tag{3}$$

where M_0 = the initial moisture contents of the seeds and M_f = the final moisture loss from the seeds at the time when no more moisture (weight) loss occurred.

As it was also very important to investigate the impact of drying air temperatures on the physical properties of seeds as it impacts the seed drying process [40], the physical appearance of the samples were also investigated. For this purpose, the drying seeds were carefully observed, and photographed using a digital photo camera (Canon, DS126061, Japan) every 24 h (1440 min) during the drying experiment for all drying temperatures.

3 Results and discussion

3.1 Moisture loss of crushed and whole seeds

Table 1 presents the dimensional properties of the whole seeds of Salmene$_3$ collection. As it could be observed from Table 1, the mean value for the seed length, width, thickness, geometric mean diameter, and arithmetic mean diameter were found to be 15.46 ± 0.74, 10.24 ± 0.54, 7.28 ± 0.57, 10.47 ± 0.501 and 10.99 ± 0.48 mm, respectively. All the seed mean dimensions found in the current study were in the range of the values determined by Mousa et al. [50] for Jatropha seeds collected from Egypt. The initial moisture content of the selected seed was also found to be 6.81%. This result demonstrated that the moisture content of the selected seed was in the range of the safe seed storage moisture content (6–10%) recommended for Jatropha seeds [12].

From the result of the drying experiment, it was found that weight loss by the CS was faster than that of the WS at the beginning of seed drying and slowed down after some hours depending on the drying temperatures. Accordingly, the weight losses (wt%) by the CS were larger than that of the WS before the drying times of around 1440, 480, 330,

Table 1 Dimensional properties of Jatropha seeds (Salmene$_3$ collection)

Type of dimension	Seed dimensions (mm)	
	Range	Mean
Length	13.5–17.0	15.46 ± 0.74
Width	9.0–11.50	10.24 ± 0.54
Thickness	6.5–9.0	7.28 ± 0.57
Geometric mean diameter	9.3–11.83	10.47 ± 0.501
Arithmetic mean diameter	9.83–12.16	10.99 ± 0.48

270 and 240 min for the drying temperatures of 313, 323, 333, 343 and 353 K, respectively. After the indicated drying times, the weight losses (wt%) by the CS was found to be lower than that of the WS for all respective temperatures. The time at which the weight losses of WS and CS became about equal for the same drying temperature, and the respective weight loss recorded are presented in Table 2.

As it is evident from Table 2, the time taken for the weight losses (wt%) by CS and WS to be about equal was the longest for the lowest temperature of drying (around 1440 min for 313 K,) and the shortest for the highest temperature (around 240 min for 353 K). This shows that the time needed for the weight losses (wt%) of CS and WS dried at 353 K to be about equal was 6 times shorter compared to that of the same samples dried at 313 K. The reason for this is that due to faster seed moisture evaporation rate at higher temperature [48], and the process rapidly reached at the falling drying rate period compared to the drying process at lower temperature.

3.2 Effects of temperatures on the physical appearances of seed samples

The experiment on the effects of drying temperatures on the physical appearance of Jatropha seed samples was conducted to observe if charring of the seeds surface would occur and prevent the moisture loss during drying the samples at higher temperature as reported for the non-pretreated whole Hass avocado seeds [40]. In the present study, after a close examination of the seeds before and after drying, and evaluating the photos taken at the same times, only a blackening of the seed coat on the WS and a similar transformation over the upper surfaces of the CS were observed. After drying, the crushed seeds seemed to be stickier than at the beginning of the study. Except those previously mentioned changes, no other major modification of physical appearances was seen as presented in Fig. 1.

Table 2 Weight loss (wt%) and the approximate time for the weight losses of whole seeds (WS) and crushed seeds (CS) to be about equal

Temperature (K)	Treatments	Weight loss (wt%)	Time (min) for weight loss to be about equal
313	WS	4.28	1440
	CS	4.21	
323	WS	4.42	480
	CS	4.47	
333	WS	4.88	330
	CS	4.80	
343	WS	5.23	270
	CS	5.23	
353	WS	6.01	240
	CS	5.99	

The results obtained in the present study was in contrast with the physical appearance of Hass avocado seeds dried at 313, 323, 333 K, 343 and 353 K, where rupturing of the seeds into two pieces, and hardening and charring of the outer surface of the seeds occurred at 333 K and higher temperatures [40]. The authors also reported that rupturing of the seeds at higher temperatures promoted moisture evaporation; however, the higher temperatures damaged the seeds due to charring and resulted in incomplete evaporation of water from the seeds at the end of drying.

3.3 Effects of temperatures and seed pretreatment on seed drying

The effect of five different drying air temperatures on the extent of moisture evaporation from the WS and CS are graphically represented in Figs. 2 and 3, respectively. As it is evident from Figs. 2 and 3, the rise in operative air temperature accelerated the drying process of the seeds. After 360 min of drying, air temperature of 353 K resulted in 6.15% reduction in the weight of the WS, which was about twice the weight reduced using 313 K at the same drying time. Weight loss of CS at drying temperature of 353 K was also much higher than that of 313 K. This behavior was in agreement with the findings in which fresh Jatropha seeds were dried at 313 and 333 K, and found that evaporation of water from the seeds at 333 K was 2 times faster than those dried at 313 K [24]. In another drying experiments using freshly collected Jatropha seeds with initial moisture content of 61% (d.b), the evaporation of water from the seeds was found to be 8 times faster when temperature was increased from 309 to 378 K [48]. In drying of fresh Hass avocado seeds (with initial moisture content of 51.2%), air temperature of 353 K resulted in 4.3 times weight reduction compared to that of 313 K after 720 min of drying time [40]. Thus, the rise in operating temperature minimizes the time required for the drying process. The larger weight reduction at higher temperature in the latter two investigations compared to the present study might be due to larger initial moisture contents of the fresh seeds.

As it could be seen from Figs. 2 and 3, for all temperatures, the weight losses of the CS and WS were found to increase with time until it reached a critical value above which there was no further increase of the weight loss. With increasing of time of drying, the rate of weight loss decreased gradually, and finally, no more weight loss was observed. This happened when moisture content of a seed would equilibrate with the relative humidity of the air surrounding it [51]; and the residual moisture remained in the seed at this time is the equilibrium moisture content (EMC)

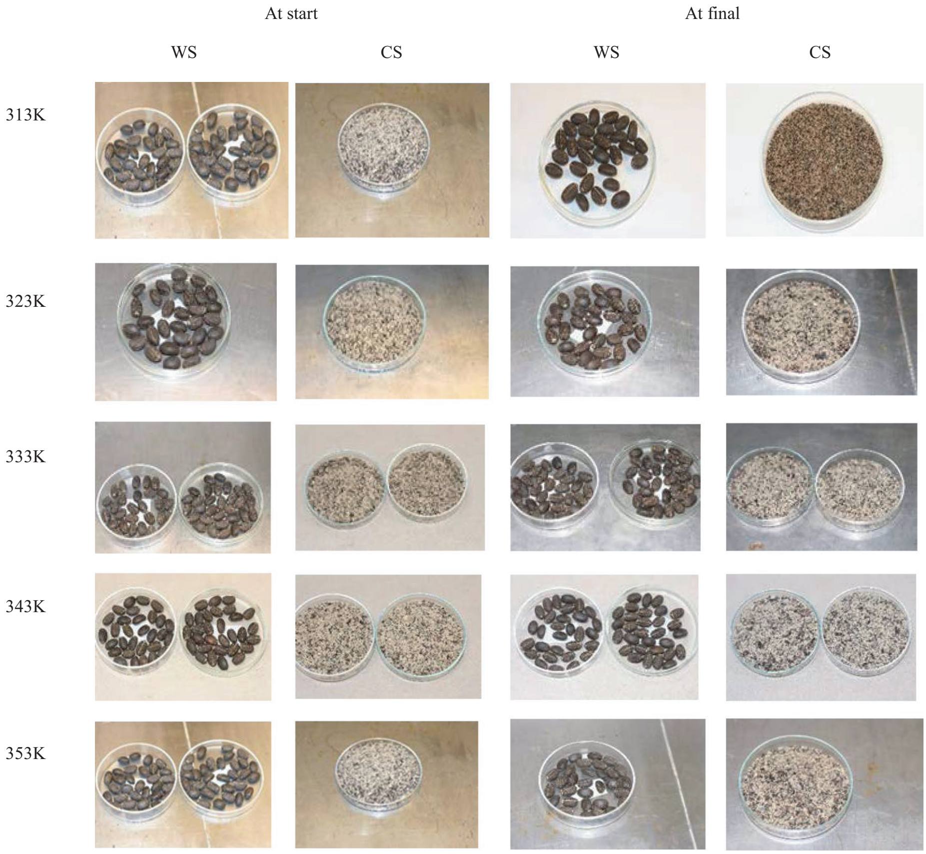

Fig. 1 Physical appearances of WS and CS at the start and final time of drying for all tested temperatures

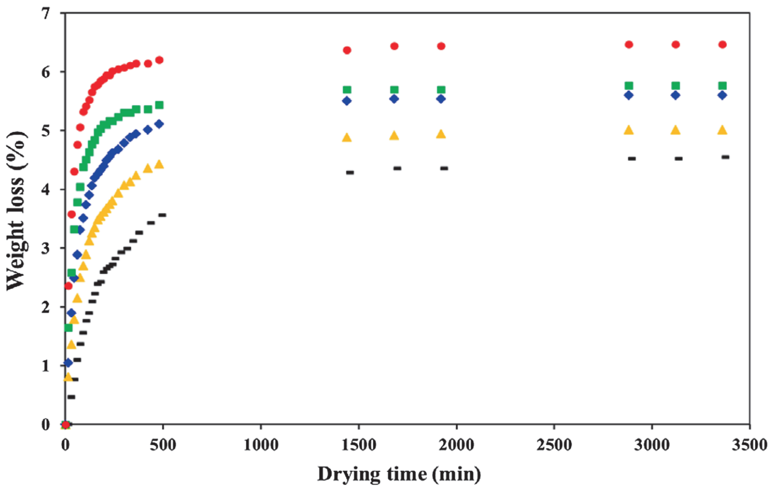

Fig. 2 Weight loss profile of the whole Jatropha seeds at drying temperatures of (▬) 313 K, (▲) 323 K, (◆) 333 K, (■) 343 K and (●) 353 K

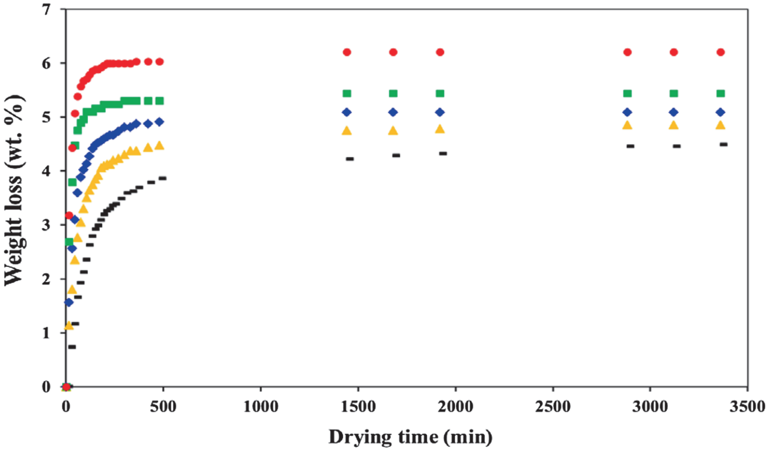

Fig. 3 Weight loss profile of crushed Jatropha seeds at drying temperatures of (▬) 313 K, (▲) 323 K, (◆) 333 K, (■) 343 K and (●) 353 K

Table 3 Final weight loss of the whole seeds (WS) and crushed seeds (CS), their EMC for different temperatures and the approximate time to reach at EMC

Temp. (K)	Treatments	Final weight loss (wt%)	EMC (wt%)	Time to reach EMC (min)
313	WS	4.61	2.19	4320
	CS	4.51	2.29	4320
323	WS	5.01	1.79	2880
	CS	4.85	1.95	2880
333	WS	5.60	1.21	2880
	CS	5.09	1.71	1440
343	WS	5.76	1.04	2880
	CS	5.44	1.36	1440
353	WS	6.47	0.34	2880
	CS	6.21	0.60	1440

of the dried seed. Table 3 shows the final weight loss (at EMC) by WS and CS, their EMC for different temperatures and the time taken to reach the EMC.

As it is evident from Figs. 2, 3 and Table 3, the weight losses (wt%) by CS were faster than that of WS for higher temperatures, particularly for 333, 343 and 353 K as the total time required to reach at EMC for WS is 2 times longer than that of CS. The results obtained in this study was in agreement with the findings reported for the drying experiment using crushed kernels (paste), kernel with particles size of 4 and 8 mm, and the whole kernels of *Buccholzia coriacea* and *Butyrospermum parkii* using drying temperatures of 318 and 333 K [52]. From this investigation, it was found that the decline in weight of the paste was very rapid compared to those of other treatments. According to the authors, the paste gave the highest drying rate, at each drying temperature compared to samples with larger particle sizes. The findings of the present study was also in line with the results reported from the drying experiments of Hass avocado seeds [40], where the weight loss of crushed avocado seeds was faster than that of the whole seeds. The faster moisture loss of crushed seeds could be due to the fact that grinding of the seeds provoked rupture of the cell membranes, thus, providing a larger surface area for rapid moisture loss to occur [52].

In the current study, although weight loss (wt%) of the CS was faster than that of the WS, the final weight losses (wt%) of the WS were larger than that of the CS, for all respective temperatures (Table 3). The maximum final weight loss of 6.47% for WS, which was obtained at 353 K, was also greater than that of the CS (6.21%). Moreover, the lowest residual moisture content (0.34%) was found in the WS dried at 353 K.

The smaller final weight loss (wt%) of the CS compared to the WS might be due to the hardening of pulverized particles of Jatropha seeds due to larger surface area that could be exposed to the drying temperatures. Some amount of moisture might also be lost by adhering to the surface of mortar and pestle during crushing the seeds [40], and to the surface of sieves during the estimation of CS particle size. These two activities were not applied to the WS prior to drying. Although the same amount of the whole and crushed seeds (15 g) and similar Petri dishes (100 mm × 15 mm) were used during the drying experiments, the thicknesses of the bed of CS and WS on the Petri dishes were different. There was also larger spaces for drying air circulation between individual whole seeds than that of the particles of crushed seeds. These might also be resulted in smaller final weight loss of the crushed seeds.

As it could be observed from Table 3, drying temperature of 353 K could reduce the moisture content of both WS and CS to below 1% while other drying temperatures could not do so. As it has been previously mentioned, reducing the moisture content of seeds to 0.912% allows the production of quality oil with FFA content of 0.9% [32] which could be directly used in alkaline catalyzed transesterification for biodiesel production [32, 33]. Dried seeds with moisture content less than 1% could also be used in alkaline catalyzed in situ transesterification for biodiesel production [35, 36]. Moreover, although the drying temperature of 353 K could reduce the moisture content of WS and CS to less than 1%, the moisture loss by WS (6.47%) was larger than that of CS (6.21%). Drying of the seed samples at a temperature higher than 353 K has not been tested based on the work done by Subroto et al. [24], where it has been shown that temperatures higher than 333 K could increase oil peroxidation in shell unprotected Jatropha seeds. Oil peroxidation reduces the quality of oil as Jatropha seed has high unsaturated oil content [24]. Therefore, drying the whole Jaatropha seeds at 353 K for 2880 min drying time was considered as optimal for satisfactory drying of Jatropha seeds for oil extraction and in situ biodiesel production.

From the above results and the information from literature, it is possible to say that reducing the moisture contents of the whole Jatropha seeds at storage to its minimum using the aforementioned methods prior to oil extraction has several benefits. For instance, reducing the moisture content of the seed to below 1% could ease oil extraction using non-polar solvents [19, 20]. It could also avoid the post extraction boiling of the oil to remove the oil moisture, and thus, it reduces the possibility of oil peroxidation. According to Subroto [24], Jatropha oil is highly unsaturated and susceptible to lipid peroxidation. Lowering the seed moisture to its minimum could also lower the amount of chemicals required during in situ transesterification process using alkaline catalysts [39]. Moreover, drying Jatropha seeds using the standard heating furnace does not require very specialized expert, and it could be easily performed.

3.4 Drying different collections of the whole seeds

Table 4 shows the initial moisture content (wt%), final moisture loss (wt%) and residual moisture contents/equilibrium moisture contents (EMC) of different whole Jatropha seeds at 353 K. As it could be seen from Table 4, all the seven seed collections had different initial moisture contents. The initial moisture contents of the seed collections named Gerbi, Salmene$_1$, Shekla, Salmene$_3$, Kurkura, Bira and Salmene$_2$ were found to be 8.72, 7.44, 7.12, 6.81, 6.80, 6.71 and 6.51% (wt%), respectively. The differences in moisture contents of the seed collections might be due to differences of the climatic conditions of the area from where the seeds were collected, stage of seed maturity [17] and differences of postharvest processing of the seeds [16]. Moreover, the moisture contents of all the seven seed collections were in the range of safe storage moisture content (6–10%) recommended for Jatropha seed [12].

Figure 4 also presents the weight loss (wt%) of different collections of the whole Jatropha seeds during drying at 353 K as the function of drying time. As it is evident from Fig. 4, the trends of weight loss in the seven seed collections was almost similar. However, the amount of moisture loss by different seed collections differed. As it could be observed from Table 4 and Fig. 4, the final moisture loss by Gerbi collection was the largest (8.58%) and that of Salmene$_2$ (5.36%) was the lowest. The differences in the amount of moisture loss (%) for different collection of Jatropha seeds might be due to the differences of the initial moisture contents, seed sizes and other physical traits for various seed collections. It was reported that seed grain size [53], porosity, shape and surface area [54] are some of the important seed physical properties that affect the drying profile of the seeds. Factors such as the climatic conditions of the seed collection sites, stage of seed maturity and the differences in postharvest processing of the seeds could also influence the moisture loss (%) of the

Table 4 Different seed collections and their initial, final and equilibrium moisture contents, and time to reach EMC

Seed collection	Initial moisture content (wt%)	Final moisture loss (wt%)	Residual moisture (EMC)	Time to reach EMC (min)
Gerbi	8.72	8.58	0.14	2880
Salmene$_1$	7.44	6.80	0.64	1440
Shekla	7.12	6.77	0.35	2880
Salmene$_3$	6.81	6.47	0.34	2880
Kurkura	6.80	6.17	0.63	1440
Bira	6.71	5.97	0.74	2880
Salmene$_2$	6.51	5.36	1.15	1440

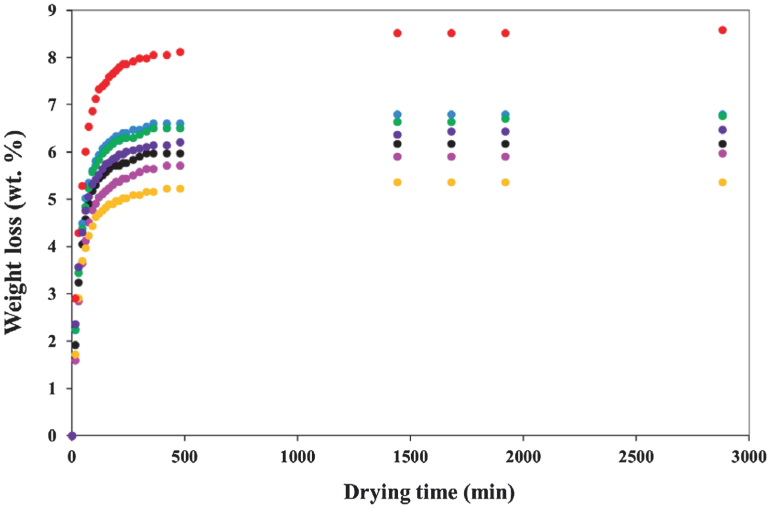

Fig. 4 Weight loss (wt%) of (●) Salmene$_2$, (●) Bira, (●) Kurkura, (●) Salmene$_3$, (●) Shekla, (●) Salmene$_1$ and (●) Gerbi collections of Jatropha seeds dried at 353 K

seed collections as these factors could affect the moisture contents of the seeds [16, 17].

As it could be seen from Table 4, drying temperature of 353 K reduced the residual moisture contents of the six seed collections to below 1%, however the residual moisture content of Salmene$_2$ (1.15%) was above the recommended value for oil extraction and in situ transesterification for biodiesel production.

4 Conclusions

Moisture content of Jatropha seeds is one of the important parameters that determine the quantity and quality of oil produced from the seeds. As it is impractical to dry oilseeds such as Jatropha to lower moisture content and keep it up at storage, drying of the stored seed for oil extraction and/or in situ biodiesel production is foremost important. From the investigation of the effects of drying air temperature ranged from 313 to 353 K on the drying process of the whole and crushed Jatropha seeds at storage condition, it was found that the rise in operating temperature accelerated the drying process of the seeds. The weight loss (wt%) of crushed seeds due to moisture evaporation was faster than that of the whole seeds, however, the drying process of the whole seed at 353 K resulted in the maximum weight loss of 6.47%, which was larger than that of the crushed seeds (6.21%). The lowest residual moisture content (0.34%) was also found in case of the whole seeds of Jatropha dried at 353 K. Thus, it could be concluded that drying the whole seeds of Jatropha at 353 K for 288 min was considered as the optimal for the satisfactory drying of the seeds for oil extraction and/or for in situ biodiesel production.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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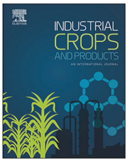

Mathematical modelling of the drying kinetics of *Jatropha curcas* L. seeds

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A B S T R A C T

Jatropha (*Jatropha curcas* L) seed contains non-edible oil, which is suitable for biodiesel production. The present research focused on the mathematical modelling of the drying kinetics of Jatropha seeds at a storage moisture content. The non-pretreated seeds (whole seeds) and pretreated seeds (crushed seeds) were dried at five different air temperatures (313, 323, 333, 343 and 353 K) in a standard heating furnace. The moisture loss from the seeds was systematically recorded, converted to moisture ratio, and fitted to four semi-theoretical drying mathematical models: Lewis, Henderson and Pabis, Page and Avhad and Marchetti models. The fitness of the models were compared using the coefficient of determination (R^2), chi-square test (X^2), root mean square error (R_{MSE}), mean bias error (MBE), and mean absolute error (MAE). It was found that an increase in the air temperature caused a reduction in the drying time of both the whole and crushed seeds. From the tested models, the Avhad and Marchetti model showed the best fitting to the experimental data with R^2 varied from 0.9914 to 0.9969 and 0.9908 to 0.9917 for all tested temperatures for the whole seeds and crushed sees of Jatropha, respectively. The Avhad and Marchetti mode showed superior fit to the experimental data at the drying temperature of 313 K with R^2 of 0.9969 for the whole seed, and at 333 K in case of crushed seeds for which the R^2 value was 0.9917. The activation energy values of 33.53 and 32.885 KJ mol^{-1}were obtained for the whole and crushed seeds, respectively when the best-fitted model was used.

1. Introduction

Biodiesel has been used as an alternative fuel to fossil engines. This importance of biodiesel has increased as a result of the depletion of world petroleum reserves, increased demand for fuels, and the negative environmental impacts of exhaust gases from fossil fuels (Kamel et al., 2018; Singh and Singh, 2010). Jatropha (*Jatropha curcas* L.) is one of the plants with promising potential for the production of biodiesel (Salehi Jouzani et al., 2018; Siqueira et al., 2012), and the production of biodiesel from the seed of this plant has been promoted due to its social, economic and environmental positive effects compared to the fossil fuels (Eckart and Henshaw, 2012; Pandey et al., 2012; Zahan and Kano, 2018). Moreover, investigations on the selection of the most promising accessions of Jatropha plants to get better oil yield, and oil with higher quality for biodiesel production are continued (Alburquerque et al., 2017; Kumar and Das, 2018).

Sustainable production oil crops and biodiesel without affecting food security is highly desirable towards meeting the increasing global energy demands (Mazumdar et al., 2018). Due to the presence of major toxic compound (the phorbol esters) in Jatropha seed oil (Amkul et al., 2017; Becker and Makkar, 2008; He et al., 2017), production of biodiesel from the seeds does not compete with human consumption (Becker and Makkar, 2008). Using non-edible biodiesels feedstocks such as Jatropha could be a good alternative to overcome the problems that could occur due to continuous conversion of edible oils to biodiesel (Atabani et al., 2012; Sajjadi et al., 2016). Jatropha can well adapt to dry and marginal lands with low soil fertility, and thus, it does not compete for arable lands (Atabani et al., 2013; Basili and Fontini, 2012).

Renewable biodiesels that can be produced within the petroleum importing countries will enable the countries to be less dependent upon the imported fossil oil. Biodiesel production also creates employment opportunity to the rural people through cultivation of oil producing plants, and this could contribute to the improvement of the domestic economy (Datta and Mandal, 2014). The seedcake produced as the by-product of oil extraction can be changed to organic fertilizer through

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Abbreviations: a, model coefficient; CS, crushed seeds; FFA, free fatty acids; k, drying constants (min^{-1}); MAE, mean absolute error; MBE, mean bias error; M_e, equilibrium moisture content; M_0, initial moisture content; MR, moisture ratio; M_t, moisture content at time t; N, model coefficient; PSCS, particle sizes of the crushed seeds; R^2, coefficient of determination; R_{MSE}, root mean square error; t, drying time (min); WS, whole seeds; wt. %, weight percentage; X^2, chi-square test

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composting and serve as an alternative to mineral fertilizer (Olowoake et al., 2018). Composted organic fertilizer is ecofriendly, and very important and useful input for the enhancement soil health, and it could reduce the N_2O emissions caused by nitrogen containing chemical fertilizers (Basili and Fontini, 2012). Moreover, biodiesel could be used as a fuel alternative in diesel engines to improve combustion efficiency and decrease emissions of the major air pollutants (Teixeira et al., 2012).

Generally, the benefits of using biodiesel include its renewability and biodegradability, low sulfur content and having natural lubricity (Sajjadi et al., 2016), non-toxicity, domestic origin and contributions to the reduction of most pollutant emissions (Firoz, 2017; Sajjadi et al., 2016).

Jatropha seeds can be harvested at different fruit maturity stages, and proper postharvest processing is required as the postharvest management of the seeds greatly affects the quality the product. One of the important factors that one has to give due consideration during postharvest processing is the moisture content of the seed, and it should be lowered just after harvest to minimize the loss of quality (Lang and Farouk, 2013). Thus, determination of the moisture content of the oilseed is an unavoidable operation during seed harvesting, transportation, storage, grinding and oil extraction as seed moisture affects the quality of the seed, the oil and biodiesel to be produced (Soltani et al., 2014). According to Brittaine and Lutaladio (Brittaine and Lutaladio, 2010), Jatropha seeds that are harvested from green, yellow and brown fruits could have different moisture contents and should be dried to a moisture content of around 6–10% prior to storage.

Lower Jatropha seed moisture contents compared to the normal seed storage moisture content were recommended by several researchers in order to obtain higher percentage of oil yield, and quality oil and biodiesel. For instance, in the extraction of Jatropha oil from ground kernel with moisture content of 0.912%, using Soxhlet extractor and hexane as solvent, Kadry (Kadry, 2015) obtained a maximum of 45% oil that contained 0.9% free fatty acids. The author reported that the oil obtained did not need pretreatment with acid for basic catalyzed biodiesel productions (Kadry, 2015) as its free fatty acid is less than 1% (Botero et al., 2017; Kombe and Temu, 2017). In biodiesel production from Jatropha seeds through in situ transesterification by alkaline catalyst, seeds with moisture content less than 1% was also used to prevent saponification (Kartika et al., 2013). Moreover, drying seed could reduce the amount of chemical input during in situ biodiesel production process. Haas and Scott (Haas and Scott, 2007) found that a reduction of 60% methanol and 56% sodium hydroxide input when soybean flakes with moisture contents of 7.4% were dried to the lowest moisture content (to around 0%) before in situ transesterification.

As the production and demand of Jatropha seeds increases, the existing and new technologies should be adjusted for the proper functioning of the machineries used for cultivation of Jatropha and postharvest processing of the seeds (Siqueira et al., 2012). Determination of the physical properties of seeds and their relation to the seed moisture content enables the improvement of the design of the equipment used for seed harvesting and postharvest processing (Kumar and Sharma, 2008).

Drying is one of the most important postharvest steps as it directly affects the quality of the oil, which is the main product of the Jatropha (Siqueira et al., 2013). Drying could be defined as the process of moisture removal due to heat and mass transfer between the biological product and the drying air through evaporation, and generally caused by temperature and air convection forces (Perea-Flores et al., 2012). Mathematical modeling of the drying process of the seeds helps to predict the behavior of moisture removal from the seeds, reduce the time and costs of seed drying, and helps in the invention of appropriate drying equipment (Siqueira et al., 2012, 2013).

A few available reports on the mathematical modeling of the drying process of Jatropha seeds and/or fruit focused on the drying kinetics of freshly collected seed or fruits, which contained relatively larger moisture compared to the seed at storage conditions. For instance, the mathematical modeling of drying kinetics of Jatropha seeds (Siqueira et al., 2012; Subroto, 2015) and fruits (Siqueira et al., 2013; Uthman and Onifade, 2016) were carried out on the freshly collected seeds and/or fruits. To the knowledge of the authors, drying kinetic studies on Jatropha seeds at a storage moisture content has not been reported. Thus, the primary objective of this research was to adjusted different drying mathematical models to experimental data from the drying of Jatropha seeds at a storage moisture content under different air temperatures for oil extraction and /or in situ biodiesel production, and select the model that best represents the drying process.

The current paper presents two new issues that have not been done in other works of mathematical modeling of the drying kinetics of Jatropha seeds. Firstly, the current paper deals with the mathematical modeling of the drying kinetics of *Jatropha curcas* L. seeds at a storage condition, and the seeds with moisture content of 6.81% (wt. %) was used for the drying experiments. The drying of seeds at storage might be done when one needs to reduce the moisture contents of the seeds to its minimum for oil extraction and /or for in situ biodiesel production. As aforementioned, in the previous studies of the mathematic modelling of the drying kinetics of Jatropha seeds or fruits, freshly collected seeds/fruits were used for the drying experiments. Secondly, Avhad and Marchetti drying mathematical model (Avhad and Marchetti, 2016), the model recently developed by the combination of the Page model and the Henderson and Pabis model, was used. This drying mathematical model has not been used in the previous studies for Jatropha seeds.

As this study deals with the mathematical modelling of the drying kinetics of Jatropha seeds, its focus is only on the process of moisture removal from the seeds at storage moisture content. Thus, the experiments on the effects of the pretreatment on the oil content and oil composition have not been done for this paper.

2. Methodology

2.1. Materials

Jatropha seed at a storage moisture content was used for the drying experiment. The detailed materials used during the drying experiments was described in the study of the effects of drying temperatures and pretreatment of the seeds on the drying process and physical appearance of different collections of Jatropha seeds and has been presented elsewhere (Keneni and Marchetti, 2018). A bowl-shaped mortar and pestle were used for crushing the pretreated Jatropha seeds. The particle sizes of the crushed seeds was estimated by three different stainless steel sieves with opening sizes of 500 μm, 1 mm and 2 mm woven cloth (Control Group, 15-D2245/J, 15-D2215/J and 15-D2185/J). Digital balance (Mettler-Toledo, PG 5002 Delta Range, Switzerland) with 0.01 mg accuracy was used to weigh the seeds samples. The samples were placed on the pyrex glass petri plates during drying. The drying experiments and determination of the initial and residual moisture contents of the seed samples were performed using a standard heating furnace (Narbetherm P300, Germany).

2.2. Seed drying experiments

The seed drying experiments were performed in the Laboratory of Norwegian University of Life Sciences (NMBU), Faculty of Science and Technology. The initial moisture contents of the Jatropha seed samples used for this experiment has been determined prior to this experiment (Keneni and Marchetti, 2018) by drying 15 g seeds at 105 °C for 24 h (Bamgboye and Adebayo, 2012; Garnayak et al., 2008; Siqueira et al., 2012; Subroto, 2015). Accordingly, the moisture content of the seeds was found to be 6.81% (wt. %), and thus, the moisture content of the seed samples used for the experiment was in the range of the recommended storage moisture content (6–10%) for Jatropha seeds (Brittaine and Lutaladio, 2010).

The pretreated (crushed seeds, CS) and non-pretreated (the whole seeds, WS) were used for the drying experiments. After crushing the seeds using mortar and pestle, the particle sizes of the pulverized seeds were estimated by three different sieves with openings of 500 μm, 1 mm and 2 mm woven cloth. For every drying experiment, ca. 15 g of Jatropha seeds were used and both treatments were duplicated. Thus, the crushed seeds used in the drying experiment was a mixture of four particles sizes. The average proportions (%) of the particle size of crushed seeds (PSCS): PSCS > 2 mm, 2 mm > PSCS > 1 mm, 1 mm > PSCS > 500 μm and PSCS < 500 μm were 14.95 ± 8.2, 29.96 ± 4.38, 35.32 ± 10.5 and 19.77 ± 4.74, respectively.

The pretreated (crushed seeds) and non-pretreated (whole seeds) seeds were placed on separate petri plates, and dried at five different drying temperatures (313, 323, 333, 343, and 353 K) in the standard heating furnace. The seed samples were weighted before inserting into the heating furnace, during the progress of the drying experiments (at the predetermined time intervals) and at the end of the drying experiments. The temperature of the heating furnace was set at the required drying temperature and maintained the set temperature for an hour before placing the samples in the furnace. This was to minimize the fluctuation of the surrounding drying air temperature during drying (Avhad and Marchetti, 2016). During the experiments, the seed samples were removed from the heating furnace at a predetermined time interval, weighted and put back into the furnace by taking less than 10 s to weigh the samples. The experiments were performed until no change in weight had been recorded for three successive weight measurements for the respective drying temperatures, which was assumed as the stage of equilibrium. Accordingly, the drying experiment at a particular temperature was carried out for four days (5760 min) in order to ensure the achievement of the critical moisture level at which no more moisture loss occurred. Every experiments were done twice and the average values were used in data analysis and reporting.

Drying data obtained from the weight measurements of the seed samples at different temperatures and drying times were changed to moisture content data in order to use it in the drying kinetics.

2.3. Mathematical modeling for the drying kinetics

Mathematical modeling of the seed drying is used to determine the optimum drying parameters and the performance of the process. It is essential to select the drying mathematical model that fits best to the drying curves under different conditions (Fudholi et al., 2012). To predict the drying kinetics of Jatropha seeds, mathematical modeling of the process of moisture evaporation from the seed is needed.

In the current study, the drying data from five different drying temperatures were fitted to three selected mathematical models: Lewis, Henderson and Pabis, and Page models. These were the most commonly used mathematical models to predict the drying process of different biological materials (Ghodake et al., 2006). The experimental data were also fitted to the Avhad and Marchetti model, which is a combination of Page model and Henderson and Pabis model and found to be best fitted to the drying kinetics of Hass avocado seeds (Avhad and Marchetti, 2016). The models mentioned above are all semi-theoretical, as in agreement with the references Chukwunonye et al. (Chukwunonye et al., 2016) and McMinn et al. (McMinn et al., 2005). These semi-theoretical models were the most commonly used and discussed models in literature for similar products, and they are used for the current study based on the information obtained from the literature.

In the present experiment, the recorded weight loss data of the seed samples at different time intervals were converted to the moisture loss data. From the initial moisture content of the seed, the moisture content data at different time intervals and the residual moisture contents for different temperatures, the dimensionless moisture ratio (MR) was calculated. Then, the MR as a function of time was used for fitting the mathematical models. The expression used to calculate the MR of Jatropha seed samples was written in Eq. (1).

$$\mathrm{MR}=\frac{\mathrm{M_t}-\mathrm{M_e}}{\mathrm{M_0}-\mathrm{M_e}} \tag{1}$$

where, $\mathrm{M_0}$, $\mathrm{M_t}$ and $\mathrm{M_e}$ refer to the initial moisture content, moisture content at time t, and the equilibrium moisture content for the seed samples, respectively. The equilibrium moisture content ($\mathrm{M_e}$) of Jatropha seeds at each temperature was obtained experimentally by drying the seed samples in the oven until no change in weight occurred for three successive weight measurements (Siqueira et al., 2012).

The activation energy that is required to start the drying process, namely water activation of the seed (Voća et al., 2007), could be found using the Arrhenius equation. It is the energy barrier that should be overcome in order to trigger moisture diffusion during drying (Perea-Flores et al., 2012). In the present study, the drying rate constant “k” and the drying activation energies (Ea) were used to analyze the change of moisture content at different temperatures. Activation energies (Ea) for the crushed and whole seeds of Jatropha were obtained from the slopes of the plots of ln(k) versus T^{-1} predicted using the experimental data for the tested models using Arrhenius equation. Then, the k values calculated from the activation energy for the respective drying temperatures were inserted into the expression of all drying mathematical models. Similarly, the rate constant k was used in the studies of drying kinetics of *Cuminum cyminum* grains (Zomorodian and Moradi, 2010), Jatropha seeds (Siqueira et al., 2012), plantain sample (Oforkansi and Oduola, 2016), and pumpkin fruit slices (Onwude et al., 2016a). Based on the information obtained from the aforementioned publications, the drying rate constant “k” and the drying activation energies (Ea) were used in this paper. Arrhenius equation is presented in Eq. (2).

$$\mathrm{k}=\mathrm{A}\exp\left(-\frac{\mathrm{Ea}}{\mathrm{RT}}\right) \tag{2}$$

where, k refers to rate constant, A is the pre-exponential factor, Ea is the activation energy (KJ $\mathrm{mol}-{}^{1}$), R is the universal gas constant (8.314 J $\mathrm{mol}^{-1}\mathrm{K}$), and T is the absolute air temperature (K).

2.3.1. Lewis model

Lewis model is the simplest model as it contains only one model constant. The model has been widely applied in describing the drying behavior of different agricultural products (Onwude et al., 2016b). According to Lewis (Lewis, 1921), the change in moisture content in the falling rate period of drying is proportional to the instantaneous difference between the moisture content and the expected moisture content when it comes into equilibrium with the humidity of the surrounding drying air. Lewis model neglects the resistance to the moisture movement from the inner to the surface of the material during drying. Although the model is simple to use, it underestimates the initial parts of drying curve and overestimates later phases (Chukwunonye et al., 2016). Lewis model was used to fit the dryings of black tea (Panchariya et al., 2002), grape seeds (Roberts et al., 2008) and strawberries (Changrue et al., 2008). The expression for the model is presented in Eq. (3).

$$\mathrm{MR}=\exp(-\mathrm{kt}) \tag{3}$$

where, k is the model constant that follows an Arrhenius equation, and t is the time.

2.3.2. Henderson and Pabis model

The Henderson and Pabis model is related to Fick’s second law, and sometimes it is named as bi-parametric exponential model (Zhang et al., 2016). The Henderson and Pabis model has produced good fit in predicting the drying of orange seed (Rosa et al., 2015), African breadfruit (Shittu and Raji, 2011) and dill leaves (Dikmen et al., 2018). The model is presented in Eq. (4).

$$\mathrm{MR}=\mathrm{a}\exp(-\mathrm{kt}) \tag{4}$$

where, a and k are the constants of the model that follow Arrhenius equation.

2.3.3. Page model

The Page model is a two constant empirical modification of the Lewis model that corrects some shortcomings (Zhang et al., 2016). Page model has been used to describe the drying process of bay leaves (Gunhan et al., 2005), cashew kernels (Shittu and Raji, 2011), mango slices (Akoy, 2014), and moringa seeds (Aremu and Akintola, 2016). The model expression can be seen in Eq. (5).

$$MR = \exp(-kt^N) \quad (5)$$

where, k and N are the constants of the model.

2.3.4. Avhad and Marchetti model

The Avhad and Marchetti model is a mathematical model that was developed by the combination of the Page model and the Henderson and Pabis model, and successfully fitted to the drying kinetics of Hass avocado seeds (Avhad and Marchetti, 2016). Avhad and Marchetti model takes into account the benefits of the three discussed models together, and that its fitness could be equally good or better. However, since the model has some parameters to be determinate due to the experimental data, it is not 100% certain that the model will always give equally good or better results. The Avhad and Marchetti model is presented in Eq. (6).

$$MR = a\exp(-kt^N) \quad (6)$$

where, a, k and N are the constants of model.

The coefficients of the drying mathematical models and the regression/statistical parameters were obtained using the optimization mechanism of Microsoft excel solver (Microsoft Excel, 2013) (Oforkansi and Oduola, 2016).

2.4. Comparison of the fitness of the models

The values of five statistical parameters were used to compare the fitness of the data predicted by the drying mathematical models to the drying curves of the experimental data. The parameters utilized include coefficient of determination (R^2), chi-square test (X^2), root mean square error (R_{MSE}), mean bias error (MBE), and mean absolute error (MAE). The statistical parameters for comparison of the models were selected based on other similar publications where these parameters were used for the selection of the most fitted model. This standard procedure has been accepted in the literature for such comparisons. For instance, in the papers of Gunhan et al. (Gunhan et al., 2005), Zomorodian and Moradi (Zomorodian and Moradi, 2010), Sridhar and Madhu (Sridhar and Madhu, 2015), Naderinezhad et al. (Naderinezhad et al., 2016), Oforkansi and Oduola (Oforkansi and Oduola, 2016), and Mazandarani et al. (Mazandarani et al., 2017) similar parameters were used to compare the fitness of different models.

R-squared or coefficient of determination (R^2) is the measures of how close the statistical data could fit the regression line (Onwude et al., 2016a). According to Gunhan et al. (Gunhan et al., 2005), the R_{MSE} provides information on the short-term performance and its value is always positive while MBE gives information on the long-term performance of the correlations by comparing the actual deviation between predicted and experimental values term by term. The author also indicated that for both R_{MSE} and MBE, the ideal value is ‘zero’.

The value of R^2 is the primary criteria for selecting the best-fit model to the drying kinetics of agricultural products (Doymaz, 2010). During the comparison of the fitness of the models to the experimental drying curves, the most fitted model must have the largest values of R^2, and conversely, it should have the smallest values of X^2, R_{MSE}, MBE and MAE (Younis et al., 2018; Zhang et al., 2016).

The statistical parameter R^2 was calculated according the expressions by Oforkansi and Oduola (Oforkansi and Oduola, 2016). The other statistical parameters were calculated using the equations used by Gunhan et al (Gunhan et al., 2005), Zomorodian and Moradi (Zomorodian and Moradi, 2010), Sridhar and Madhu (Sridhar and Madhu, 2015), Naderinezhad et al. (Naderinezhad et al., 2016), Oforkansi and Oduola (Oforkansi and Oduola, 2016), Avhad and Marchetti (Avhad and Marchetti, 2016), and Mazandarani et al. (Mazandarani et al., 2017). The expression for these statistical parameters were written in Eqs. (7)–(11) as:

$$R^2 = 1 - \left(\frac{\sum_{i=1}^{N}(MR_{pre,i} - MR_{exp,i})^2}{\sum_{i=1}^{N}(MR_{exp,i} - \bar{MR}_{exp})^2}\right) \quad (7)$$

$$X^2 = \frac{\sum_{i,=1}^{N}(MR_{ex,i} - MR_{pr,i})^2}{N - z} \quad (8)$$

$$E_{RMS} = \left[\frac{1}{N}\sum_{i,=1}^{N}(MR_{ex,i} - MR_{pr,i})^2\right]^{\frac{1}{2}} \quad (9)$$

$$MBE = \frac{1}{N}\sum_{i=1}^{N}(MR_{ex,i} - MR_{pr,i}) \quad (10)$$

$$MAE = \frac{1}{N}\sum_{i=1}^{N}|MR_{ex,i} - MR_{pr,i}| \quad (11)$$

where, $MR_{exp,i}$ is the i^{th} experimental moisture ratio; $MR_{pre,i}$ is the i^{th} predicted moisture ratio; $\bar{MR}_{exp}$ is the mean of the experimental moisture ratio; N refers to the number of observations; z represents the number of constants in the models.

3. Results and discussion

3.1. Moisture ratio and seed drying process

The weight loss data collected during Jatropha seed dryings were converted to moisture ratios and their variations as a function of drying time were plotted. Fig. 1a and b show the moisture ratio versus drying time at the drying temperatures of 313, 323, 333, 343 and 353 K. As it

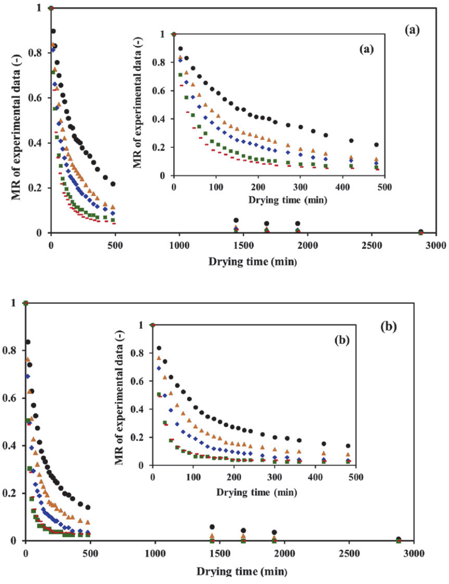

Fig. 1. (a) Moisture ratio vs. drying time at different air temperatures for the whole seeds: (●) 313 K, (▲) 323 K, (◆) 333 K, (■) 343 K and (–) 353 K; (b) Moisture ratio vs. drying time at different air temperatures for the crushed: (●) 313 K, (▲) 323 K, (◆) 333 K, (■) 343 K and (–) 353 K.

can be observed from Fig. 1a and b, rises in the dying temperature resulted in the increasing of the rate of moisture evaporation from the seed samples. Similar behavior was observed in a number of agricultural products such as grape seeds (Roberts et al., 2008), pumpkin seeds (Jittanit, 2011), caster bean (Perea-Flores et al., 2012), fresh Jatropha seeds (Siqueira et al., 2012), sorghum grains (Resende et al., 2014), orange seeds (Rosa et al., 2015) and Hass avocado seeds (Avhad and Marchetti, 2016). According to Siqueira et al. (Siqueira et al., 2012) and Rosa et al. (Rosa et al., 2015), rising in temperature increases the difference between the vapor pressure of the drying air and that of the seed samples, thus, higher temperature results in greater and faster water removal.

As it could be seen from Fig. 1a, in the WS of Jatropha, the drying time required to reduce the moisture ratio to below 0.5 when using 313 K was about 5 times more than that required at 353 K drying temperature. The time taken to reduce the moisture ratio of CS to below 0.5 at 313 K was also 6 times longer than when it was dried at 353 K, as it can be seen in Fig. 1 b. Moreover, the reduction of moisture ratios of the WS to below 0.5 when drying at 313 K and 353 K required twice more times compared to that of the CS dried at the respective temperatures. The greater moisture evaporation rate for the CS compared to that of the WS might be due to the greater surface area exposed to the drying temperature in the case of the CS.

In the drying of the whole seeds (Fig. 1a) and the crushed seeds (Fig.1b) of Jatropha, the moisture evaporation rate was faster at the beginning due to high level of water to be removed, and decreasing as the equilibrium moisture content approached. According to Sandeepa et al. (Sandeepa et al., 2013), in the drying experiment, the decreasing of drying rate from the initial to the end of drying shows the non-existence of constant rate period or the existence of constant rate for an insignificant period of time relative to the entire time of drying. During drying, the rate of moisture evaporation will be higher at the early stage of drying due to larger moisture content of the seeds, and reduces as the moisture content decreases.

3.2. Determination of activation energy

Fig. 2a and b show the plot of ln(k) versus T^{-1} for WS and CS of Jatropha, respectively at the five drying temperatures when Avhad and Marchetti model (Avhad and Marchetti, 2016) was used. The computed value of the activation energies and pre-exponential factors for the employed models are also presented in Table 1. As it can be seen from Table 1, the activation energy value for the whole seeds and crushed seeds of Jatropha varied from 23.67 to 36.06 and 32.88 to 45.75 KJ mol^{-1}, respectively for all mathematical models used. The activation energies of the WS and CS of Jatropha were in line with those reported for other agricultural products such as sorghum (Resende et al., 2014), grape seeds (Roberts et al., 2008), sliced, and crushed Hass avocado seeds (Avhad and Marchetti, 2016) and castor oil seeds (Perea-Flores et al., 2012).

As it can be observed from Table 1, the activation energy of the CS was greater than that of the WS and this was unexpected as the rate of water evaporation in the crushed seed was faster than that of the WS. In the study of activation energy of water release rate from corn kernel, Voća, et al. (Voća et al., 2007) found that the drying rate constant k significantly increased with the increasing of drying air temperature, and described activation energy as the energy that needs to be supplied to kernels for initiating the moisture release. The authors concluded that if the activation energy is higher, the moisture release from the kernels became slower. Generally, the values of activation energy are related to the nature of a materials to be dried, and thus, if water is more strongly bounded to the structure of the material, it will be more difficult to removed it (Bezerra et al., 2015). The present result was in contrary to the finding of Avhad and Marchetti (Avhad and Marchetti, 2016) in which the activation energy of the crushed Hass avocado seeds (24–32 KJ mol^{-1}) was found to be less than that of the sliced (34–36 KJ mol^{-1}) and non-pretreated (43–129 KJ mol^{-1}) seeds.

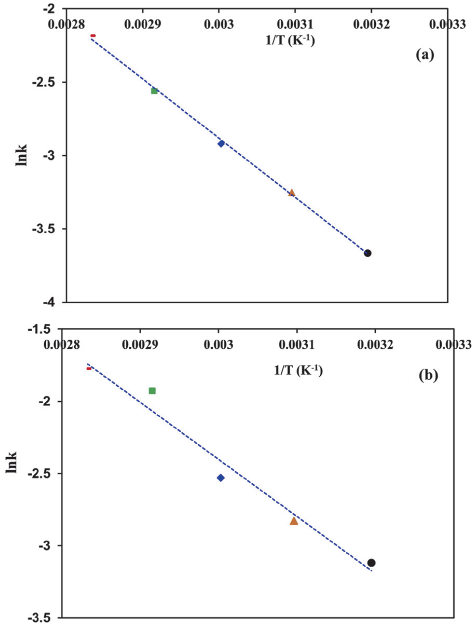

Fig. 2. (a) Arrhenius plot between ln(k) versus 1/T for the whole seeds of Jatropha using Avhad and Marchetti model: (●) 313 K, (▲) 323 K, (◆) 333 K, (■) 343 K and (–) 353 K; (b) Arrhenius plot between ln(k) versus 1/T for the crushed seeds of Jatropha: (●) 313 K, (▲) 323 K, (◆) 333 K, (■) 343 K and (–) 353 K.

Table 1
Estimated activation energy and pre-exponential factor for the whole seeds and crushed seeds of Jatropha.

Models	Whole seeds		Crushed seeds	
	Ea (KJ mol^{-1})	A	Ea (KJ mol^{-1})	A
Lewis	35.5956	3.8372×10^3	42.333	8.253×10^4
Henderson and Pabis	36.063	3.891×10^3	45.753	2.563×10^5
Page	23.6706	2.8911×10^4	35.7759	3.468×10^4
Avhad and Marchetti	33.533	1.0064×10^4	32.885	1.288×10^4

3.3. Mathematical modeling of seed drying

The predicted data by the employed mathematical models were fitted to the drying curves of the experimental data of the WS and CS of Jatropha to select a model that best describe the drying process of the seeds. Figs. 3a–c and 4 a–c show the comparison of the four drying mathematical models and the experimental data obtained for the WS and CS of Jatropha, respectively at 313 K (the lowest), 333 K (medium) and 353 K (the highest) air temperatures of the experiments. As it could be seen from the graphical presentations, all the employed models could describe the drying kinetics of the Jatropha seeds. However, the selection of best fit mathematical model was based on the values R^2, X^2, R_{MSE}, MBE and MAE, and as it was aforementioned, the selection of best fit is primarily based on the values of R^2 (Doymaz, 2010). In the mathematical modelling of the drying kinetics castor oil seeds, Perea-

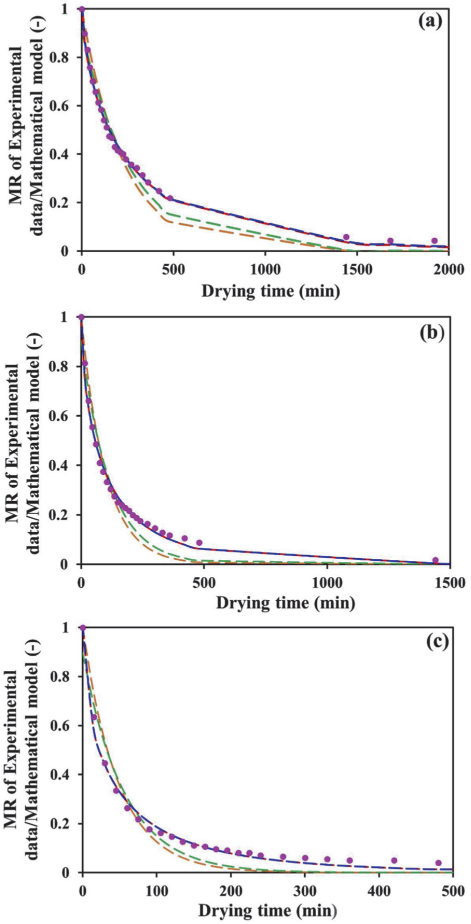

Fig. 3. Comparison of the experimental and predicted moisture ratios using the four different drying mathematical models at (a) 313 K, (b) 333 K and (c) 353 K for the whole seeds of Jatropha: (●) Experimental data, (—) Lewis model, (—) Henderson and Pabis model, (—) Page model and (—) Avhad and Marchetti model.

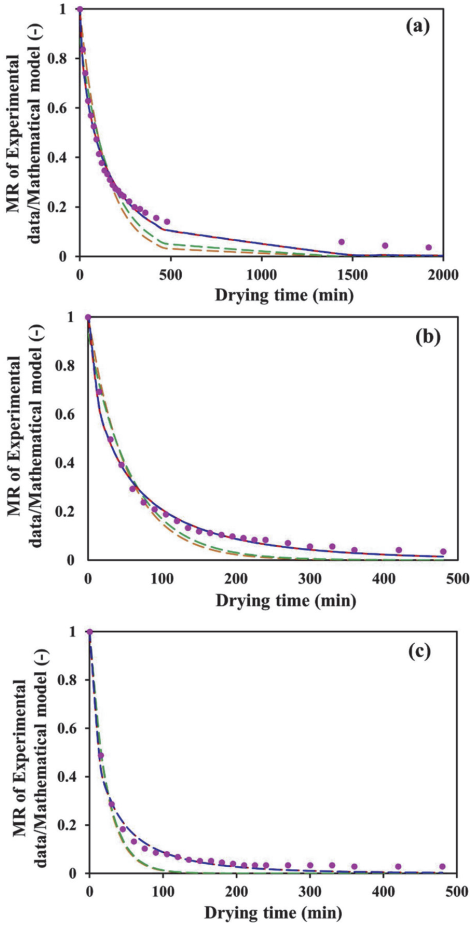

Fig. 4. Comparison of the experimental and predicted moisture ratios using the four different drying mathematical models at (a) 313 K, (b) 333 K and (c) 353 K for the crushed seeds of Jatropha: (●) Experimental data, (—) Lewis model, (—) Henderson and Pabis model, (—) Page model and (—) Avhad and Marchetti model.

Flores et al. (Perea-Flores et al., 2012) accepted the mathematical models with R^2 values greater than 0.97 as fit models to the experimental data.

The calculated statistical parameters for the WS and CS of Jatropha for all the four models and the drying air temperatures (313–353 K) is presented in Table 2. As it can be seed from Table 2, the values of R^2, X^2, R_{MSE}, MBE and MAE for the WS of Jatropha for all the drying models and drying temperatures ranged from 0.9278 to 0.9969, 2.37×10^{-4} and 4.29×10^{-3}, 0.01454 and 0.06427, $1.95 \times 10^{-3}$and 2.97×10^{-2}, and 0.01171 and 0.05559, respectively. In the CS of Jatropha, the R^2, X^2, R_{MSE}, MBE and MAE values changed between 0.9361 and 0.9917, 4.18×10^{-4} and 4.01×10^{-3}, 0.02039 and 0.06224, 3.64×10^{-3} and 0.04043, and 0.01639 and 0.05318, respectively.

From the four mathematical models, the Avhad and Marchetti model was found to show best fit to experimental data, with the values of coefficient of determination ranging from 0.9914 to 0.9969 and 0.9908 to 0.9917 for the WS and CS of Jatropha, respectively when analyzing all temperature ranges. In the drying of the WS, the values of R^2 for Avhad and Marchetti model were the closest to 1 when compared to that of all other models used. The maximum value of R^2 (0.9969) and the smallest values of X^2 (2.37×10^{-4}), R_{MSE} (0.01454), MBE (1.95×10^{-3}) and MAE (0.01171) were obtained when the whole seeds were dried at 313 K and the Avhad and Marchetti mode (Avhad and Marchetti, 2016) was employed. Moreover, in the drying of crushed seeds of Jatropha, the maximum R^2 value (0.9917) was obtained when the seeds were dried at 333 K and Avhad and Marchetti model was used. The smallest values of E_{RMS} (0.02039) and MBE (3.64×10^{-3}) for crushed seeds were also found when Avhad and Marchetti model was used.

The Page model was found to have a satisfactory fitting with the experimental data as well. Although the fitness of Page model was comparable to that of Avhad and Marchetti, the latter model was found to be superior to fit to the experimental data. As it could be seen from Table 2, the value of R^2 for Avhad and Marchetti model were slightly larger than that of Page model while the X^2 and other statistical parameters for Avhad and Marchetti model were found to be smaller

Table 2
Results obtained from the statistical analysis of the four selected drying mathematical models at 313–353 K temperatures for the whole seeds and crushed seeds of Jatropha.

Model	Temperature (K)	Whole seeds					Crushed seeds				
		R^2	X^2	E_{RMS}	MBE	MAE	R^2	X^2	E_{RMS}	MBE	MAE
Lewis	313	0.9607	2.82×10^{-3}	0.05217	0.005330	0.045256	0.9361	4.01×10^{-3}	0.06224	0.01201	0.05318
	323	0.9397	3.75×10^{-3}	0.06008	−0.00946	0.05189	0.9372	3.61×10^{-3}	0.05898	0.02363	0.05199
	333	0.9278	4.29×10^{-3}	0.06427	0.02604	0.05559	0.9441	3.12×10^{-3}	0.05467	0.03314	0.05066
	343	0.9356	3.48×10^{-3}	0.05787	0.01858	0.05071	0.9442	2.69×10^{-3}	0.05077	0.00717	0.04071
	353	0.9304	3.40×10^{-3}	0.05724	0.02972	0.05056	0.9536	2.19×10^{-3}	0.04577	0.04043	0.04231
Henderson and Pabis	313	0.9775	1.67×10^{-3}	0.03948	0.00908	0.03426	0.9583	2.72×10^{-3}	0.05026	0.01408	0.04218
	323	0.9646	2.29×10^{-3}	0.04601	0.00555	0.03742	0.9539	2.76×10^{-3}	0.05055	0.02205	0.04356
	333	0.9506	2.82 × 10-3	0.05318	0.02124	0.04627	0.9534	2.72×10^{-3}	0.04990	0.03018	0.047441
	343	0.9495	2.84×10^{-3}	0.05123	0.01991	0.04371	0.9508	2.48×10^{-3}	0.04763	0.01527	0.04081
	353	0.9412	2.99×10^{-3}	0.05262	0.027791	0.04715	0.9563	2.16×10^{-3}	0.04444	0.03820	0.04131
Page	313	0.9964	2.63×10^{-4}	0.01563	3.63×10^{-3}	0.01223	0.9908	5.98×10^{-4}	0.02356	6.61×10^{-3}	0.01881
	323	0.9959	2.65×10^{-4}	0.01565	3.37×10^{-3}	0.01366	0.9913	5.19×10^{-4}	0.02190	6.01×10^{-3}	0.01889
	333	0.9926	4.55×10^{-4}	0.02051	438×10^{-3}	0.01554	0.9915	4.96×10^{-4}	0.02128	4.81×10^{-3}	0.01639
	343	0.9912	4.91×10^{-4}	0.02130	5.89×10^{-3}	0.01760	0.9888	5.66×10^{-4}	0.02274	0.01128	0.02052
	353	0.9918	4.18×10^{-4}	0.01965	5.78×10^{-3}	0.01590	0.9907	4.18×10^{-4}	0.02046	7.58×10^{-3}	0.01676
Avhad and Marchetti	313	0.9969	2.37×10^{-4}	0.01454	1.95×10^{-3}	0.01171	0.9913	5.86×10^{-4}	0.02288	5.51×10^{-3}	0.01877
	323	0.9962	2.53×10^{-4}	0.01496	2.48×10^{-3}	0.01336	0.9916	5.23×10^{-4}	0.02152	4.81×10^{-3}	0.01917
	333	0.9931	4.45×10^{-4}	0.01985	3.03×10^{-3}	0.01589	0.9917	5.08×10^{-4}	0.02101	3.64×10^{-3}	0.01701
	343	0.9914	5.00×10^{-4}	0.02104	5.04×10^{-3}	0.01791	0.9889	5.88×10^{-4}	0.02262	1.09×10^{-2}	0.02039
	353	0.9919	4.31×10^{-4}	0.01952	5.36×10^{-3}	0.01610	0.9908	4.78×10^{-4}	0.02039	7.48×10^{-3}	0.01721

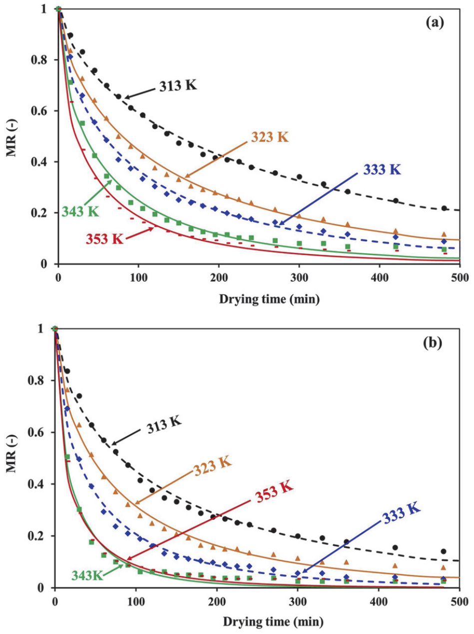

Fig. 5. (a) Comparison of the experimental and predicted moisture ratios using the Avhad and Marchetti drying mathematical model at 313–353 K air temperatures for whole seeds of Jatropha: (●) Experimental data, () model; (▲) Experimental data, (—) model; (♦) Experimental data, (—)model; (■) Experimental data, (—) model; (—) Experimental data, (—) model. (b) Comparison of the experimental and predicted moisture ratios using the Avhad and Marchetti drying mathematical model at 313–353 K air temperatures for crushed seeds of Jatropha: (●) Experimental data, () model; (▲) Experimental data, (—) model; (♦) Experimental data, (—)model; (■) Experimental data, (—) model; (—) Experimental data, (—) model.

Table 3
Constants of the Avhad and Marchetti model for the whole seeds and crushed seeds of Jatropha.

Temperature	Whole seeds			Crushed seeds		
	k (min^{-1})	a	N	k (min^{-1})	a	N
313	0.0255	1.0263	0.6663	0.04186	1.0219	0.6459
323	0.0379	1.0186	0.6684	0.0619	1.0244	0.6399
333	0.0552	1.0267	0.6349	0.0894	1.0241	0.6258
343	0.0786	1.0180	0.6264	0.1264	1.00028	0.6538
353	0.1098	1.0092	0.5936	0.1752	1.0068	0.5725

compared to that of the Page model.

Fig. 5a and b show the fitness of Avhad and Marchetti model with the experimental data for temperatures varying from 313 K to 353 K for the WS and CS of Jatropha. The values of the constants (k, a and N) obtained for the Avhad and Marchetti model are also presented in Table 3. As it can be seen from Table 3, the values of the drying rate constants k (moisture release rate constant) found to increase with the drying temperature for both the WS and CS as expected. The estimated values for the parameter a and N were not constant and found to vary with the drying air temperature, and both parameters tend to decrease with the rising of the drying temperatures and increasing of drying rate constant k. In contrary to the present finding, Simal et al.(Simal et al., 2005) reported the study in which the calculated value for N parameter for Page model did not exhibited temperature dependence, and considered as a constant parameter (N = 0.796).

Figs. 6a–c and 7 a–c show the predicted moisture ratio by Avhad and Marchetti model versus experimental moisture ratio of the WS and CS of Jatropha, respectively at 313 K (the lowest), 333 K (medium) and 353 K (the highest) air temperatures of the experiments. As it is evident from Figs. 6a–c and 7 a–c, the predicted moisture ratio by Avhad and Marchetti model generally banded around the straight line which showed the suitability of the model in describing the drying behavior of the WS and CS of Jatropha, respectively.

4. Conclusions

In this study, to describe the drying kinetics of Jatropha seeds at a storage moisture content, non-pretreated (whole seeds) and pretreated

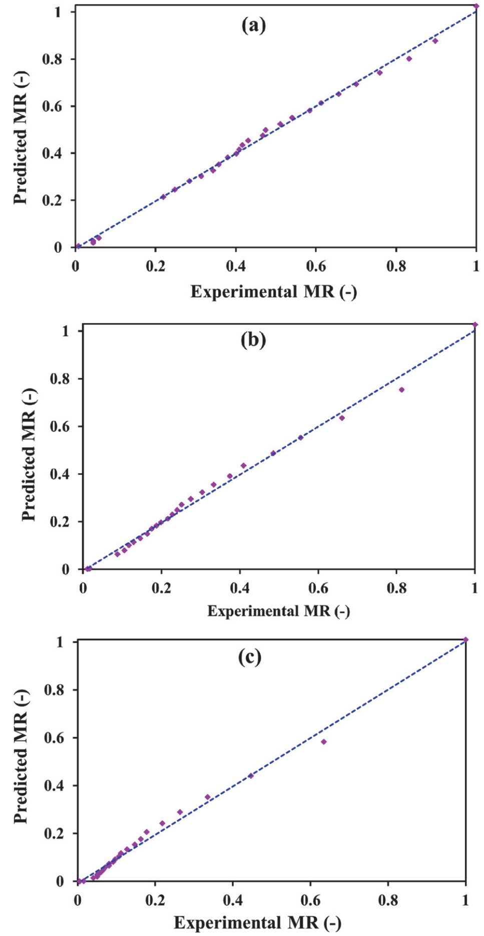

Fig. 6. Predicted moisture ratio by Avhad and Marchetti model versus experimental moisture ratio of the whole seeds of Jatropha at the drying temperatures of (a) 313k, (b)333 K, (c) 353 K: (◆) predicted moisture ratio and (–) regression line.

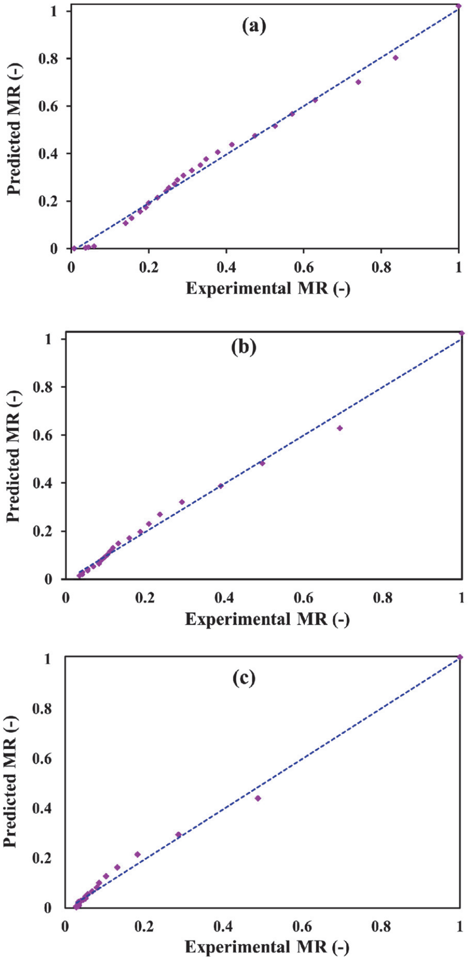

Fig. 7. Predicted moisture ratio by Avhad and Marchetti model versus experimental moisture ratio of the crushed seeds of Jatropha at the drying temperatures of (a) 313k, (b)333 K, (c) 353 K: (◆) predicted moisture ratio and (–) regression line.

(crushed seeds) seeds were dried at temperatures ranged between 313 and 353 K. The fitness of four different semi-theoretical mathematical models (Lewis model, Henderson and Pabis model, Page model and Avhad and Marchetti model) to drying curves were compared by employing coefficient of determination, chi-square test, root mean square error, mean bias error, and mean absolute error. It was found that the moisture removal rate increased with the rising of the oven air temperature and decreased with time due to the reduction of the seed moisture content. Avhad and Marchetti model and the Page model gave better and a more comparable fit to the experimental data than the other models. However, the Avhad and Marchetti model with R^2 ranged from 0.9914 to 0.9969 and 0.9908 to 0.9917 for the whole seeds and crushed seeds, respectively for all the drying temperatures and models was found to show best fit to the drying kinetics of the Jatropha seeds at a storage moisture content. The Avhad and Marchetti model showed superior fit to the experimental data at the drying temperature of 313 K with R^2 of 0.9969 for the whole seed, and at 333 K in case of crushed seeds for which the R^2 value was 0.9917. The activation energies of the whole and crushed seeds of Jatropha when using Avhad and Marchetti model were found to be 33.53 and 32.885 KJ mol^{-1}, respectively.

Declarations of interest

The authors declare no competing financial interest.

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Paper IV

Effects of different extraction solvents on the amount of oil extracted from Jatropha seeds from Ethiopia and the potential of de-oiled seed residues as a heat provider

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Abstract

The present study focuses on the determination of oil contents of thirteen different Jatropha seed collections from Ethiopia. The oil was extracted with Soxhlet extractor using hexane which was selected out of four different solvents: ethanol, hexane, diethyl ether and heptane. Cotton and thimble were used as filter for the extractions. Oil properties of the oil of Chali seed collection and a sample of mixed oils (a mixture of equal volume of oils from thirteen different seed collections) were determined. The energy contents of selected de-oiled Jatropha seed residues were also estimated. In the extraction with cotton and thimble, the largest amount of oils was obtained from Dana seed (48.29%) and Chali seed (45.79±0.54%) collections, respectively. The acid value (1.32±0.14 mg KOH/g) and percentage of free fatty acids (%FFA) (0.66±0.07%) of Chali seed oil were lower than the acid value (2.12±0.15 mg KOH/g) and %FFA (1.06±0.07%) of the mixed oil, and thus, the former oil is more suitable for alkaline catalyzed biodiesel production. The iodine values of both Chali seed oil (116.02±3.50 g/100 g) and mixed oil (109.24±0.05 g/100 g) did not exceed the maximum standard for biodiesel according to the European EN 14214 specification, and the oils could be used for biodiesel production. The gross calorific values of de-oiled Jatropha seed residues after oil extraction was found to range from 18.57- 24.03 MJ kg-1, and with the average value of 19.64 MJ kg-1. Thus, the de-oiled seed residues can be used as the source of heat.

Keywords: Calorific value. Jatropha (*Jatropha curcas* L.) seed. Oil content. Seed collection. Soxhlet extraction

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1. Introduction

Jatropha (*Jatropha curcas* L.) is a poisonous semi-evergreen perennial tree or shrub that belongs to the family Euphorbiaceae and reaching a height of up to 6 m [1], but can attain a height of 8-10 m under favorable conditions [2]. It is native to central America and has naturalized in many tropical and subtropical areas including Asia, Africa and North America [3]. Originating in the Caribbean, Jatropha was spread as a useful hedge plant to Africa and Asia by Portuguese merchants [1,3,2], and now the plant is found abundantly in many tropical and sub-tropical regions of the world [2].

Different parts of Jatropha plant have various uses and thus, this plant is considered as a multipurpose shrub [4-6]. Jatropha has the potential to be used for the production of biodiesel, cleaning agents, cosmetics, dyes, organic fertilizers and different medicines [5,6]. The seeds are known to contain high amount of oil that is not edible due to the presence of a toxic compound, the phorbol ester, and this made the oil of the plant a very attractive source of biodiesel [7]. Production of biodiesel from non-edible seed oils such as Jatropha has been given due consideration in the past decade as these oils are renewable, biodegradable and non-toxic alternative to fossil fuels [8,9].

The amount of oil that could be extracted from Jatropha seed and seed kernel could vary from 20-60% and 40-60%, respectively [10,11]. The oil contents of Jatropha seeds may vary from provenance to provenance [12] and for different agro-ecological zones [13]. The seed residue remains after oil extraction (seed cake) also has various attributes. For instance, it has a potential to be used as animal feed and organic fertilizer because of its high protein content [14]. It has also been reported that in comparison to standard woody pellets, Jatropha seed cake reaches similar or better physical and chemical properties of the European standard EN 14961-1 to be used as solid biofuels [15].

One of the important steps in biodiesel production is oil extraction. The three most commonly employed conventional oil extraction methods are mechanical, chemical/solvent and enzymatic extraction methods [16,9]. Besides these, accelerated solvent extraction, supercritical fluid extraction and microwave-assisted extraction methods are frequently used [16]. For commercial oil extraction, solvent extraction and mechanical pressing are the most commonly used methods [9]. Each oil extraction method has its own advantages and limitations. For instance, extraction of oil from Jatropha seeds using n-hexane as solvent, results in the largest percentage oil yield compared to mechanical and enzymatic extractions. However, using hexane as extraction solvent has negative environment impacts [9]. Oil extraction with enzymatic method is ecofriendly, but it takes longer time as the rate of oil extraction by this method is very slow compared to that of the solvent extraction methods [17]. Moreover, in supercritical fluid extraction, oil produced has very high purity and the time needed is also very short; however, the operating and investment cost is higher [18].

A number of solvents can be used to extract oil individually or as mixture of solvents from plant seeds. Hexane, petroleum-ether, diethyl ether, ethanol, n-heptane, isopropanol, acetone, chloroform, methanol and 1-butanol were some of the most commonly used and reported solvents for oil extraction [19,18,20-23]. The oil extraction efficiency, environmental impacts and renewability of different solvents vary. It was also reported that different solvents yielded different natural compounds from the material taken and the extract composition differs from solvent to solvent [24]. Therefore, selection of a solvent for oil extraction is the most critical step in oil extraction by chemical methods, and particularly, in the most commonly used Soxhlet extraction [25].

Soxhlet extraction is one of the most traditional techniques still being used to extract oil from solid samples using different volatile solvent. It is a popular method and used as a reference for several existing modern extraction techniques [24]. However, compared to the newly developed modern oil extraction techniques such as supercritical fluid extraction, microwave-assisted extraction and accelerated solvent extraction, Soxhlet extraction is an older extraction technique [26].

Except a few researches on oil extraction using hexane and petroleum ether, no research has been reported on oil extraction from Jatropha seeds from different parts of Ethiopia using different pretreatments and solvents. The objective of the present research was to determine the amount of oil that could be extracted from different Jatropha seed collections from Ethiopia using different pre-treatments and solvents and measure the energy contents of the de-oiled seed residues.

2. Materials and methods

2.1. Materials

Thirteen different collections of Jatropha seeds used for the experiments were collected from Ethiopia. From these, seven seed collections (Kurkura, Bira, Salmene$_1$, Salmene$_2$, Salmene$_3$, Shekla and Gerbi) were collected from the north-central part of the country while the rest collections (Dimeka, Chali, Kako, Mulato, Dana and

Awwaaragamaa) were harvested from the southern part. These collection sites were the areas where large cultivation of Jatropha has been practiced by the local farmers relative to other parts of the country.

After collecting Jatropha fruits, the seeds were recovered from the fruits mostly with hands by splitting open the fruit shells, and rarely by cracking the fruits carefully using small stones. The procedures used to remove the seeds from the fruits were adopted from the practices of the local farmers (farmers living around the seed collection areas). The collected seeds were air and sun dried for storage. Then, the dried seeds were transported to the Biodiesel Laboratory of Norwegian University of Life Sciences (NMBU), Faculty of Science and Technology, and stored at room temperature (about 293K) until used for oil extraction. During oil extraction, the seeds at storage were dried using a heating furnace (Narbetherm P300, Germany) by placing the seed samples on Pyrex Petri dishes (100 mm × 15 mm). The dried seeds were crushed using mortar and pestle before oil extraction was performed. Information of the seed collection sites, maturation stages of the fruits, and the respective seed collection years are presented in Table 1.

The organic solvents (ethanol, hexane, diethyl ether and heptane) used for oil extraction were standard grades. Diethyl ether, ethanol, phenolphthalein, potassium hydroxide, chloroform, Wijs solution, potassium iodide, sodium thiosulphate ($Na_2SO_3.5H_2O$), potato starch and sulfuric acid used for the determination of the chemical properties of the oils were also analytical reagent grades. Moreover, Plain Jacket bomb calorimeter (Model 1341, Parr Instrument Company, USA) was used to measure the energy contents of the de-oiled seed residues produced after oil extraction.

Table 1 Information of seed collection sites, seed maturation stages and time of collection.

Geographical region	Districts	Local name of sampling sites	Code for seed collections	Fruit maturity	Collection year	Location (coordinate)	Altitude (a.s.l. (m)
North-central	Bati	Kurkura	Kurkura	Yellow	2016	11° 14' 2.86" N, 40° 0' 18.5" E	1412
		Birra	Bira	Unkown[a]	2016	11° 12' 48.14" N, 40° 0' 38.83" E	1720
		Salmene	Salmene$_1$	Yellow	2016	11° 10' 47.74" N, 40° 0' 34.36" E	1668
			Salmene$_2$	Yellow	2016	11° 10' 34.59" N, 40° 0' 33.55" E	1596
			Salmene$_3$	Yellow	2016	11° 10' 35.02" N, 40° 0' 34.18" E	1603
	Dawa Chefa	Shekla	Shekla	Dried dark	2016	10° 47' 59.29" N, 39° 50' 8.62" E	1466
		Gerbi	Gerbi	Dried dark	2016	10° 44'5.42" N, 39° 50'11.38" E	1426
Southern part of Ethiopia	Hammer	Dimeka	Dimeka (dried fruit)[b]	Dried dark	2017	05˚10.437'N, 036˚32.795'E	1116
		Dimeka	Dimeka (yellow fruit)[c]	Yellow	2017	05˚10.437'N, 036˚32.795'E	1116
	Benatsemai	Chali	Chali	Yellow	2017 & 2018	05˚40.431'N , 036˚42.896'E	1340
		Kako	Kako	Yellow	2017	05˚39.416'N, 36˚39.317'E	1396
	Mi'erab Abaya	Mulato	Mulato	Yellow	2017	06˚27.997'N, 037˚45.106'E	1210
	Kucha	Dana	Dana	Yellow	2017	06˚34.112'N, 037˚33.070'E	1270
	Shalla	Awwaaragamaa	Awwaaragamaa	Yellow	2017	07˚16.573'N, 038˚27.292'E	1687

[a] The maturity stage of Bira seed collection was not known as it was purchased from a farmer after collection.

[b] Dimeka (dried fruit) and [c] Dimeka (yellow fruit) were seeds of the same collection but collected at different fruit maturity stages: Dimeka (dried fruit) and Dimeka (yellow fruit) seeds were collected from dried brown fruits and newly matured yellow fruits, respectively.

2.2. Experimental procedures

During oil extraction, the whole seeds (WS) at storage were dried in a heating furnace before crushing them for extraction. Accordingly, the WS with their seed coats were placed on Petri dishes and dried in the furnace at 353K for 2880 minutes to reduce their moisture content to the minimum following the previously published work [27]. According to Subroto [28], exposing the seed coat unprotected seed to temperatures higher than 333K might cause Jatropha oil peroxidation, and thus, in the current work, drying the WS with its seed coat and crushing it just before oil extraction was preferred.

After drying, the WS were crushed mechanically by hand using mortar and pestle. Then, the particle sizes of the crushed seeds (PSCS) were estimated using three different stainless steel sieves with openings of 500 µm, 1 mm and 2 mm woven cloth (Control Group, 15-D2245/J, 15-D2215/J and 15-D2185/J) following the studies published elsewhere [27,29]. Accordingly, the pulverized seeds used for this experiment was a mixture of four different particles sizes. The average proportions (%) of different PSCS: PSCS >2 mm, 2 mm > PSCS >1 mm, 1 mm > PSCS >500 µm and PSCS<500 µm were about 14.95±8.2, 29.96±4.38, 35.32±10.5 and 19.77±4.74%, respectively.

All seed samples were weighed using sensitive electronic balance having 0.0001 mg accuracy (AD, GR-202-EC, A&D Instruments, Japan). Oil extraction from the crushed seeds (CS) was performed with Soxhlet extractor having an extractor column and oil-collecting round bottom flak of 200 ml and 250 ml, respectively. The preliminary oil extraction processes were employed using cotton as filter due to its easy availability and cheaper cost compared to the extraction thimbles. Two types of thimbles were also used for the extraction: thimble with single thickness (37x130 mm) and a relatively thicker thimble (Hahnemühle FineArt, Germany, 40x150 mm). Heating mantle (LabHeat, SAF, KM-MER 250 ml) was employed during oil extraction to heat the round bottom flask of the Soxhlet extractor at the temperature around the boiling points of the extraction solvents. Rotary evaporator (Rotary Vapo R-3, Butchi Labortechnik AG, CH-9230, Switzerland) with vacuum pump (Shanghai Eyela CO. LTD Aspirator A.1000S, China) was also used to separate the oil and the solvents after oil extraction.

The experimental procedures of oil extraction was started with Salmene$_3$ collection, which was selected from the seeds collected from north-central Ethiopia. Oil extraction from the seeds was performed using four different solvents (ethanol, hexane, diethyl ether and heptane) and cotton as filter. Salmene$_3$ collection was selected for the indicated experiment as it was collected from yellow fruits. It has been reported that maximum physiological quality and lipid content of Jatropha seeds occur at physiological seed maturity, which corresponds to the seeds obtained from yellow fruits [30,31]. This experiment was carried out to compare the amount of oil (%) that could be extracted with the indicated solvents and identify the most efficient solvent for oil extraction. By comparing the oil extraction potentials of the extraction solvents in the preliminary experiment, the solvent that extracted the largest amount of oil was selected to extract oil from all seed collections. In all experiments of oil extraction, 50 g dried CS was used, except in the case of oil extraction from non-dried Dana seed collection in which non-dried WS and CS (50 g of each sample) were extracted using hexane and ethanol as solvents, and cotton as filter.

After determining the average oil extracted (%) from the seeds collected from the north-central and the southern part of the country separately, the seeds collected from the southern Ethiopia were selected for oil extraction with thimble for further investigations as larger amount of oil was obtained from these collections during the preliminary experiments. Oil sample from the selected seed collection (oil from Chali seed collection) and a sample of mixed oils (the mixture formed from oils of all the thirteen seed collections) were characterized. The energy contents of the selected de-oiled seed residues produced after oil extraction with hexane using cotton was also determined by bomb calorimeter. Fig. 1 shows the schematic diagram of Jatropha seed processing for oil extraction, oil extraction procedures and the post extraction process. The procedures in the schematic diagram (Fig. 1) and other additional experiments of oil extraction from Kako and Salmene$_2$ seed collections were described in the next part.

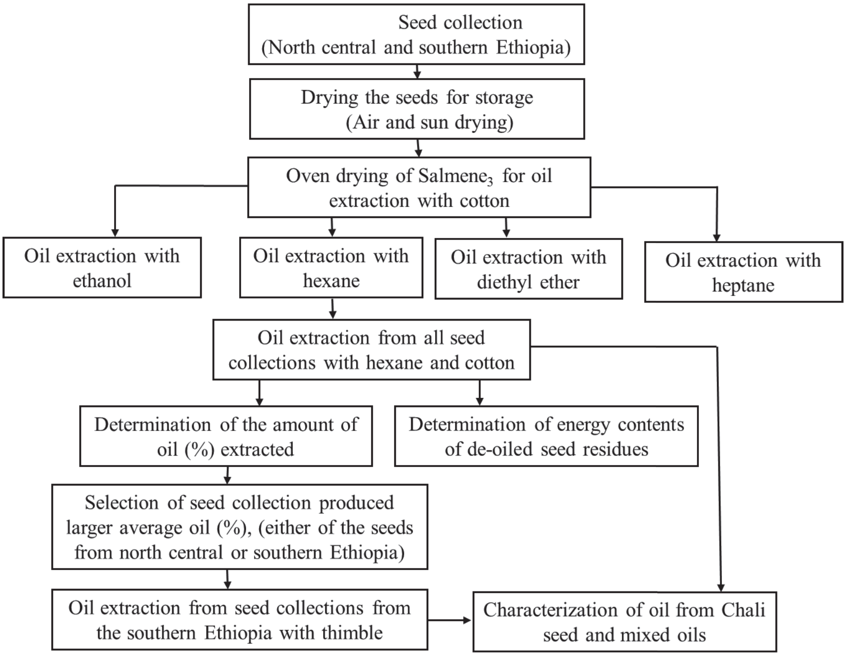

Fig.1 Schematic diagram for Jatropha seed collection, oil extraction and post extraction processes.

2.2.1. Extraction of oil from the seeds

Oil extraction using cotton

During the oil extraction from Salmene$_3$ to identify the solvent that could extract the largest amount (%) of oil from the seeds, the WS were dried, crushed and extracted with ethanol, hexane, diethyl ether and heptane using cotton as filter. Depending on the amount of oil (%) extracted from Salmene$_3$ using these solvents, the solvent that extracted the largest amount of oil was selected. Then, the samples of all seed collection were treated with the selected solvent. Accordingly, all the thirteen seed collections were extracted with the selected solvent using cotton after drying the WS and crushing them [27].

In oil extraction with cotton, the seed samples were placed in Soxhlet extractor column in between two cotton layers with uniform thickness. After adding 240 ml of the respective solvents to the round bottom flask, the flask was placed on the heating mantle and all the Soxhlet extractor parts were fitted to each other to complete the full setup. Then, the solvents were heated to their respective boing points for the oil extraction to occur. The oil extraction proceeded until five cycles of washes to occur. In this paper, the extraction duration is expressed in terms of the number of cycles of washes occurred using the Soxhlet extractor. Based on the results of the trial experiments performed to check the number of cycles of washes to be applied during the oil extractions to extract almost all the oil available for extraction from the crushed seeds using different solvents, five and ten cycles of washes were employed for the extraction with cotton and thimbles, respectively. After extraction, the extract (the mixture of oil and solvent) was filtered using Whatman filter paper. The solvents were recovered from the extract using rotary evaporator with vacuum by heating the extract to the temperature around the boiling points of solvents for 2.5 hours. After the removal of the solvents, the remaining oil was weighed and its amount was determined in terms of the percentage of oil obtained, using equation 1. This equation was also used to determine amount of oil extracted (%) from all seed samples presented in this paper.

$$Percentage\ of\ oil\ = \frac{W_{Oil}}{W_{CS}} x100 \qquad (1)$$

Where: W_{Oil} is weight of oil and W_{CS} is the weight of crushed seed just before oil extraction.

Besides extracting the oil by drying the whole seeds (WS) and crushing them, the non-dried WS and crushed seeds (CS) of Dana seed collection were extracted with hexane and ethanol using cotton as filter, and by employing five cycles of washes. This experiment was performed to check if hexane and ethanol or either of them could extract any oil from the whole seeds. The experiment was also aimed to compare the amount oil (%) that could be extracted from the non-died CS (crushed seeds from non-dried WS) using the two solvents.

Oil extraction using thimbles

Triplicated WS samples from the seeds from southern Ethiopia were dried, crushed and extracted using the selected solvent and thimble with single thickness (37x130 mm) for ten cycles of washes. Moreover, from the seeds collected from southern Ethiopia, Kako seed collection was purposively selected for oil extraction by ethanol using thicker thimble (40x150 mm) and cotton. The experiment was conducted to compare the amount of oil (%) that could be extracted by ethanol and thimble, and also to investigate the effects of extraction time (cycles of washes) with thimble on the amount of oil (%) extracted. Ethanol was selected for the extraction of oil from Kako seed collection as ethanol is non-toxic and renewable, and it is preferable in terms of the environmental health and utilization of bio-solvent which is renewable [32]

Oil extraction from seeds stored at different temperatures

From the seven seeds collected from the north-central Ethiopia, $Salmene_2$ which was also collected at a physiological maturity stage of the fruit (from yellow fruit) was selected for the storage temperature experiments. In this case, three samples of $Salmene_2$ were stored at three different temperatures to investigate the effects of the storage temperature on the percentage of oil that could be extracted. Accordingly, each of the three samples was placed at the room temperature (293K), cool temperature (277K) and freezing temperature (255K), respectively for 18 months (from September 2016 to February 2018). After the indicated period, triplicated samples of the seed stored at the respective temperatures were dried [27], crushed and extracted with Soxhlet extractor using hexane and cotton.

2.2.2. Characterization of the extracted oils

Two different oil samples: the sample from Chali seed collection extracted with Soxhlet extraction using thimble (Chali oil) and a sample of mixed oils (the mixture formed by mixing equal volumes of oils extracted from all the thirteen seed collections) were characterized for physical and chemical properties. The Chali oil was selected for analysis as the amount of oil (%) extracted from this collection using hexane and thimble was found to be the largest of the oils extracted from all the six Jatropha seeds collected from southern Ethiopia using the same method. The properties selected were acid value, percentage of free fatty acids (%FFA), Iodine value, saponification value and oil density. During oil analyses, the experiments were done twice for all oil properties and the average values of the two experiments were reported in this article.

Acidity and percentage of free fatty acids

The acid value (AV) and percentage of free fatty acid (%FFA) of both oil samples were determined following the procedures used by Asmare and Gabbiye [33] to determine these parameters for castor bean oil and biodiesel. Accordingly, 25 ml of diethyl ether and ethanol (1:1) mixture was added to 5 gm of oil in a 250ml conical flask and shacked well. After adding 5 drops of phenolphthalein indicator, the solution was titrated with 0.1N ethanolic KOH with consistent shaking until the end point of the titration was confirmed (change from colorless to pink). The volume of 0.1N ethanoic KOH (V) consumed during the titration was recorded. The total acidity of the sample in mg KOH/g was calculated using the following expression.

$$AV = \frac{56.1 * N * V}{W} \qquad (2)$$

Where, N = the normality of ethanolic KOH used, V= the volume (ml) of ethanolic KOH, and W = the weight (g) of oil sample.

The %FFA was also calculated from the acid value of the oil using the following equation.

$$\%FFA = AV/2 \qquad (3)$$

Iodine value

To determine the iodine value (IV) of the oils samples, the procedures used by Amabye and Bezabh [14] was adopted. Accordingly, 0.25 g of oil sample was measured and placed in 250 ml flask, and 20 ml of chloroform was added into the flask to dissolve the oil sample. Then, 20 ml Wijs reagent, the iodine monochloride solution, was added to the mixture using a pipette. The flask was stoppered and kept in dark place for 1 hour with intermittent shaking. After 1 hour, the mixture was taken out of the dark and 10 ml of 15% potassium iodide solution and 50 ml of distilled water were added and shaken well by inserting the stopper properly to the flask. Then, the liberated iodine was titrated with 0.1 N sodium thiosulphate ($Na_2S_2O_3.5H_2O$ solution) with gently stirring the mixture until the yellow color changed to a light straw. Finally, 5 drops of 1% starch indicator was added to the mixture and the titration was continued until the blue color disappeared. The blank titration was also conducted side by side to use it in the calculation to determine the parameter.

The iodine value of the oil sample was determined using the following equation.

$$IV = \frac{V_b - V_s}{M} * 12.69 * N \qquad (4)$$

Where, Vb= volume (ml) of sodium thiosalphate used for the blank, Vs = volume (ml) of sodium thiosalphate used for the sample, N = normality of sodium thiosuphate, and W =the mass of the sample used (g).

Saponification Value

The saponification value (SV) was determined according to Ogbunugafor et al.[34]. 50 ml of 0.5N ethanolic potassium hydroxide (KOH) was added into a conical flask containing 1g of Jatropha oil. The flask was connected to the condenser and the mixture was heated to reflux with gentle stirring for 45 minutes. Then, the mixture was cooled to room temperature, after which it was titrated with 0.5N sulfuric acid (H_2SO_4) by adding 5 drops of phenolphthalein indicator until the pink color of the indicator just disappeared. The blank test was also carried out under the same conditions. The saponification value of the sample was calculated using the following equation.

$$SV = \frac{V_b - V_s}{W} x\ Nx\ 56.1 \qquad (5)$$

Where, Vb = volume (ml) of sulfuric acid used for the blank, Vs = volume (ml) of sulfuric acid used for the sample, N = normality ethanolic potassium hydroxide (KOH) and W =the mass (g) of the sample.

Density

The volumetric flask with capacity of 50 ml was dried well before using it for the determination of the densities of the oil samples. The dried flask was placed on sensitive electronic balance and the reading of the balance with the flask was adjusted to zero. Then, the oil sample was added to the volumetric flasks using pipette until the volume of the oil reached 50 ml, and the weight (g) of the oil was recorded. Finally, the density of the oil was determined from the weight reading and the volume of the oil. The measurement was duplicated, and the average value of the measurements was reported. The densities of the oil samples were determined at 293 K.

2.2.3. Determination of the energy contents of the de-oiled seed residues

The energy content of biomass is determined by its calorific value, and the calorific value is influenced by biomass elemental composition, moisture and ash contents [35]. Upper calorific value (gross calorific value) is the amount of heat per unit of weight released by complete combustion of the fuel (biomass) in the pressure vessel built in the calorimeter under compressed oxygen at 25ºC (298K). In the calorimetric vessel, the sample is totally burned and the values of temperature jump were converted to the net energy value. Net calorific value is the gross calorific value minus the heat of vaporization of water, resulting from the fuel during combustion [15]. Accordingly, after the extraction of oil from the crushed Jatropha seeds with cotton, the de-oiled residues of some selected seed samples were dried under fume hood for five days. The energy content of de-oiled residue of Kako seed collection that was extracted with ethanol and thicker thimble (by employing five cycles of washes) was also determined for comparison. Then, the upper calorific values (gross calorific values) of the residues were estimated by bomb calorimeter, using benzoic acid as a standard. The objective was to compare the calorific values of different analyzed de-oiled seed residues with each other and with that of other crop residues from literature.

2.3. Statistical analysis

The data of oil content of six Jatropha seed collections from southern Ethiopia that were extracted by thimble with single thickness and that of Salmene$_2$ stored at three different temperatures were subjected to the analysis of variance (ANOVA test). Significant difference among the amount of oil produced (%) from the six different seed collections from southern Ethiopia and those of Salmene$_2$ stored at three different temperatures, respectively were analyzed at $p \leq 0.05$. Duncan's post hoc test ($p \leq 0.05$) was used to determine the homogeneity subsets whenever significant differences existed among the treatments. The statistical software used was SPSS for windows, version 20.

3. Results and discussion

3.1. Extraction of oil using different solvents

As it was mentioned in the methodology part, Salmene$_3$ seed collection was extracted with different solvents using cotton as filter to compare the efficiency of different solvents to extract the oil from CS. Table 2 shows the percentage of oil extracted from Salmene$_3$ using different organic solvents by employing five cycles of washes. As it can be seen from Table 2, in the extraction of oil using four different organic solvents (ethanol, hexane, diethyl ether and heptane), the percentage of oil extracted using hexane (41.24%) was found to be the largest. In their comprehensive reviews on oil extraction techniques and biodiesel production technologies, Atabani, et al. [36] and Bhuiya, et al. [16] indicated that oil extraction using n-hexane method results in the highest oil yield which makes it the most common solvent used.

Based on the results presented in Table 2, hexane was selected as the best solvent in terms of the amount of oil extracted and thus, it was used for the determination of the oil contents of all collections of Jatropha seeds used in this study. However, using ethanol as solvent is more preferable in terms of environmental health and being renewable [20], because ethanol is environmentally less toxic, and renewable (it can be produced from renewable resources by fermentation of sugar-containing feeds, starchy feed materials or lignocellulosic materials) [20,32].

Table 2 Percentage of oil extracted from Salmene$_3$ using different organic solvents and cotton as filter

No.	Solvents used	Amount of oil extracted (%)
1	Hexane	41.24
2	Ethanol	25.92
3	Diethyl ether	34.92
4	Heptane	38.95

3.2. Extraction of oil from different seed collections

3.2.1. Oil extraction from crushed seeds using hexane and cotton

Table 3 shows the percentage of oil extracted from Jatropha seeds collected from the north-central Ethiopia after drying and crushing the seeds. Extraction was done with Soxhlet extractor using hexane and cotton as solvent and filter, respectively, and by applying five cycles of washes. By using this method, the amount of oil (%) extracted from the seven seed collections ranged from 26.05 to 41.51%, and the average was found to be 34%. The amount of oil extracted from Salmene$_2$ seed collection (41.51%) was the largest and that obtained from Salmene$_1$ (26.05%) was found to be the smallest. The difference in the amount of oil extracted from different seed collections might be due to the existence of some genetic variations among the seed collections and/or relative differences in the environmental conditions of the seed collection sites.

In the study of oil extraction from Jatropha seeds collected from 40 different sites (provenances) of Ethiopia, Beemnet et al. [12] reported that from the existing Ethiopian Jatropha provenances growing in different testing sites, 15.79% of the provenances demonstrated oil content value of > 35%, 71.05% between 30 and 35% and the remaining 13.16% demonstrated oil content value of < 30%. The authors also wrote that the differences for the oil obtained from Jatropha seeds collected from different provenances might be due to the variations of the existing growing conditions and some genetic variations. In their review of the influences of abiotic factors on plant lipids, Singer et al. [37] mentioned that besides plant genotype, seed oil concentration can be affected by the environmental conditions such as temperature, which modifies seed oil concentration and the fatty acid composition through changes in grain filling dynamics and biosynthetic activity.

Table 3 Percentages of oil extracted from Jatropha seeds collected from north-central Ethiopia using hexane and cotton as solvent and filter, respectively.

No.	Seed collection	Oil extracted (%)
1	Kurkura	31.59
2	Bira	31.92
3	Salmene_1	26.05
4	Salmene_2	41.51
5	Salmene_3	41.24
6	Shekla	34.75
7	Gerbi	30.94
	Average	34.00

Table 4 shows the percentage of oil extracted from Jatropha seeds collected from southern Ethiopia using Soxhlet extractor with five cycles of washings. The WS were oven dried and extracted using hexane and cotton as solvent and filter, respectively. As it can be seen from Table 4, the largest amount of oil (48.29%) was obtained from Dana seed collection, follow by Dimeka seed collected from dried fruit (44.18%). The average oil extracted in this experiment was calculated to be 40.43%. The smallest amount of oil (30.66%) was obtained from Kako collection. The differences of the amount of oil extracted from different seed collections could be due to the climatic differences of the collection sites and the genetic variation of the seeds [37].

Table 4 Oil extracted (%) from Jatropha seeds collected from southern Ethiopia, using hexane and cotton

No.	Seed collection	Oil extracted (%)
1	Dimeka (dried fruit)	44.18
2	Dimeka (yellow fruit)	36.29
3	Chali	43.48
4	Kako	30.66
5	Mulato	43.86
6	Dana	48.29
7	Awwaaragamaa	36.31
	Average	40.43

It was also found that the amount of oil extracted from Dimeka seed collected from yellow fruit (36.29%) was less than that of the seed obtained from dried fruit (44.18%). The oil yield obtained from Dimeka seed collected from yellow fruit in the present experiment was in contrary to the values reported by Santoso et al.[38]

in which 36.9 and 35.8% oil was obtained from Jatropha seeds (Indonesian genotype) collected from yellow and black-dry fruits, respectively. From the study of oil contents of Jatropha seeds collected from Botswana at different fruits maturity stages, Jonas et al [31] also reported that Jatropha seeds from yellow fruits had the highest yield of seed oil, least %FFA level and yielded biodiesel with relatively highest energy content.

During seed collection from southern Ethiopia (in October 2017), the majority the fruits of Jatropha plants at the Dimeka site had dried and turned to brown due to lower altitude and dry climate of the area, and only a few lately produced fruits were found at the yellow stage. Thus, both seeds from the lately produced yellow fruits and those from dried fruits were collected from the Dimeka site and used for the experiment. Therefore, the lower oil yield of Dimeka seeds collected from the yellow fruit compared to that obtained from dried fruit might be due to the lately produced abnormal yellow fruits collected and used for the experiment.

When the amount of oils extracted (%) from the seed collections from north-central Ethiopia (Table 3) were compared with those obtained from the seed collections from southern Ethiopia (Table 4), generally, the average oil extracted from the seed collections from southern Ethiopia (40.43%) was greater than that of the seed collections of north-central Ethiopia (34%). The maximum (48.29%) and minimum (30.66%) oil extracted from the seed collections from southern Ethiopia were also greater than the maximum (41.51%) and minimum (26.05 %) oil obtained from those of the north-central part of the country, respectively. The difference in the amounts of oil extracted from the seed collections from the southern and north-central parts of the country might be due to the differences of the growing conditions (altitude, climatic and soil conditions) and some genetic differences of the Jatropha plants growing in the southern and north-central parts of the country [12,37,39,40].

Based on the average oil extracted (%) from Jatropha seed collections from the two geographical regions (north-central and southern parts) of Ethiopia, the seed collections from the southern part of the country which gave larger average oil (40.43%) were selected to be extracted with extraction thimble for further investigations.

3.2.2. Oil extraction from the whole and crushed Dana seed collection

The amount of oil extracted from crushed non-dried Dana seed collection with cotton using hexane (41.82%) was larger than the one extracted from the same seed with ethanol (29.93%). No oil was obtained when the non-dried WS was extracted with hexane and ethanol, respectively. Table 5 shows the amount of oil extracted from non-dried WS and CS of Dana seed collection using hexane and ethanol as solvent, cotton as filter, and by applying five cycles of washes. From Table 4 and Table 5, it can be seen that the amount of oil extracted from the WS of Dana seed collection dried, crushed and extracted using hexane and cotton (48.29%) was greater than the amount of oil extracted from the non-dried CS of the same seed (41.82%) with similar methods of extraction. In line with this result, in the extraction of oil from Moringa (*Moringa oleifera*) seeds with Soxhlet extractor using hexane, Omosuli et al.[41] obtained the oil yield of 30.30, 32.21 and 33.11% from the milled seed flour of raw (non-dried), sundried and oven dried Moringa seeds, respectively. From the results of the current experiment, it could be suggested that drying the WS of Jatropha before crushing it for oil extraction might increase the leaching of the oil from the pulverized seeds during oil extraction.

Table 5 Oil extracted from non-dried whole seeds (WS) and crushed seeds (CS) of Dana seed collection using hexane and ethanol

No.	Solvent used	Types of seed extracted	Amount of oil extracted (%)
1	Hexane	WS	0
		CS	41.82
2	Ethanol	WS	0
		CS	29.93

3.2.3. Oil extraction from seeds from Southern Ethiopia with thimble

Fig. 2 presents the mean oil extracted (%) from Jatropha seeds collected from southern Ethiopia using hexane and thimble with single thickness. As it can be seen from Fig. 2, the mean oil extracted ranged from 37.14±0.46 to 45.79±0.54%. The mean oil extracted from Chali seed collection (45.79±0.54%) was not significantly different ($p \leq 0.05$) from that of Dimeka seed collected from dried fruit (43.91±0.71%). However, it was significantly larger ($p \leq 0.05$) than the mean oil extracted from of Kako (37.14±0.46%), Awwaaragamaa (38.04±1.24), Mulato (41.61±0.21) and Dana (43.29±0.12) seed collections. The mean oil extracted from Kako (37.14±0.46%) and Awwaaragamaa (38.04±1.24%) were significantly lower ($p \leq 0.05$) than those of the other seeds collected from southern Ethiopia and extracted with thimble with single thickness. Moreover, the overall average oil extracted (%) from all the six Jatropha seeds shown in Fig. 2 was calculated to be 41.63±0.54%.

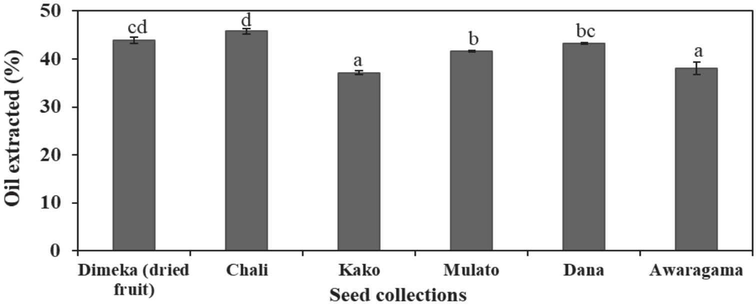

Fig. 2 Mean oil extracted (%) from seeds collected from southern part of Ethiopia using hexane and thimble with single thickness and extracted by ten cycles of washes. Bars show means ±SE (standard errors) and different letters indicate significant differences among the mean oil extracted from the seed collections (Duncan's post hoc test at $p \leq 0.05$).

In the study carried out by Beemnet, et al. [12] to determine the oil contents of the Ethiopian Jatropha populations from five regional states of the country, it was found that the averaged oil extracted by Soxhlet extractor using hexane as solvent ranged from 29.88% to 34.34%. The authors also reported that the oil obtained from Jatropha seed collected from the Southern Nation Nationalities and Peoples Regional State (from southern Ethiopia), by extracting using Soxhlet extractor with thimble, varied from 31.18 to 35.91%, and with average of 34.34%. Thus, the average oil obtained in the present experiment from all seeds collected from southern Ethiopia (41.63±0.54%) was larger than the values reported [12].

The larger average oil obtained in the present experiment compared to the previously reported value might be caused by the difference in the pretreatment of the seeds for oil extraction, the thickness of thimbles used, and the particle sizes of the CS used for the experiments. In the present study, the whole Jatropha seeds were dried before crushing at 80ºC until no more moisture loss occurred, and the filter used was thimble with single thickness (37x130 mm). However, in the oil extraction by Beemnet, et al. [12], no seed drying procedure and the thickness of the extraction thimble used was reported. By extracting Jatropha seed kernel from Northern Ethiopia, using Soxhlet extractor and petroleum ether as solvent, Amabye and Bezabh [14] obtained the oil yield of 42.19% which was also less than the mean oil extracted from Chali (45.79±0.54%), Dimeka (43.91±0.71%) and Dana (43.29±0.12%) seed collections in of the present study.

Table 6 shows the amount of oil (%) extracted from Kako collection by ethanol, using thicker thimble (40x150 mm) and cotton for different extraction time (for different number of cycles of washes). As it can be seen from Table 6, oil extracted with cotton for 5 cycles of washes (28.17%) was found to be the largest. When the cycle of wash increased from 5 to 10 using thimble with the same thickness, the amount of oil extracted (%) increased from 11.99% to 26.73%. This shows that the amount of oil (%) extracted increased to more than double when the number of washing cycles increased from 5 to 10.

Table 6 Kako seed collection extracted by ethanol using thinker thimble and cotton, and with different washing cycles for the thimble.

No.	Filter used	Cycles of wash	Amount of oil extracted (%)
1	Thicker thimble (40x150 mm)	5	11.99
2	Thicker thimble (40x150 mm)	10	26.73
3	Cotton	5	28.17

Concerning the increment of Jatropha oil yield with extraction time (the number of cycles of washes in the current work), Santos et al. [42] reported that the oil yield increased with the time of extraction until reaching equilibrium (saturation of the solvent), for all the temperatures, moisture contents, and average particle sizes of the extracted seed. In the study of oil extraction from Jatropha seed using hexane and petroleum ether as solvent, Sayyar et al. [19] also reported that oil yield increased with extraction time until the optimum extraction time of 8 hours was reached. Moreover, in the extraction of oil from Spent Coffee Grounds, the highest oil yield was achieved at 8 hours of solvent extraction, but the yield was considerably low when the duration of extraction was less than 2 hours [43]. The reason for this could be that the short duration of extraction might not allow sufficient time for the recirculating solvent to extract the total available oil from the feedstock [43,44].

As it can be seen from Table 6, the extraction with cotton produced larger oil yield only with five cycles of washes compared to the thimble. Thus, using cotton could shorten the extraction time by reducing the number of cycles of washes needed to extract the oil available for extraction using the extraction method used. Cotton could also be easily available and cheaper than the extraction thimbles. However, in the extraction with cotton, the cycles of washes (particularly, the time taken for the consecutive cycles of washes to occur) were observed to be less uniform compared to that of extraction thimble in the successive batches of extraction. This might occur due to the difference in thickness and compression of the cotton placed in the Soxhlet column for the respective batches of extraction. Moreover, cotton did also absorb more solvents than thimble and resulted in less solvents recovery. Averagely, about 10% of the solvent was lost in case of extraction with cotton compared to the amount of solvent recovered in the extraction using thimble.

3.3. Oil extraction from seeds stored at different temperatures

Fig. 3 shows the mean oil extracted from Salmene$_2$ seed collection that was stored at three different temperatures. As it can be observed from Fig. 3, the mean percentage oil extracted from Salmene$_2$ stored at 255K (43.55±1.46%) was found to be slightly higher than those of the seeds stored at 277K (43.09±1.32%) and 293K (41.51±1.89%). However, the oil extracted from the seeds stored at the three different temperatures did not significantly differ ($p \leq 0.05$).

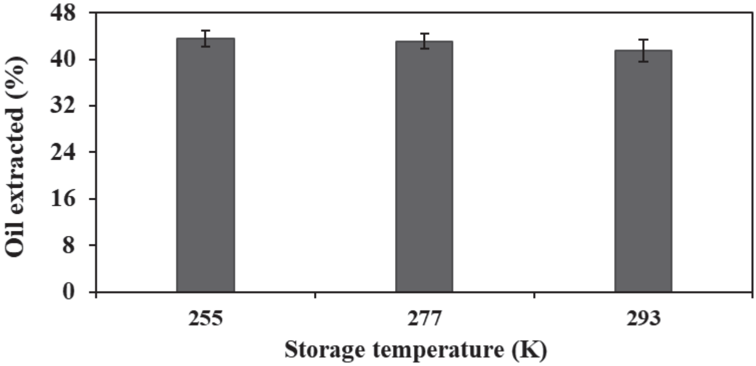

Fig. 3 Mean oil extracted from Salmene$_2$ stored at room temperature (293K), cool temperature (277K) and freezing temperature (255K). Bars show means ±SE.

From the study of the effects of Jatropha seed storage on the quantity of oil, Sushma [45] reported that the seed stored at 278K gave the highest amount of oil (29.12%) after 15 months of storage compared to 22.11, 17.39, and 12.27% oil contents for those seeds stored at room temperature (288.5 K), 273K and 268K, respectively. However, in the present study there was no such significant difference among the amount of oil obtained from the seeds stored at the three different temperatures. The results of this experiment demonstrated that all the seed samples stored at three different temperature gave almost similar amount of oil and thus, the storage temperatures might not significantly affect the amount of oil in the seed samples and/or the process of oil extraction.

3.4. Physico-chemical analysis of the oils

Experimental values for some properties of the oil of Chali collection (Chali oil) and mixed oil samples and the values reported in literature for the same parameters of oils from different origin (countries) are presented in Table 7. As it can be seen from Table 7, the acid value and free fatty acids for Chali oil and the mixed oil samples were found to be 1.32±0.14 and 2.12±0.15 mg KOH/g and 0.66±0.07 and 1.06±0.07%, respectively. Acid value indicates the amount of FFA found in fat or oil, and it provides information about how much generation of free fatty acids has taken place. The age of oil sample and oil exposure to atmospheric oxygen could increase acid value of the oil [46,47]. The higher acid value and %FFA for the mixed oil compared to that Chali oil in the present study could be due to the age of the seeds as mixed oil contained oils from thirteen different Jatropha seed collections that were collected in 2016, 2017 and 2018 while Chali oil was extracted from the seed that was collected in 2018.

Table 7 Some properties of Chali and mixed oils of Jatropha from the experimental results and values reported for Jatropha oils from different origins (countries)

Properties	Experimental values		Values reported for Jatropha oils from different origin (counties)							
	Chali oil	Mixed oil	Malaysia [48]	Ethiopia [14]	South Africa [49]	Indonesia [49]	Nigeria [47]	Egypt [50]	Sudan [51]	Indian [49]
Acid value (mg KOH/g oil)	1.32±0.14	2.12±0.15	1.50	1.38	0.9	3.8	36.2	2.3	9.537	1.9
FFA (%)	0.66±0.07	1.06±0.07	1.03	0.74	0.4	1.9	18.1	0.9	4.769	0.9
Iodine value (g I_2/100g oil)	116.02±3.50	109.24±0.05	135.85	129.66	138.1	122.2	105	−	114.64	113.4
Saponification value (mg KOH/g)	191.40±3.11	205.77±3.81	208.50	114.49	193.4	196.6	190	200	193.40	197.1
Density(g/ml)	0.906±0.001	0.9104±0.001	−	−	0.914	0.917	0.913	0.912	0.943	0.914

Compared to the values of the acid vale and %FFA of Jatropha oil reported in literature and listed in Table 7, the values obtained for Chali oil in the current study was lower than that of all the values reported, except for the one from South Africa. The reported values of acid value and %FFA for the oil of Jatropha seeds from South Africa was 0.9 mg KOH/g and of 0.4%, respectively [49]. However, the values of the same parameters for the mixed oil from the present experiment were found to be larger than that of the values reported for Jatropha oil extracted from Jatropha seeds of Malaysian [48], Ethiopian [14], South African[49] and Indian [49] origins. As mentioned earlier, the larger acid vale and %FFA of the mixed oil of the present study could be due to the age of the seeds from which the component oils of the mixed oil were extracted. Differences in the acid vale and %FFA the Jatropha oils from different seeds might also be due to the differences in maturation stage of the fruits from which the seeds were collected [31]. Mazumdar et al. [52] mentioned that among all the fuel properties studied for Jatropha oil collected from different geographical location of world, acid value is found to vary widely, and the causes of such variation in the acid value may be due to some genetic variations, differences in seed maturation stages, seed storage, and edaphic condition of the regions [53].

Technically, acid value is the mass of potassium hydroxide (KOH) in milligrams that is needed to neutralize one gram of chemical substance. Larger acid value shows the presence of more amount of free fatty acid (FFAs) in the oil and the presence of which interferes biodiesel production, particularly, when basic catalysts are used in the transesterification process. The yield of biodiesel is dependent on the acid value as oil with lower acid value produces higher biodiesel throughput [46]. From the results of the current study, Chali oil sample, which had lower acid value than that of the mixed oil, was found relatively to be a better feedstock to be used in base catalyzed transesterification process.

The Iodine value of Chali oil and mixed oil samples were found to be 116.02±3.50 and 109.24±0.05 g/100 g, respectively, and thus, the value for Chai oil was larger than that of the mixed oil. Compared to the literature values listed in Table 7, the iodine values for both Chali oil and mixed oil samples were moderate, and within the range of the values reported in the listed literature.

The iodine value is a measure of the degree of unsaturation of the oil and the larger the iodine value, the greater the degree of unsaturation [28,54]. The maximum iodine value for biodiesel is 120 g/100 g according to the European EN 14214 specification. The maximum limit of unsaturation is necessary because heating higher unsaturated fatty acid results in polymerization of glycerides, and this could lead to the formation of deposits and deterioration of the lubricating properties [55]. Higher unsaturated fatty acids have also a negative impact on oil stability [49]. Vegetable oil with iodine value between 100 and 130 belongs to the groups of semi-drying oil. This group of oil absorbs atmospheric oxygen slowly, partially hardens and form a soft film after prolonged exposure to air [47,28]. Accordingly, Jatropha oils is classified under semi-drying oil group, and the higher iodine value of Jatropha oil is caused by high content of unsaturated fatty acid such as oleic acid and linoleic acid [55]. Thus, the iodine values obtained for both Chali oil and mixed oil samples in the current study suggested that both oils were classified under semi-drying oil group and could also be used as the feedstock for biodiesel as their iodine value were not exceed the maximum values for biodiesel in the European EN 14214 specification.

Saponification is the hydrolysis of fats and oils in the presence of alkaline solution such as potassium hydroxide or caustic soda to produce glycerol and the corresponding salt of fatty acids. Saponification value of an oil is the number of mg of potassium hydroxide required to saponify 1 gram of oil/fat. It indicates the nature of fatty acids available in triacylglycerol. The longer the carbon chain of the fat hydrolyzed, the reduced the quantity of acid liberated per gram of sample and hence the reduced the saponification value of such oil sample [46]. As it is presented in Table 7, the saponification value of Chali oil and mixed oil were 191.40±3.11 and 205.77±3.81 mg KOH/g, respectively. This shows that the saponification vale for the mixed oil was larger than that of Chaali oil. The saponification values of both Chali and mixed oil samples were high and in the range of the literature values listed in Table 7 for Jatropha oils of different origin. According to Rania et al. [51], Jatropha oil is usually associated with high saponification value due to the fact that the oil contains normal triglycerides, and such oils with high saponification numbers are very useful in production of liquid soap and shampoo industries [55]

Density is the mass per unit volume of the oil at a particular temperature. The density of vegetable oil is lower than that of water and the differences between the densities of vegetable oils are quite small, particularly amongst the common vegetable oils [51]. The densities of Chali oil (0.906±0.001 g/ml) and that of the mixed oil (0.9104±0.001 g/ml) of the present study were about equal. The values for both oil samples were in line with the literature values listed in Table 7, except for the density reported for the Jatropha oil from Sudan (0.943g/ml), which was reasonably higher than both experimental values.

3.5. Energy contents of seed residues

The energy contents of selected de-oiled Jatropha seed residues were determined and compared with each other and the values from literature. Table 8 shows the gross calorific value of the de-oiled seed residues left after oil extraction using different solvents. As it can be seen from Table 8, the upper calorific values (gross calorific values) of the analyzed samples ranged from 18.57- 24.03 MJ kg^{-1}, and with an average of 19.64 MJ kg^{-1}. The gross calorific values of all the de-oiled seed residues analyzed in the present study and their average were in the range of the gross calorific values (14.3-25.4 MJ·kg^{-1}) determined by Gravalos et al. [35] for different agroforestry species and bio-based industry residues.

In the current experiments, the largest gross calorific value (24.03 MJ kg^{-1}) was obtained from the residue of Kako WS that was dried, crushed and extracted by thicker thimble and ethanol, by employing five cycles of washes (KWDCS/TEth5). The smallest gross calorific value (18.57 MJ kg^{-1}) was recorded in the case of the residue of Salmene$_2$ WS that was stored at 277K, dried, crushed and extracted with hexane (S$_2$WS(4°C)DCS/Hex). The second smallest gross calorific value (18.77 MJ kg^{-1}) was also obtained from the de-oiled residue of Dana seed collection that was extracted by hexane and cotton by applying five cycles of washes (DnWSDCS/Hex).

As it is shown in Table 6, the de-oiled seed residue KWDCS/TEth5, the residue that produced the largest gross calorific value (24.03 MJ kg^{-1}), was the residue of the seeds from which only 11.99% oil (the lowest amount of oil) was extracted. The de-oiled seed residue that produced the second smallest gross calorific value (18.77 MJ kg^{-1}) was also the de-oiled seed residue of the seeds from which 48.29% oil (the largest amount of oil) was extracted (DnWSDCS/Hex) (Table 4). These results showed that the de-oiled seed residues that was produced after the extraction of the smallest amount of oil (%) gave the largest gross calorific value and vice versa. This suggested that the residual oil in de-oiled seed residue could impact their gross calorific values. However, the gross calorific values of the other de-oiled seed residues (Table 8) did not consistently follow the same trend. This might be due to the interactions of other factors that determine the gross calorific value of the de-oiled seed residues [35].

The average gross calorific value of Jatropha seed residues found from the present experiment (19.64 MJ kg^{-1}) was in accordance to the value reported for the cake of Jatropha seed by Kavalek et al. [15], which was 19.11 MJ kg^{-1}. However, it was greater than the values 18.76, 18.2 and 17.7 MJ/kg^{-1}, which were reported by Steinbrück et al.[56], Achten et al. [57] and Sharma and Sheth [58], respectively. As the cake of Jatropha seed has very low moisture content and its residual oil content does not tend to take in water, it is suitable for direct combustion [15]. Moreover, it was reported that the gross calorific value for the Jatropha seed (with 0% moisture content) and Jatropha oil were 20.85 and 37.83 MJ kg^{-1}, respectively [59]. Furthermore, Makkar and Becker [60] reported that the gross calorific value for Jatropha oil could vary from below 37 MJ/kg to 39.5 MJ/kg.

Table 8 Energy content of the selected de-oiled residue of Jatropha seeds after oil extraction with different solvents

No	Description for the de-oiled seed residues	Codes used for the seed residues	Upper/gross calorific values (MJ kg^{-1})[d]
1	Kako WS, dried, crushed, extracted by thicker thimble and ethanol with five washes	KWDCS/TEth5	24.03
2	Kako WS, dried, crushed and extracted by hexane	KkWSDCS/Hex	20.72
3	Awwaaragamaa WS, dried, crushed and extracted by hexane	AwWSDCS/Hex	20.07
4	Dimeka WS (from dried fruit), dried, crushed and extracted by hexane	DkWS(d)DCS/Hex	19.77
5	Salmene$_2$ CS, dried and extracted by hexane	S$_2$CSD/Hex	19.67
6	Salmene$_2$ stored at -18°C, WS dried, crushed and extracted by hexane	S$_2$WS(-18°C)DCS/Hex	19.66
7	Salmene$_3$, crushed seed, dried and extracted by hexane	S$_3$CSD/Hex	19.52
8	Gerbi CS, dried and extracted by hexane	GCSD/Hex	19.50
9	Chali WS, dried, Crushed and extracted by Hexane	ChWSDCS/Hex	19.47
10	Dimeka WS (from yellow fruit), dried, crushed and extracted by hexane	DkWS(y)DCS/Hex	19.44
11	Salmene$_3$ WS, dried, crushed and extracted by heptane	S$_3$WSDCS/Hept	19.40
12	Mulato WS, dried, crushed and extracted by hexane	MWSDCS/Hex	19.39
13	Shekla CS, dried and extracted by hexane	ShCSD/Hex	19.30
14	Salmene$_3$ WS, dried, crushed and extracted by diethyl ether	S$_3$WSDCS/DE	19.22
15	Salmene$_2$ WS stored at room temperature, dried, crushed and extracted by hexane	S$_2$WS(RT)DCS/Hex	18.93
16	Salmene$_2$ WS, dried, crushed and extracted by hexane	S$_2$WDCS/Hex	18.84
17	Salmene$_3$ WS, dried, crushed and extracted by hexane	S$_3$WSDCS/Hex	18.81
18	Dana WS, dried, crushed and extracted by hexane	DnWSDCS/Hex	18.77
19	Salmene$_2$ WS stored at 4°C, dried, crushed and extracted by hexane	S$_2$WS(4°C)DCS/Hex	18.57
	Average		19.64

[d] Calorific values are arranged from the largest (number 1) to the smallest (number 19).

Elemental composition (particularly due to difference in carbon content as it is the main energy source), ash (non-combustible material) and moisture contents are the main factors that determine the gross calorific values of crop residues [35]. Accordingly, seeds and kernels have higher gross calorific values than the seed shell, husks, cakes and other residues as the seeds and kernels have higher unit mass and higher lipid content compared to the residues [35]. Concerning the conversion of residues of Jatroppha such as Jatropha oil cake, seed shell, fruit husk and pruned twigs to useful energy source, Steinbrück et al. [56] wrote that the conversion of these residues into marketable products would contribute to broadening the circumstances under which the Jatropha crop is profitable.

4. Conclusion

In the extraction with cotton, the largest amount of oil (48.29%) was obtained from Dana seed collection whereas in case of extraction with thimble, the largest amount of oil (45.79±0.54%) was obtained from Chali seed collection. The study suggested that Chali seed oil is more suitable for alkaline catalyzed biodiesel production as its acid value and free fatty acid contents were lower than that of the mixed oil. The iodine values of both Chali and mixed oils did not exceed the maximum standard value for biodiesel (120 g/100 g) according to the European EN 14214 specification and thus, both oils could be used as the biodiesel feedstock. The average gross calorific values of the de-oiled Jatropha seed residues after oil extraction was found to be 19.64 MJ kg^{-1}. Thus, the seed residues could be used as the source of heat.

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Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflict of interest.

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Full Length Article

Optimization of the production of biofuel form Jatropha oil using a recyclable anion-exchange resin

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ABSTRACT

The study of an anion-exchange resin (Amberlyst A26 (OH)) catalyzed transesterification of Jatropha (*Jatropha curcas* L.) oil was conducted to determine the effects of three variables: reaction temperature, ethanol: oil molar ratio and catalyst amount, on Jatropha oil conversion (X_{JO}) and fatty acid ethyl esters yield's (Y_{FAEEs}). The modified central composite design that involved three independent factors (temperature, ethanol: oil molar ratio and the catalyst present) with two levels, but not included the non-linear stage, was employed to optimize the process. From the main factors and their interactions, the ethanol: oil molar ratio was found to highly affect the X_{JO} and Y_{FAEEs}. In this study, the statistical analysis showed that curvature is not significant ($p \leq 0.05$), and thus, from the model regression equations, linear model was found to be more suitable to optimize the responses. By using the regression analysis and the response surface plots, the optimum X_{JO} and Y_{FAEEs} of 37.63% and 36.31%, respectively were predicted to be obtained at the optimum temperature of 55 °C, ethanol: oil molar ratio of 35:1 and catalyst amount of 15%. Employing higher amount of catalyst reduced the X_{JO} and Y_{FAEEs}, particularly, when the variable interacted with the reaction temperature.

1. Introduction

Biodiesel is produced by the transesterification of triglycerides, which are one of the main constituents of both edible and non-edible vegetable oils, and an alcohol [1]. Biodiesel from non-edible and wasted oils is considered to potentially be a vital renewable energy alternative to current fossil based fuel as it is nontoxic, bio-degradable, with low greenhouse gas emission and higher lubricating quality [1–3].

Some of the promising alternative processes for biodiesel production are still unprofitable. This is due to their limitations, which includes long reaction times, difficulties in the separation of the products, unaffordable amounts of solvents and generation of large amounts of wastewater [4,5]. For instance, the homogeneous alkaline catalysts such as NaOH and KOH are generally used for the industrial production of biodiesel [1,4]. However, these catalysts require refined oil that contains less than 0.5% free fatty acids (FFAs), and anhydrous conditions as water favors the formation of FFAs by hydrolysis of the triglycerides of the oil. Oil with FFA higher than the indicated limit results in an undesired side reaction, saponification. It also allows emulsions to occur between the obtained biodiesel and the byproduct glycerol, which requires a long settling time for separation. Moreover, alkaline catalysts need to be neutralized with mineral acids, and this results in a dirty glycerol that requires an expensive washing and purification procedure [1,4,6].

The commonly used homogenous acid catalysts such as HCl and H_2SO_4 were found to be more efficient in terms of overcoming the problematic saponification side reactions [1]. However, homogeneous acid catalysts are difficult to recycle and operate at high temperatures and also cause serious environmental and corrosion problems, and thus, are not efficient [1,7,8]. The catalytic enzymes, such as lipase, have high reaction selectivity and can be immobilized in a support material. However, enzymes are very expensive, and have unstable activities and slow reaction kinetics [1,9]. A catalyst-free supercritical method of biodiesel production produces quality biodiesel, and with a very high rate of production. However, the method is expensive as it requires a higher temperature and pressure [1].

Using of heterogeneous catalysts for biodiesel production offers many advantages over homogeneous alternatives, such as simple catalyst recovery, catalyst reusability, simple product purification, less energy and water consumption, lower costs of purification, and simple glycerol recovery [1,4,10]. Thus, to minimize the drawbacks observed in the utilization of homogeneous catalysts, several heterogeneous

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catalysts such as clays, zeolites, oxides and polymer resins (ion exchange resins) have been evaluated for transesterification of vegetable oils [8,11].

Ion exchange resins are suitable catalysts for etherification, esterification, and transesterification reactions [12–14]. The main advantage of using the resins over other heterogeneous catalysts is the opportunity to prepare tailor-made materials by controlling the polymerization conditions [8]. For instance, ion exchange resins can be prepared with different particle sizes and porosity degrees, and a wide variety of functional groups can also be introduced in these polymeric resins to prepare different materials [11]. Moreover, ion exchange resins can be easily separated from the biodiesel produced as they have relatively larger sizes [14].

From several literature reports on the catalytic activities of heterogenous catalysts in the transesterification of vegetable oils, only a few reports were found for that of ion exchange resins. Some of these investigations report that anionic ion exchange resins were more effective in the transesterification of oil than the cationic resins. For instance, Li et al. [14] and Shibasaki-Kitakawa et al. [1] investigated the transesterification of oil with methanol and ethanol respectively, using different types of ion exchange resins as catalysts and the catalytic activities of these resins were then compared. From these studies, it was reported that in general the anionic resins were more efficient in their catalytic activities than the cationic resins under the same conditions for the respective studies. Similarly, in the study of the catalytic activities of Amberlyst 15Wet (cationic resin) and Amberlyst A26 (OH) (anionic resin) on the transesterification reactions of Brazilian soybean oil with methanol and ethanol, the anionic resin was found to be more efficient than the cationic resin for the production of biodiesel under similar conditions [11].

The use of Amberlyst A26 (OH) to catalyze the transesterification of Jatropha (*Jatropha curcas* L.) oil to biodiesel is of interest due to the resin's ability to be recovered, regenerated, and reused. Amberlyst A26 (OH) resin can carry out both esterification and transesterification reactions consecutively, and it is very important to reduce the saponification side reactions in cases of biodiesel production from oils containing free fatty acids [15]. It is a macroporous ion-exchange resin with quaternary ammonium functional groups that impart a strongly basic and reactive surface [15]. The quaternary ammonium functional group in the resin is known to ease transesterification and to remove free fatty acids [15,16].

Only a few research reports were found, from literature, concerning the catalytic activities of Amberlyst A26 (OH) in the transesterification of vegetable oils. For instance, in the transesterification of sunflower oil with methanol using ion-exchange resins (anionic Amberlyst A26 (OH) and A27 (OH) and cationic Amberlyst 15), Vicente et al. [17] obtained a conversion that was less than 1% with each resin. By employing Amberlyst A26 (OH) in the transesterification of Brazilian soybean oil using ethanol, Oliveira et al. [11] obtained the oil conversion of 100% by using 50 mol % of resin, alcohol: oil molar ratio of 150:1 and a reaction time of 24 h. This shows that the catalytic activities of Amberlyst A26 (OH) in the transesterification of oil vary for different vegetable oils, the reaction conditions and needs much amount of alcohol and the catalyst. Moreover, to our knowledge, no research investigation has been performed on the transesterification of Jatropha oil using Amberlyst A26 (OH) in the presence of ethanol.

The objective of this study is to investigate the catalytic transesterification of Jatropha oil using Amberlyst A26 (OH) (a heterogeneous ion-exchange resin) and to determine the effects of reaction temperature, the ethanol: oil molar ratio and the catalyst percent on the conversion of the oil and the yield of biodiesel, and to optimize the process. For this purpose, a Design of Experiment (DOE) and Response Surface Methodology (RSM) have been implemented on the most significant operational variables.

2. Materials and methods

2.1. Reagents and materials

Jatropha oil that was extracted from Ethiopian seeds with Soxhlet extractor using hexane as solvent was used for the experiments. The oil's physico-chemical properties, such as density, iodine number, composition, etc., has already been carried out and the results were submitted elsewhere [18]. The Amberlyst A26 (OH). in wet form, was purchased from Dow Chemical Company, it was used as received, no pretreatment was done to it. The absolute ethanol, tetradecane, pyridine, acetone, methanol and hexane used were purchased from Sigma-Aldrich and with a purity of higher than 99% and used as received.

2.2. Experimental setup for the reactions

The reaction of Jatropha oil with absolute ethanol using Amberlyst A26 (OH) as the catalyst, was performed in a three-neck glass reactor from Quark Glass, with a volume capacity of 500 ml. A cooling condenser, connected to tap water, was inserted into the middle neck of the reactor to enable the refluxing of evaporated ethanol into the reactor. A thermostat attached to the digital heating plate on which the reactor was standing was inserted into the glass reactor, through one of the side necks, to measure the temperature of the reacting mixture. The third neck of the glass reactor was plugged with a rubber cork through which the samples of the reaction mixture were periodically taken using a syringe. The lower part of the reactor was connected to a thermostatic water bath that regulated the temperature of the reacting mixture by circulating the water through the reactor.

Before the reaction time was started, 50 g of Jatropha oil and the calculated amount of ethanol were added to the glass reactor and heated to the required temperature by vigorously stirring the mixture at a rate of 200 rotations per minute (rpm). When the mixture reached the pre-set temperature, a measured amount of Amberlyst A26(OH) was added to the mixture. This was registered as the starting time of the transesterification reaction. The stirring intensity of 200 rpm was maintained for all experiments to overcome the mass-transfer limitations. The aliquots (about 0.5 ml) of the reaction mixture were withdrawn using a syringe at specified time intervals (0, 5, 10, 15, 20, 30, 45, 60, 90, 120, 180, 240, 300, 420, 480 and 540 min) to investigate the progress of the reaction. This total amount of liquid removed from the reactor represents a small quantity in comparison with the total volume, and therefore a constant volume batch system can be assumed. After the reaction, the mixture was filtrated by placing the filter paper on the separatory funnel to separate the resin from the other constituents of the mixture. The filtrate mixture collected in the separatory funnel was then allowed to stand overnight to form different layers of the constituents of the mixture for separation. The resin remaining on the filter paper was washed by acetone and ethanol to be reused for another transesterification reaction [11]. After the separation of the resin, the samples were prepared for analysis, no pre analysis treatment was performed. The solid resin was used once, even though there is an established process to recover the catalysts, its reuses has not been tested so far.

2.3. Analysis of the reaction samples

The reaction samples were analyzed using the gas chromatography (GC) analyzer (Bruker scion 436 chromatograph) equipped with an autosampler (CP-8400), a flame ionization detector (FID) and using a 5-phenyl-methylpolysiloxane capillary column (DB-5HT column, Agilent Technologies). The GC column has a length of 15 m, a diameter of 0.32 mm and a thickness of 0.10 µm. The injection system was split-splitless, and helium was used as carrier gas with a flowrate of 1 ml min^{-1}. The temperature of the injector was set at 320 °C while that of detector was adjusted at 350 °C. The initial temperature in the oven was 80 °C and it was programmed to raise with 10 °C per minute until it reached a final temperature of 360 °C. The GC samples were prepared following the AOAC (2003). Accordingly, tetradecane and pyridine were used as the internal standard and solvent for the GC samples, respectively. The GC analysis was performed by injecting 1 µl of the prepared samples into the equipment.

Using the area obtained for a given weight of the sample and internal standard from the chromatogram, the weight was converted to molar values with the help of standards and the response factors using equations (1) and (2) [19].

$$m_{EE} = \frac{m_{is} \times A_{EE}}{R_{EE} \times A_{is}} \tag{1}$$

$$\eta_{EE} = \frac{m_{EE}}{M_{EE}} \tag{2}$$

Where m_{EE} = mass of ethyl ester (g), m_{is} = mass of internal standard (g), A_{EE} = peak area of ethyl ester, R_{EE} = response factor of ethyl ester, A_{is} = peak area of internal standard, η_{EE} = number of moles of ethyl ester and M_{EE} = molar mass of ethyl ester (g mol^{-1}).

The equation used to calculate Jatropha oil conversion (X_{JO}) is expressed as:

$$X_{JO} = \frac{Initialmolesofoil - Finalmolesofoil}{Initialmolesofoil} x100 \tag{3}$$

Moreover, the fatty acid ethyl esters yield (Y_{FAEEs}) obtained was calculated using the expression below following the study by Wang et al. [20].

$$Y_{FAEEs} = \frac{FAEE(\%)}{\mathrm{TG}(\%) + \mathrm{DG}(\%) + \mathrm{MG}(\%) + \mathrm{FAEE}(\%) + \mathrm{FAA}(\%)} x100 \tag{4}$$

Where FAEE, TG, DG, MG, and FAA refer to fatty acid ethyl ester, triglycerides, diglycerides, monoglycerides and free fatty acids, respectively.

2.4. Experimental design and statistical analysis

2.4.1. Response surface Methodology

Response Surface Methodology (RSM) is a collection of statistical and mathematical techniques that are useful for the modeling and analysis of problems in which a response of interest is influenced by several variables, and the objective of using RSM is to optimize this response [21,22]. It is used to evaluate operation variables that may or may not have a significant effect in the main responses [21]. The design procedures of RSM involve:

i) developing an original design of experiment for adequate and reliable measurement of the selected responses (the conversion of the oil to biodiesel and biodiesel yield in the current study),
ii) developing equations of a statistical model with best fittings,
iii) obtaining the optimal set of experimental parameters that results in the maximum value of responses, and
iv) presenting the direct and interactive effects of the parameters using response surface plots.

2.4.1.1. Experimental design. In the present study, the modified central composite design (CCD) that excluded the star points (the non-linear stage) was applied to determine the influences of three different factors and their interaction on the conversion of Jatropha oil to FAEE (biodiesel) and the Y_{FAEEs}, and to optimize the process. The non-linear stage of the CCD was not included in the current experiment as the statistical analyses of the responses of factorial (linear) points and replicated central points showed that curvature was not significant, and thus, the linear model was used [23]. The design of the experiment involved three independent factors with two levels (2^3 factorial). The selected factors were reaction temperature (T), ethanol: oil molar ratio (R) and the catalyst percent (C) whereas the X_{JO} and Y_{FAEEs} were the two chosen responses. The reaction time and stirring speed were kept constant at 540 min (9 h) and 200 rpm, respectively.

The selected factors have been chosen based on the previous transesterification reaction studies by Sánchez et al. [5] and Ayoola et al. [24], where the temperature, methanol: oil molar ratio and catalyst percent were found to be the most significant variables. The values for the factors were also selected based on the information from the product data sheet of the catalyst and a few related previous studies on ion-exchange resins [8,11,25]. As it was indicated on the product data sheet of the current catalyst (Amberlyst A26(OH)), its maximum operating temperature is 60 °C and thus, the maximum reaction temperature was kept below 60 °C. The design of the experiment consisted of eight factorial (linear) point and six center point experiments, respectively. Running replicated central points is important to measure the accuracy of the study, and it is also used in checking for the presence of curvature [23]. The values of the selected factors and their associated levels in the modified central composite design are presented in Table 1.

Table 1
Values of the factors at different levels in the modified central composite design.

Factors	Levels		
	−1	0	1
Temperature (°C)	45	50	55
Molar ratio (-)	15	25	35
Catalyst amount (%)	15	20	25

2.4.1.2. Statistical analysis. The statistical analyses were performed by designing the sets of different experiments using the Statgraphics Centurion 17 (Statgraphics Technologies, Inc USA). The analyses allowed us to determine the influences of the main factors and their interactions on the conversion of Jatropha oil to biodiesel and yield of the biodiesel. The equations of the regression models were used to interpret the effects of the main factors and their interactions on the selected responses and predict the optimum conditions needed to maximize the responses.

The presence of curvature in the response surface when the selected model equation used was tested statistically using the responses of the factorial points and that of the replicated center points, by employing the statistical equations 5–7 [23,26]. Then, the p value associated with the calculated F value was determined to test the significance of the curvature ($p \leq 0.05$).

$$SS_{pure\ quadratic} = \frac{n_F n_C (\bar{y}_F - \bar{y}_C)^2}{n_F + n_C} \tag{5}$$

$$MS_E = \frac{\sum_{Central\ points} (y_i - \bar{y}_C)^2}{n - 1} \tag{6}$$

$$\mathrm{F} = \frac{\mathrm{SS_{purequadiratic}}}{\mathrm{MS_E}} \tag{7}$$

Where: $SS_{pure\ quadratic}$ = sum of square for pure quadratic curvature, and MS_E = mean square error of central points. $\bar{y}_F$and $\bar{y}_C$ are the average of responses of factorial and central points, respectively. n_F and n_C are number of factorial and central points, respectively. y_i refers to the responses of the central points and $n_C - 1$ is the degree of freedom for central points. F = F-statistic, the test statistic for F-tests.

3. Results and discussion

3.1. Design of the experiment and the experimental responses

As already mentioned, the present study investigated the influences

Table 2

Linear and central point experiments of the design of the experiments and the X_{JO} and Y_{FAEEs}.

Stage/types of experiments	Run number	Temperature (°C)	Molar Ratio	Catalyst (wt%)	X_T	X_R	X_C	X_{JO} (%)	Y_{FAEEs} (%)
Linear (factorial) stage	1	45	15	15	−1	−1	−1	16.91	16.14
	2	55	15	15	1	−1	−1	19.66	18.79
	3	45	35	15	−1	1	−1	31.61	30.41
	4	55	35	15	1	1	−1	38.12	36.81
	5	45	15	25	−1	−1	1	18.14	17.32
	6	55	15	25	1	−1	1	20.53	19.63
	7	45	35	25	−1	1	1	36.91	35.61
	8	55	35	25	1	1	1	34.55	33.29
Center stage	9	50	25	20	0	0	0	29.33	28.19
	10	50	25	20	0	0	0	32,22	31,01
	11	50	25	20	0	0	0	26.76	25.68
	12	50	25	20	0	0	0	27.03	25.94
	13	50	25	20	0	0	0	26.73	25.65
	14	50	25	20	0	0	0	28.42	27.31

of the three selected factors and their interaction on the conversion of Jatropha oil to biodiesel and the biodiesel yield. The modified central composite design (CCD) with three factors and two levels factorial (2^3) that consisted of only two stages (eight factorial/linear points and the central points that were replicated six times). Accordingly, the experiments of the linear stage and the central points were carried out randomly, and the obtained X_{JO} and Y_{FAEEs} were recorded. The natural and coded factors and the resulting X_{JO} and Y_{FAEEs} for the experiments were presented in Table 2.

As it can be seen from Table 2, the largest experimental X_{JO} (38.12%) and Y_{FAEEs} (36.81%) were obtained when the reaction was carried out at the reaction temperature of 55 °C, ethanol: oil molar ratio of 35:1 and 15% catalyst.

3.2. Effects of the reaction variables

During the experiment, four reactions were carried out by varying the temperature, ethanol: oil molar ratio and catalyst amount one at a time and keeping the other reaction conditions constant (at the value of the central points) to investigate the effects of the respective factors on the responses. Fig. 1a-c shows the effects of temperature, ethanol: oil molar ratio and catalyst amount on the X_{JO} and Y_{FAEEs} by keeping two of the three factors constant. As it can be seen from Fig. 1a, the raising of reaction temperature from 41.6 to 55 °C resulted in the increase of X_{JO} and Y_{FAEEs} by 5.39% and 5.27%, respectively. The raising of the ethanol: oil molar ratio from 8.18:1 to 35:1 found to increase the X_{JO} and Y_{FAEEs} by 33.71% and 32.88%, respectively (Fig. 1b). Moreover, increasing the catalyst amount from 11.6 to 25% resulted in the increase of X_{JO} and Y_{FAEEs} by 2.42 and 2.37%, respectively (Fig. 1c). Thus, the results of these experiments showed that from the influences of the three investigated reaction factors, the effects of ethanol: oil molar ratio on both responses are the largest.

3.3. Results from the statistical analysis

The statistical analysis was performed by considering the reaction temperature, ethanol: oil molar ratio and the catalyst amount. The effects of the main factors and their interactions on X_{JO} and Y_{FAEEs} were determined using Statgraphics Centurion 17, and the $SS_{\text{pure quadratic}}$, MS_E and the value of F statistics were determined using equations 5–7 [23,26] to test the presence (significance) of curvature ($p \leq 0.05$) in the response surface plot as previously mentioned. Table 3 shows the results obtained from the statistical analysis of the experimental responses. From the results depicted in Table 3, ethanol: oil molar ratio was found to be the factor with the highest positive impact. The reaction temperature and the catalyst percent were found to have a very small positive impact on the transesterification process compared to that of ethanol: oil molar ratio. Moreover, the effects of all the binary interactions on the transesterification process were found to be small and negative.

The experimental results from Fig. 1 and Table 3 showed that ethanol: oil molar ratio has the highest positive impact on the transesterification Jatropha oil. According to the stoichiometry, three molecules of ethanol react with one molecule of triglyceride to produce three moles of FAEE. However, an excessive amount of alcohol is generally employed to promote the forward reaction to increase the oil conversion and yield of the esters [27,28] and to facilitate the glycerin separation [27]. This is in line with literature reports for transesterification of different vegetable oils using ion-exchange resins as catalyst, in which an increase in the molar ratio of alcohol to oil ratio highly influenced the transesterification of the oils. For example, in the transesterification of soybean oil with ethanol, Oliveira, et al. [11] reported an increase of oil conversion from 50% to 100% when the alcohol to oil molar ratio raised from 50:1 to 150:1.

There are also reports from literature about the requirement of very high alcohol: oil molar ratio for the transesterification of soybean oil with ethanol and methanol by using ion exchange resins. In the study of the influence of methanol: oil molar ratio on the conversion of babaçu coconut oil by using Amberlyst 15 wet as catalyst, Reis et al. [25] found the need of a high alcohol amount to produce ester. Accordingly, the authors reported that the conversion of oil to biodiesel reached around 70% only by employing an alcohol: oil molar ratio of 300:1, which is very high.

From an industrial perspective, increasing the amount of alcohol has several disadvantages, technical as well as economical. The higher amount of alcohol produced that the reaction equipment is of bigger size, increasing the investment cost, there is more energy consumed due to heating of reactors, pumping of streams, storage of products, etc. as well more time and money consumed separating the alcohol from the products, recirculation of the unreacted material, among other disadvantages.

In order to make this new technology more commercially attractive, it is imperative to improve the reaction, decreasing the amount of alcohol to almost stoichiometric quantities, reducing the cost of reactant, the cost of recycling material as well as making the equipment as efficient as possible. However, this needs to go hand in hand with producing the desired product at the desired quality and with the desired conversion and selectivity.

In the current study, compared to the influence of ethanol: oil molar ratio, the impacts of the reaction temperature and catalyst amount on the oil conversion and biodiesel yield are very low (Fig. 1 and Table 3). According to Yatish et al. [29], generally, temperature has a positive impact on the transesterification of different vegetable oils although this depends on the type of catalyst and the experimental range studied.

The natural values of the experimental variables were used to predict the suitable mathematical regression models for the described

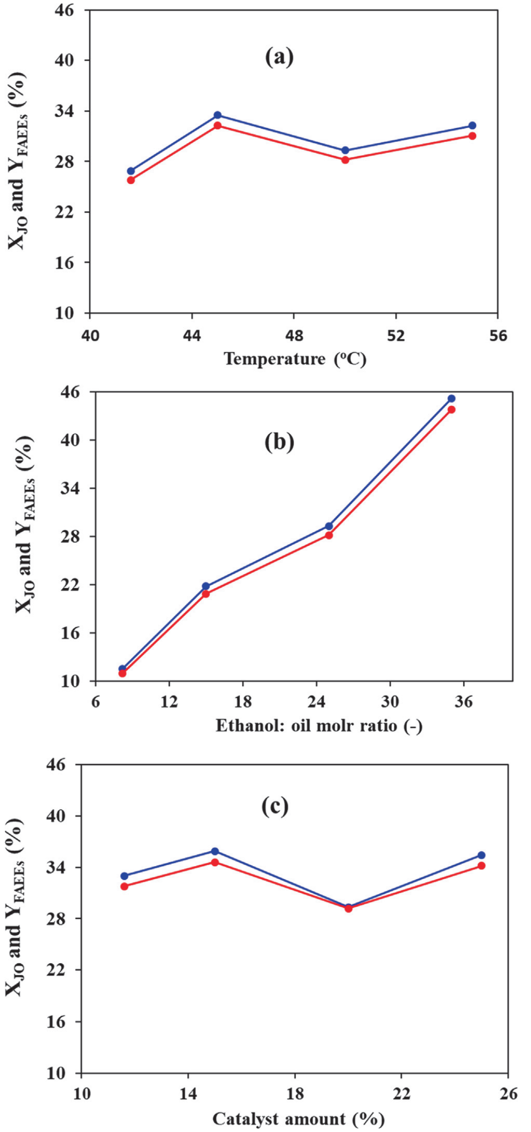

Fig. 1. (a) Effect of reaction temperature (•) on X_{JO} and (●) Y_{FAEEs} at ethanol: oil molar ratio of 25:1, catalyst amount: 20 wt%. (b) Effect of ethanol: oil molar ratio (•) on X_{JO} and (●) Y_{FAEEs} at reaction temperature: 50 °C and catalyst amount: 20 wt%. (c) Effect of catalyst amount (•) on X_{JO} and (●) Y_{FAEEs} at reaction temperature: 50 °C and ethanol: oil molar ratio: 25:1. The stirring intensity: 200 rpm and reaction time: 540 min were common for all the three cases.

transesterification of Jatropha oil using Amberlyst A26 (OH). As the curvature for both responses is not significant (Table 3), the first order mathematical model (linear model) was found to be suitable to be used for the optimization of the transesterification process [23,26]. Accordingly, the linear regression models that express the X_{JO} and Y_{FAEEs} under the current experimental range are presented in equation (8) and (9), respectively.

Table 3
Results from the statistical analysis of the experiments.

Parameters	Responses Oil conversion	Biodiesel yield
Main effects and interactions	$\bar{y}$ = 27.63	$\bar{y}$ = 26.55
	I_T = 2.32	I_T = 2.26
	I_R = 16.48	I_R = 16.06
	I_C = 0.95	I_C = 0.92
	I_{TR} = -0.24	I_{TR} = -0.22
	I_{TC} = -2.31	I_{TC} = -2.26
	I_{RC} = -0.092	T_{RC} = -0.08
Significance of curvature (at p ≤ 0.05)		
Mean response (factorial points, $\bar{y}_F$)	27,053	26.00
Mean response (center points, $\bar{y}_C$)	28.415	27.29
Curvature	−1.36	−1.29
$SS_{pure\ quadratic}$	6.35	5.76
MS_E	4.56	4.35
F calculated	1.39	1.32
p value	0.291	0.301
Significance of curvature (p ≤ 0.05)	Not significant	Not significant

Where: T = temperature, R = ethanol: oil molar ratio, C = catalyst percent, I_{TR} = interaction of temperature and molar ratio, I_{TC} = interaction of temperature and catalyst percent and I_{RC} = interaction of molar ratio and catalyst percent.

$$X_{JO} = -56.20 + 1.21T + 0.96R + 2.42C - 0.0024TR - 0.046TC - 0.00092RC \quad (8)$$

$$Y_{FAEE} = -55.14 + 1.18T + 0.93R + 2.37C - 0.0022TR - 0.045TC - 0.00085RC \quad (9)$$

Based on the regression models, three-dimensional (3D) response surface plots were produced to illustrate the binary interaction effects of the reaction temperature, ethanol: oil molar ratio and catalyst percent (Figs. 2-4). From the binary factor interactions (I_{TC}, I_{TR} and I_{RC}), the effect of the interactions of temperature and catalyst percent on the responses was relatively larger and negative while that of the interaction of ethanol: oil molar ratio with catalyst amount was the smallest (Table 3). As aforementioned, generally, the effects of the binary interactions of the experimental factors on the X_{JO} and Y_{FAEEs} were found to be low. The negative impact of the interaction of the temperature and catalyst amount on the responses might be due mass-transfer limitation at higher concentration of the catalyst (Table 3 and Fig. 4a and b).

As it can be seen from Fig. 2a and b and Fig. 3a and b, in the interactions of temperature and ethanol: oil molar ratio (at catalyst amount of 20%) and those of the catalyst percent and ethanol: oil molar ratio (at constant temperature, 50 °C), the effects of the factors on both responses were dominated by the alcohol: oil molar ratio. As the ethanol: oil molar ratio raised from its minimum (15:1) to the maximum (35:1) of the experiment, the X_{JO} and Y_{FAEEs} increased linearly whereas the impacts of the temperature and catalyst amount, respectively were relatively lower. Accordingly, when the ethanol: oil molar ration raised to 35:1, both responses were predicted to reach above 33% even at the minimum experimental temperature (45 °C) and catalyst amount (15%), respectively (Fig. 2a and b and Fig. 3a and b). Moreover, the linearity and continuous increasing of both responses with the raising of the alcohol: oil molar ratio up to the maximum value of the experiment suggested that further increasing of ethanol: oil molar ratio than the experimental maximum could result in higher X_{JO} and Y_{FAEEs} compared to those obtained in the current experiments.

In the binary interactions of reaction temperature and catalyst amount (Fig. 4a and b), the maximum X_{JO} and Y_{FAEEs} were predicted to be obtained when the reaction temperature raised form the minimum (45 °C) to the maximum (55 °C) experimental ranges but at the

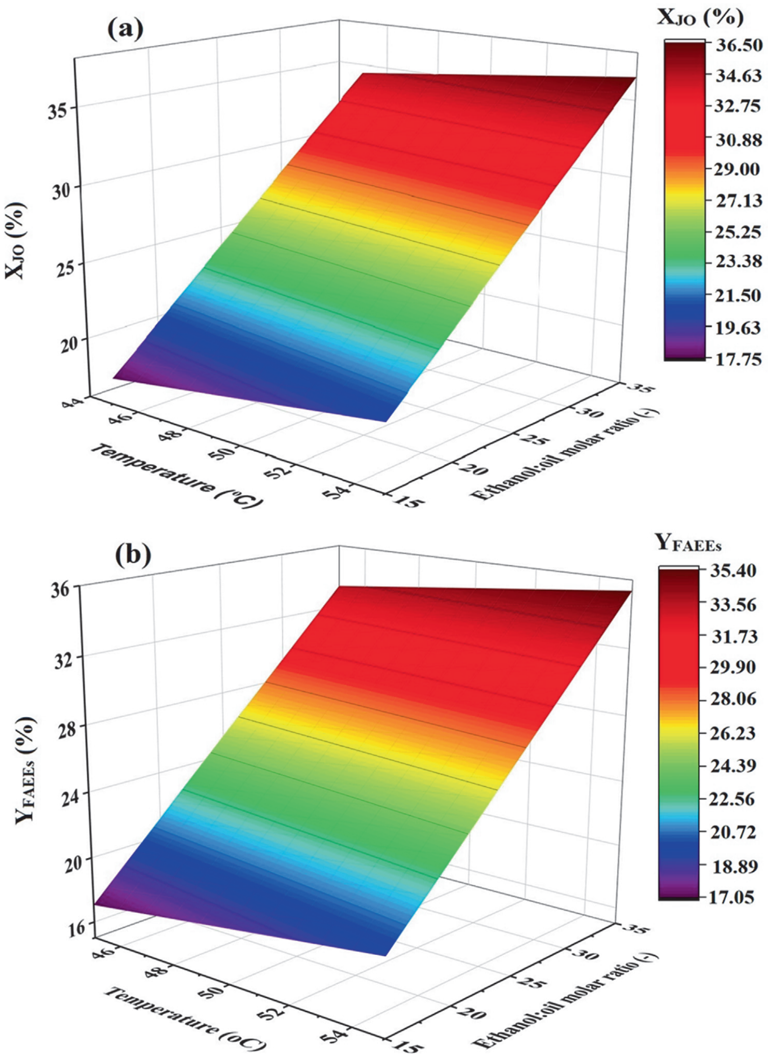

Fig. 2. Response surface 3D plot indicating the influence of temperature and ethanol: oil molar ratio on (a) the X_{JO} and (b) Y_{FAEEs}. Catalyst amount = 20% (temperature and ethanol: oil molar ratio refer to the actual values).

minimum catalyst amount (15%). The amount of catalyst utilized in the present experiment varied from 15 to 25%. Although the variable, generally, has slight positive effects on the transesterification process of the oil (Table 3), its interaction with temperature at the average ethanol: oil molar ratio (25:1) had a negative impact on both responses. As it can be seen from Fig. 4a and b, when the catalyst amount raised from the minimum (15%) to the maximum (25%) range of the experiment, both the X_{JO} and Y_{FAEEs} slowly decreased. The decreasing of the X_{JO} and Y_{FAEEs} with the simultaneous raising of the catalyst amount and temperature at the average ethanol: oil molar ratio (25%) might be due to the lower ethanol: oil molar ratio than the optimum alcohol: oil molar ratio value predicted (35:1) (Table 4) and the mass-transfer limitation that could be occurred as the catalyst amount increased.

By using the linear model equations and the response surface plots, the optimum X_{JO} and Y_{FAEEs} of 37.63% and 36.31%, respectively were predicted to be obtained at the optimum temperature of 55 °C, ethanol: oil molar ratio of 35:1 and catalyst amount of 15% (Table 4). During the experiment, the X_{JO} and Y_{FAEEs} of 38.12% and 36.81%, respectively were obtained at the same reaction conditions (reaction temperature of 55 °C, ethanol: oil molar ratio of 35:1 and catalyst amount of 15%) (Table 2), and thus, the experimentally obtained values are in agreement with those predicted for the optimal operational conditions.

The graphical representation for the predicted values and experimental results of X_{JO} and Y_{FAEEs}, are presented in Fig. 5a and b, respectively. As it can be seen from Fig. 5a and b, the predicted X_{JO} and Y_{FAEEs} generally banded around the predicted straight line and this shows the better correlation of the predicted values with the experimental results.

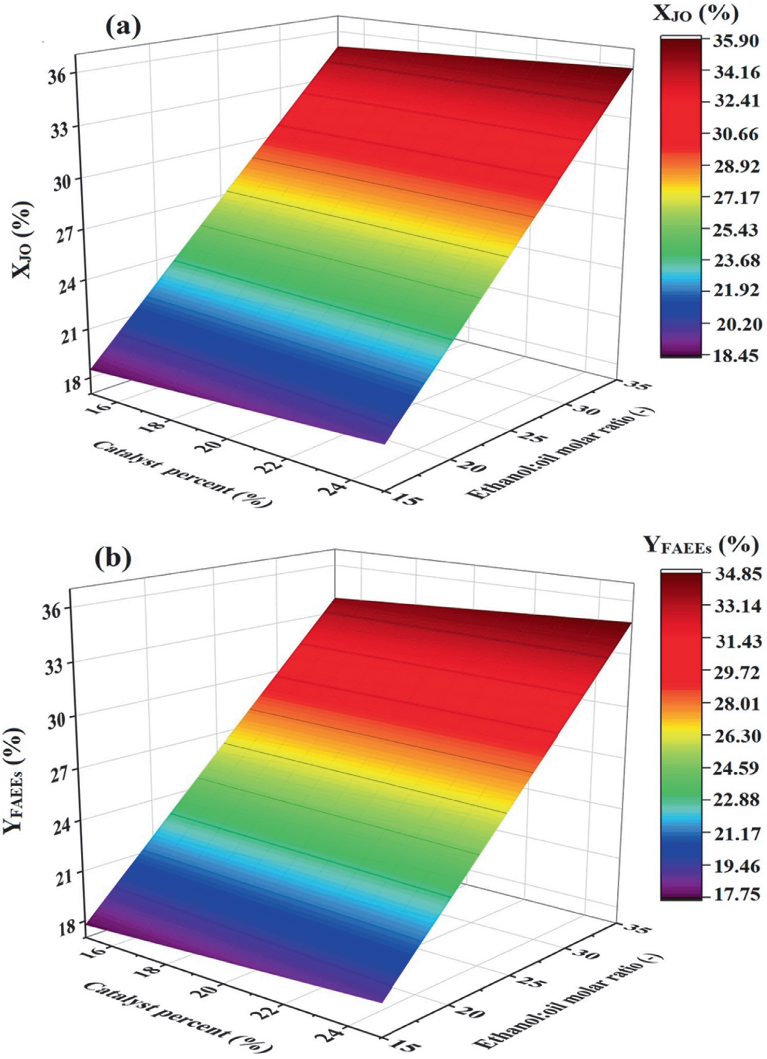

Fig. 3. Response surface 3D plot indicating the of influence of catalyst percent and ethanol: oil molar ratio on (a) the X_{JO} and (b) Y_{FAEEs}. Temperature = 50 °C (catalyst percent and ethanol: oil molar ratio refer to the actual values).

4. Conclusion

This study was carried out to investigate the catalytic transesterification of Jatropha oil using Amberlyst A26 (OH) wet (a heterogeneous ion-exchange resin) as catalyst and determine the impacts of the reaction temperature, ethanol: oil molar ratio and catalyst amount on the X_{JO} and Y_{FAEEs}, and to optimize the process. Accordingly, the modified central composite design from which the non-linear stage excluded was used to optimize the reaction process. From the main factors and their interactions, ethanol: oil molar ratio was found to highly influence the X_{JO} and Y_{FAEEs}. From the model regression equations, the linear model was found to be suitable to optimize the responses. The optimum X_{JO} and Y_{FAEEs} of 37.63% and 36.31%, respectively were predicted to be obtained at the optimum temperature of 55 °C, ethanol: oil molar ratio of 35:1 and catalyst amount of 15%. Using a catalyst amount higher than 15% reduced the X_{JO} and Y_{FAEEs}, particularly, when the variable interacted with the reaction temperature, and this might be due to the mass-transfer limitation. The result hereby presented are limited to the domain where they have been obtained. Any extrapolation based on the models needs to be done carefully since the models are valid for the domain used to developed them.

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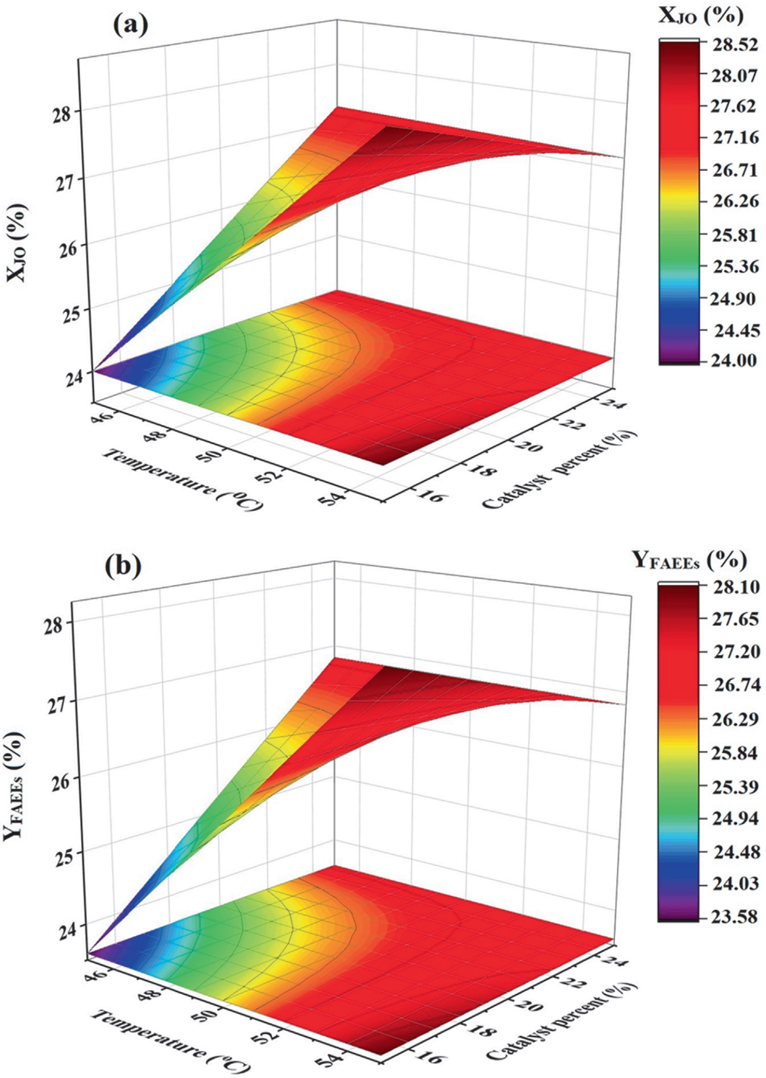

Fig. 4. Response surface 3D plot indicating the influence of temperature and catalyst percent on the X_{JO} and (b) Y_{FAEEs}. Ethanol: oil molar ratio = 25 (temperature and catalyst percent refer to the actual values).

Table 4
Optimum conditions predicted for maximum conversion of Jatropha oil and Y_{FAEEs}, and the optimum responses.

Factors	Conversion Optimum factors	Optimum response (%)	Yield Optimum factor	Optimum response (%)
Temperature (°C)	55.00		55.00	
Molar ratio (-)	35.00	37.63	35.00	36.31
Catalyst amount (%)	15.00		15.00	

CRediT authorship contribution statement

Yadessa G. Keneni: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Software, Validation, Writing - original draft, Writing - review & editing, Visualization. **Anne Kathrine (Trine) Hvoslef-Eide:** Conceptualization, Methodology, Validation, Visualization, Supervision, Project administration, Funding acquisition. **Jorge M. Marchetti:** Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Software, Validation, Writing - review & editing, Visualization, Supervision, Project administration.

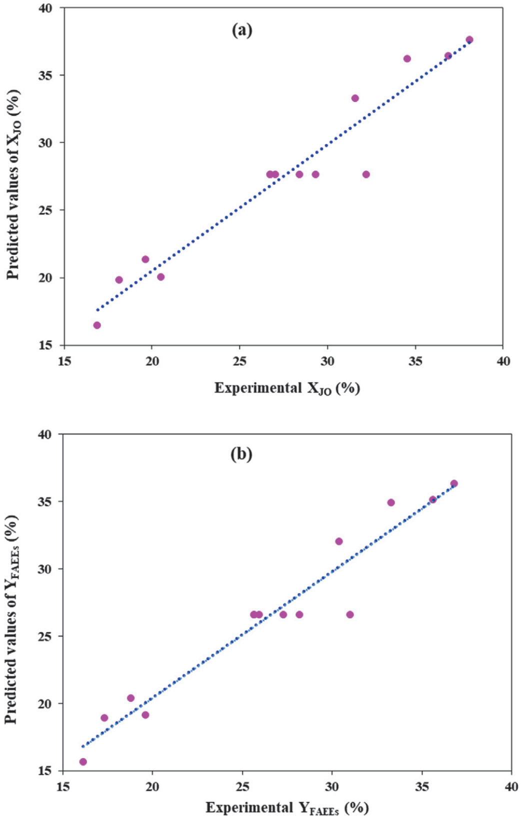

Fig. 5. Predicted versus experimental values of (a) X_{JO} and (b) Y_{FAEEs}, respectively.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Paper VI

Butanolysis of Jatropha oil using glycerol enriched non-calcined calcium oxide: optimization of the process

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Abstract

The study of butanolysis of Jatropha oil using glycerol enriched non-calcined calcium oxide as heterogenous catalyst was carried out to investigate the effects of reaction temperature and butanol: oil molar ratio on Jatropha oil conversion using butanol (X_{JOB}) and yield of fatty acid butyl esters (Y_{FABEs}). The central composite design that involved two factors (reaction temperature and butanol: oil molar ratio) and two levels factorial (2^2) was used to determine the effects of the factors on X_{JOB} and Y_{FABEs} and to optimize the process. From the main factors and their interaction, reaction temperature was found to highly affect both the X_{JOB} and Y_{FABEs}. As curvatures are statistically significant ($p \leq 0.05$), the second order regression models (quadratic models) were found to be more suitable for the optimization of the butanolysis process. Based on the regression analysis models and the response surface methodology, the maximum X_{JOB} (98.16%) and Y_{FABEs} (95.79%) were predicted to be obtained at the optimum temperatures of 87.35 and 90.48 ^{o}C and butanol: oil molar ratios of 9.13:1 and 13.24:1, respectively. The maximum Y_{FABEs} of 95.64% was also experimentally obtained at the optimum conditions predicted for Y_{FABEs}. From the results obtained for the experimental ranges investigated, the present study suggested that glycerol enriched non-calcined calcium oxide can be used as good alternative catalyst for biodiesel

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production using butanol. More studies are also suggested for upscaling the reaction process of the current experiments by using more integrated reaction factors.

Keywords: Biodiesel; butanolysis; calcium oxide; glycerol; *Jatropha curcas* L. oil; optimization

1. Introduction

The interest of using fuels from renewable sources, such as biodiesel, has increased in recent years due to political and economic instability of the fossil fuel market, and also because of the positive environmental benefits of the fuels from renewable sources [1, 2]. Biodiesel contributes less to global warming and contains less contaminant in its emission due to the renewable nature and organic origin of the feedstocks [3].

Biodiesel is a liquid fuel that consists of mono alkyl esters of long chain fatty acids derived from lipid such as vegetable oils, animal fats and microalgae oils [1, 4, 5]. It is usually produced through the transesterification reactions of the oils with shot-chain alcohols using homogeneous or heterogeneous catalysts [1, 5]. The catalysts used can be either acidic, basic or enzymatic in nature and employing each kind of catalyst has its own benefits and limitations [5].

Biodiesel has still difficulties to be competitive with petroleum diesel without fiscal incentives, mostly due to the price of the raw materials and the processing costs [6]. The cost of feedstock alone accounts about 75% of the overall biodiesel production cost [7, 8], and hence using inexpensive feedstocks such as non-edible oils, wasted oils and animal fats has been identified as a promising solutions in this regard [7-9]. The other alternatives to reduce the price of biodiesel is employing cost effective biodiesel manufacturing process, particularly by using low-cost catalysts [10].

The majority of biodiesel is produced through homogeneous base catalyzed transesterification of edible vegetable oils using methanol, and the most commonly used catalysts are KOH and NaOH [5]. These catalysts result in fast reaction rates under mild reaction conditions [11], however, the oil and the alcohol must be substantially anhydrous, and the free fatty acid (FFA) content of the oil should be low to avoid the saponification side reaction [12, 13]. Generation of large amount of wastewater to purify the products and incapability of catalyst reuse are also among the limitations of using these catalysts [14]. Homogenous acid catalysts such as HCl and H_2SO_4 are efficient in terms of overcoming the saponification side reactions [15], but difficulties of catalyst recycling, requirement of higher temperature and alcohol to oil molar ratio, and serious environmental and corrosion problems are some of the limitations of these catalysts [15-17]. Moreover, enzymatic catalysts are less sensitive to FFA and moisture content of the oil [15, 17], however, the requirement of more stringent reaction conditions, long reaction time and being expensive are some of the disadvantages of using enzymes [14, 17]. One of the possible solutions to overcome these problems is using heterogenous catalysts [11].

Using heterogeneous catalysts might significantly reduce the processing costs associated with homogeneous catalysis [6] as they can be reused, ease separation of products and avoids the extensive product washing steps [15, 17-19]. Heterogenous basic catalysts are more reactive than heterogenous acid catalysts as the basic ones require relatively shorter reaction time and lower reaction temperature [20]. Among the basic heterogeneous catalysts, CaO has been extensively used for transesterification reactions as it processes high basicity, low solubility in alcohols and low cost [20]. It can be reused, has tolerance to moisture and FFA content of the oil and is non-corrosive and environmentally friendly [14]. CaO can be used in various forms such as single oxide [1, 21, 22], mixed oxides [23, 24] and supported [25-27] forms. Moreover, the glycerol-CaO complex form of CaO which is designated as glycerol-enriched CaO or calcium diglyceroxide (CaDg) has been used as a catalyst for biodiesel production [6, 28, 29].

Concerning the formation of CaDg in CaO catalyzed transesterification reaction, several studies reported the structural transformation CaO catalyst during the progress of the reaction [30-32]. At the beginning of the reaction, CaO is the active phase, however, as the transesterification reaction proceeds, the produced glycerol ($C_3O_8H_3$) reacts with CaO and produces CaDg ($Ca(C_3O_7H_3)_2$) [30, 32]. Kouzu et al. [31, 32] found that the probability of CaDg formation in the transesterification reaction matrix is higher than that of calcium methoxide as glycerol is more reactive with CaO than methanol. CaDg consists of an isolated tetramer ($Ca_4(C_3H_7O_3)_8$) and is bound by a complex H-bond network [30] and this structure of CaDg contributed to its outstanding physiochemical properties and good catalysis ability [33]. CaDg catalyst has been reported to show superior catalytic activity in biodiesel production compared to CaO because the presence of basic oxygen anions, formed due to the interruption of the surface crystal structure, which can easily abstract protons from the -OH groups of methanol and form methoxide ion on the surface [34].

Transesterification has been generally carried out using methanol or ethanol as these alcohols are considered as good fatty acid acyl acceptors [35]. Accordingly, investigations of biodiesel production using glycerol-enriched CaO as catalyst have focused on the transesterification of oil with methanol or ethanol [6, 28-30, 36] using calcined CaO [6, 28-30]. On the contrary, butanol has not been so extensively studied [37]. However, butanol is less corrosive and less soluble in water, and thus, has a greater miscibility with the oil phase [38]. Using butanol for transesterification has several advantages over methanol or ethanol since its longer chain favors the properties biodiesel produced and its blending with conventional diesel. For instance, the butyl ester has a higher energy value than the analogues methyl or ethyl esters since it contains more carbon atoms [37]. Moreover, butanol can be produced from different biological resources, including organic wastes, through fermentation and, thus, it is renewable [39, 40]. Hence, regarding these promising properties of butanol in biodiesel production, more research work is needed [37]. In several studies, commercial CaO was calcined prior to utilizing it as catalyst for transesterification to activate the active site that might be poisoned by CO_2 and H_2O from the air [21, 41, 42], and this might add some cost to the overall biodiesel production process. To our knowledge, no research has been performed on the transesterification of non-edible oils such as Jatropha oil using glycerol-enriched non-calcined commercial CaO using butanol.

The objective of the present study is to investigate the catalytic butanolysis of Jatropha oil using glycerol-enriched non-calcined commercial CaO, and to determine the effects of variations of reaction temperature and butanol: oil molar ratio on oil conversion and fatty butyl ester yield and optimize the process.

2. Materials and methods

2.1. Reagents and materials

Jatropha (*Jatropha curcas* L.) oil that was extracted from the seed collected from Ethiopia was used for the experiment. The oil was extracted from the seeds with Soxhlet extractor using hexane as solvent and thimble with single thickness (37x130 mm). The physico-chemical properties of the oil was determined and the results were submitted elsewhere [43]. The calcium oxide used for the reaction was purchased from Honeywell Company. The 1-butanol, glycerol, tetradecane, pyridine, acetone, methanol and hexane used were purchased from Sigma-Aldrich. A rotary evaporator (Rotary Vapo R-3, Butchi Labortechnik AG, CH-9230, Switzerland) with vacuum pump was used to separate butanol from the reaction mixture after transesterification reaction.

2.2. Experimental setup for the reactions

Both the synthesis of the glycerol-enriched CaO and transesterification of Jatropha oil with butanol using glycerol enriched CaO as catalyst, were performed in a three-necked glass reactor from Quark Glass, with a capacity of 500ml. A cooling condenser connected to a tap water was inserted into the middle neck of the reactor to cool the evaporated butanol during the reaction and reflux it into the reactor. A thermostat that was attached to the digital heating plate was inserted into the glass reactor via one of the side necks to measure the temperature of the reaction mixture. The third neck of the glass reactor was connected to a syringe through which the samples of the reaction mixture were taken. The lower part of the reactor was also connected to a water bath that was thermostatically regulating the temperature of the reacting mixture.

2.2.1. Synthesis of the glycerol-enriched CaO

Before starting the transesterification reaction, the synthesis of glycerol-enriched CaO (glycerol-CaO complex) was performed in an airtight the three-necked glass reactor as previously mentioned. Measured amount of glycerol (15% by wt% of CaO) was added to the inner bottom surface of the glass reactor. Then, about 70 g of Jatropha oil and 10.5 g of non-calcined commercial CaO (15% by wt% of the oil) were added to the reactor and heated to 60°C by vigorously stirring the mixture at 200 rpm for 60 min under ambient pressure. The amount of the glycerol and the temperature used for the synthesis of glycerol-CaO complex was adapted from the previous related works [28, 29, 36]. The synthesis of glycerol-enriched CaO was performed in the presence of Jatropha oil, but without adding any butanol to avoid the possibility of the formation of calcium butoxide [28, 29, 31]. After the activation of CaO with glycerol, the mixture in the glass reactor was heated to the desired temperature.

2.2.2. Transesterification reactions

When the temperature of the mixture in glass reactor (the mixture contained glycerol-enriched CaO) reached at the set temperature, a measured amount of 1-butanol heated separately to the reaction temperature was added to the mixture. This time was taken as the initial time (t=0) for the glycerol- enriched CaO catalyzed transesterification of Jatropha oil. About 0.5 ml samples of the reacting mixtures were withdrawn at predetermine time intervals (0, 10, 20, 30, 60, 90 minutes) to follow up the progress of the reaction. At the end of the reaction, the mixture was centrifuged to separate CaO and other components. The butanol in the mixture was also removed through distillation using a rotary evaporator attached to a vacuum pump. The glycerol and fatty acid butyl esters (biodiesel) were separated by decantation using separatory funnel.

2.3. Analysis of the reaction samples

The reaction samples were analyzed by the gas chromatography (GC) analyzer (Bruker scion 436 chromatograph) having an autosampler (CP-8400) and a flame ionization detector (FID) and using a capillary column with 5-phenyl-methylpolysiloxane (DB-5HT column, Agilent Technologies). The length, diameter and thickness of GC column were 15m, 0.32mm and 0.10μm, respectively. Helium was used as carrier gas with a flowrate of 1ml min^{-1}, and the injection system employed was split-splitless. The temperature of the injector and detector were set at 320 and 350 ^{o}C, respectively. The temperature of the oven was started from 80 ^{o}C and programmed to raise by 10 ^{o}C per min until the final temperature of 360 ^{o}C was reached. The GC samples were prepared according to AOAC Official Method (2003). Hence, tetradecane was used as the internal standard while pyridine was utilized as a solvent for the GC samples. The analysis was done by injecting 1μl of a sample into the equipment.

From the areas of the chromatogram recorded for a given weight of the sample and the internal standard of the components in the sample, the weight of the components and their molar values were calculated with the help of the standards and the response factors employing equation 1 and 2 [28].

$$m_{BE} = \frac{m_{is} \times A_{BE}}{R_{BE} \times A_{is}} \tag{1}$$

$$\eta_{BE} = \frac{m_{BE}}{M_{BE}} \tag{2}$$

Where m_{BE} = mass of butyl ester (g), m_{is} = mass of internal standard (g), A_{BE} = peak area of butyl ester, R_{BE} = response factor of butyl ester, A_{is} = peak area of internal standard, η_{BE} = number of moles of butyl ester and M_{BE} = molar mass of butyl ester (g mol^{-1}).

Jatropha oil conversion using butanol (X_{JOB}) was calculated using Equation 3.

$$X_{JOB} = \frac{Initial\ moles\ of\ oil - Final\ moles\ of\ oil}{Initial\ moles\ of\ oil}\ x\ 100 \tag{3}$$

The yield of fatty acid butyl esters (Y_{FABEs}) obtained was also calculated using Equation 4 which was also used by Wang et al. [44].

$$Y_{FABEs} = \frac{FABE\ (\%)}{TG(\%) +\ DG(\%) + MG\ (\%) + FABE(\%) + FAA(\%)}\ x\ 100 \tag{4}$$

Where FABE, TG, DG, MG, and FAA represents fatty acid butyl ester, triglycerides, diglycerides, monoglycerides and free fatty acids, respectively.

2.4. Experimental design and statistical analysis

2.4.1. Response surface methodology

Response Surface Methodology (RSM) is a collection of statistical and mathematical approach which are useful for developing, improving, and optimizing processes and product designs [45-47]. RSM deals with the analysis and modelling of problems in which a response of interest is affected by several factors, and the main objective is to optimize this response [45, 46]

According to Muriithi et al. [45], the major procedures needed in RSM include designing of the experiment with adequate and reliable measurement of the selected responses, developing equations of statistical model with best fittings, obtaining the optimal experimental conditions to maximize the responses, and presenting the direct and interactive effects of the parameters using response surface plots.

2.4.2. Experimental design

The experiment of the transesterification reaction catalyzed by glycerol enriched CaO was carried out to determine the effects of two selected factors (reaction temperature and butanol: oil molar ratio) with two levels on jatropha oil conversion in the reaction with butanol (X_{JOB}) and the yield of fatty acid butyl esters (Y_{FABEs}). Accordingly, the central composite design (CCD) that involved two factors and two levels full factorial (2^2) was used to determine the impacts of the factors on the X_{JOB} and Y_{FABEs}, and to optimize the process. The design of the experiment contained three stages: factorial (linear) and non-linear stages which consisted of four experiments each as well as the four times replicated center points. Running the replicated center points is important to measure the accuracy of the study, and it is also used to statistically test for the presence or significance of curvature [48]. The values of the selected factors and their associated levels for the reactions catalyzed with non-calcined CaO are presented in Table 1. The amount of CaO employed was kept constant at 15% (wt%) of the oil while the glycerol used was 15% (wt%) of the catalyst. The amounts of catalyst and glycerol used were adopted from the results obtained by Avhad et al. [28]. Reaction time and stirring speed of 90 min and 200 rpm, respectively were used for all experiments.

Table 1

Values of the factors at different levels of the design for the reaction catalyzed with CaO.

Factors	Levels				
	-α	-1	0	1	α
Temperature (°C)	65.9	70	80	90	94.10
Molar ratio (-)	4.77	6	9	12	13.23

The temperature range used for the present work was selected based on the study by Navas et al. [2] where transesterification reactions of castor oil with butanol were carried out using the supported oxides, MgO/ γ-Al_2O_3 and ZnO/ γ-Al_2O_3 catalysts by employing the reaction temperature of 80°C and obtained the fatty acid butyl ester yield of 97% and 85%, respectively. The boiling point of 1-butanol is 117.5 °C [49] and the butanolysis involving heterogeneous catalysts requires relatively higher temperature compared to the transesterification with shorter chain alcohols such as methanol and ethanol [2, 37, 50].

2.4.3. Statistical analysis

The statistical analyses were performed by designing the sets of experiments using CCD by employing Statgraphics Centurion 17 software (Statgraphics Technologies, Inc USA). The analyses enabled us to determine the significances of the influences of the main factors and their interactions on the X_{JOB} and Y_{FABEs}. The suitable equation of regression model was also developed to interpret the influences of the main factors and their interactions on the selected response and predict the optimum conditions required to maximize the responses [45].

After running the experiments of factorial and center points (totally eight experiments) and determining the X_{JOB} and Y_{FABEs} of each experiment, the significance of curvature in the response surface plot when the selected model equation used was statistically tested by employing the statistical equations 5-7 [48, 51]. Then, using the calculated F value, the associated p value was determined to test the significance of curvature ($p \leq 0.05$).

$$SS_{pure\ quadratic} = \frac{n_F n_C(\bar{y}_F - \bar{y}_C)^2}{n_F + n_C} \quad (5)$$

$$MS_E = \frac{\sum_{Central\ points}(y_i - \bar{y}_C)^2}{n-1} \quad (6)$$

$$F = \frac{SS_{pure\ quadiratic}}{MS_E} \quad (7)$$

Where: $SS_{\text{pure quadratic}}$ is the sum of square for pure quadratic curvature and MS_E is the mean square error of center points. $\bar{y}_F$ and $\bar{y}_C$ are the average of responses of factorial and center points, respectively. n_F and n_C are number of factorial and center points, respectively. y_i represents to the responses of the center points while $n_C - 1$ refers to the degree of freedom for center points. F represents the F-statistic, the test statistic for F-tests.

3. Results and discussion

3.1. Experiments of different stages and the responses

As previously mentioned, butanolysis of jatropha oil using glycerol enriched CaO as catalyst was performed to investigate the effects of reaction temperature and butanol: oil ratio and their interaction on X_{JOB} and the Y_{FABEs}. The CCD with two factors and two levels factorial (2^2) that consisted of three stages was used to optimize the process. Accordingly, a total of twelve experiments, four experiments for the linear stage, center points and non-linear stage, respectively were carried out randomly, and the obtained responses were recorded. The natural and coded factors and X_{JOB} and Y_{FABEs} found for the respective experiments are presented in Table 2.

Table 2

Stages of the CCD design and the Jatropha oil conversion using butsnol (X_{JOB}) and yield of fatty acid butyl esters (Y_{FABEs}).

Stage/types of experiments	Run	Temperature (T) (ºC)	Molar ratio (R)	XT	XR	X_{JOB} (%)	Y_{FABEs}(%)
Linear (factorial) stage	1	90	12	1	1	89.70	86.70
	2	90	6	1	-1	96.39	93.13
	3	70	12	-1	1	22.80	9.46
	4	70	6	-1	-1	47.88	45.71
Center point stage	5	80	9	0	0	92.11	85.04
	6	80	9	0	0	87.68	81.73
	7	80	9	0	0	85.44	75.78
	8	80	9	0	0	92.97	88.30
Non-linear stage	9	94.1	9	1.41	0	90.16	86.86
	10	65.9	9	-1.41	0	38.16	13.88
	11	80	13.23	0	1.41	94.46	88.87
	12	80,00	4.77	0	-1.41	90.07	84.49

As it is evident from Table 2, the maximum experimental X_{JOB} (96.39%) and Y_{FABEs} (93.131%) were obtained when the reaction run at the reaction temperature of 90ºC, butanol: oil molar ratio of 6. The smallest X_{JOB} (22.80%) and Y_{FABEs} (9.46%) were found when the reaction was performed at the reaction temperature of 70ºC and butanol: oil molar ratio of 12. When the reactions run at 65.9 and 70ºC, the oil conversion and biodiesel yields were found to be less than 50% despite of the variation of the values of butanol: oil molar ratio. However, for the reactions that occurred at the average temperatures (80ºC) and above, both the oil conversions and biodiesel yields obtained were more than 80% regardless of the differences in the butanol: oil molar ratio. Thus, the results from Table 2 suggested that the impact of reaction temperature on both responses was higher than that of the alcohol: oil molar ratio. Moreover, for all experiments, the values of

X_{JOB} were larger than that of the Y_{FABEs}, and this might be due to some unreacted diglycerides and monoglycerides remaining in the reaction mixture at the end of the reaction.

3.2. Statistical analysis and optimization of the responses

3.2.1. Results from statistical analysis

The statistical analysis was performed to determine the influences of the reaction temperature (T) and butanol: oil molar ratio (R), and their interactions (TR) on the responses of the butanolysis process. The effects of the main factors and their interactions on X_{JOB} and Y_{FABEs} were determined using Statgraphics Centurion 17, and the presence (significance) of curvature ($p \leq 0.05$) in the response surface plot was also tested [48, 51]. Table 3 shows the results obtained from the statistical analysis of the experimental responses.

As is can be seen from Table 3, reaction temperature was found to be the factor with the highest positive impact whereas butanol: oil molar ration had a slight negative effect on the butanolysis process. The positive effect of reaction temperature on the butanolysis process could be due to the improvement of the miscibility and reactivity between the reactants with rising in temperature [29]. The influences of butanol: oil molar ratio (I_R) on both responses was negative. However, the interaction of temperature and alcohol: oil molar ratio (I_{TR}) was found to have a medium positive impact on both responses. Moreover, the influences of I_T, I_R and I_{TR} on the Y_{FABEs} were higher compared to their respective impacts on X_{JOB} (Table 3). Furthermore, based on ANOVA test, it was determined that the reaction temperature and its interaction with itself (T^2) had a significant effect ($p \leq 0.05$) on the described butanolysis process.

The values of R-squared (R^2) and R^2-adjusted for X_{JOB} and Y_{FABEs} were found to be 88.37 and 78.68 % and 93.54 and 88.16%, respectively (Table 3). This shows that the estimated models satisfactorily fit the experimental data for both responses. It has been suggested that for a good fit of a model, the R^2 should be at least 80% [52]. Moreover, the R^2 and R^2-adjusted for Y_{FABEs} were larger than the R^2 and R^2-adjusted of X_{JOB}, respectively, and this shows that the fitness of the estimated model to the experimental data in case of Y_{FABEs} was better than that of X_{JOB}.

Table 3

Results from the statistical analysis of the experimental responses.

Parameters and types of tests	Responses	
	X_{JOB} (%)	Y_{FABEs}(%)
	$\bar{y}$ =89.55	$\bar{y}$=82.71
Main effects and interactions	I_T = 47.23	I_T = 56.96
	I_R= -6.39	I_R= -9.12
	I_T^2= -32.40	I_T^2= -37.23
	I_{TR}= 9.19	I_{TR}= 14.91
	I_R^2= -4.29	I_R^2= -0.92
Test for significance of variables (ANOVA test, $p \leq 0.05$)		
Significant variables	T and T^2	T and T^2
R^2 and R^2 adjusted (%)		
R^2 (%)	88.37	93.54
R^2 adjusted (%)	78.68	88.16
Test for significance of curvature		
Mean response (factorial points, $\bar{y}_F$)	64.19	58.75
Mean response (center points, $\bar{y}_C$)	89.55	82.71
Curvature	-25.35	-23.96
$SS_{pure\ quadratic}$	1286.19	1148.22
MS_E	12.87	28.53
F calculated	99.89	40.24
p value	0.0021	0.00094
Significance of curvature ($p \leq 0.05$)	Significant	Significant

Where: T refers to temperature, R is butanol: oil molar ratio, and I_{TR} represents interaction of temperature and alcohol: oil molar ratio and R^2 refers to R-squared.

From the calculated parameters to test the presence of curvature, it was found that curvature is significant ($p \leq 0.05$) for both oil conversion and biodiesel yield (Table 3). Thus, in addition to the linear and the center stages, the non-linear stage of the design of experiments was also taken into consideration to fit the experimental data with a quadratic model.

3.2.2. Regression models and optimization of the responses

The natural values of the experimental factors were used to predict the suitable regression models that best described butanolysis of jatropha oil using glycerol enriched CaO as catalyst. As curvature is significant ($p \leq 0.05$) for both X_{JOB} and Y_{FABEs} (Table 3), the second order regression model (quadratic model) was found to be suitable to be used for the optimization of the butanolysis process [48, 51]. Hence, the suggested quadratic regression models for X_{JOB} and Y_{FABEs} under the present experimental ranges are presented in equation 8 and 9, respectively.

$$X_{JOB} = -1035.61 + 26.90T - 9.03R - 0.16T^2 + 0.15TR - 0.23R^2 \tag{8}$$

$$Y_{FABE} = -1148.06 + 30.39T - 20.48R - 0.18T^2 + 0.24TR - 0.051R^2 \tag{9}$$

To show the effects of the binary interaction of the reaction temperature and butanol: oil molar ratio on the X_{JOB} and Y_{FABEs}, the three-dimensional (3D) response surface plots were produced based on the respective regression models presented above. The response surface plot for the effects of the interaction of reaction temperature and butanol: oil molar ratio on the X_{JOB} and Y_{FABEs} are shown in Fig. 1 and Fig. 2, respectively. As it can be seen from Fig. 1 and Fig. 2, generally, raising in the reaction temperature increased both the X_{JOB} and Y_{FABEs} until the optimum values (the temperature at which the maximum responses obtained) would be reached regardless of the amount of butanol: molar ratio employed. However, at the lower temperature, raising in the butanol: oil molar ratio highly reduced both the X_{JOB} and Y_{FABEs}. As the reaction temperature raised from its experimental minimum (65.9°C) to around the optimum values for both X_{JOB} (87.35°C) and Y_{FABEs} (90.48°C) (Table 4), the negative impacts of butanol: oil molar ration on both responses rapidly decreased, and then, started to positively contribute to maximize the responses as the optimum amount of butanol: oil molar ratio would approach.

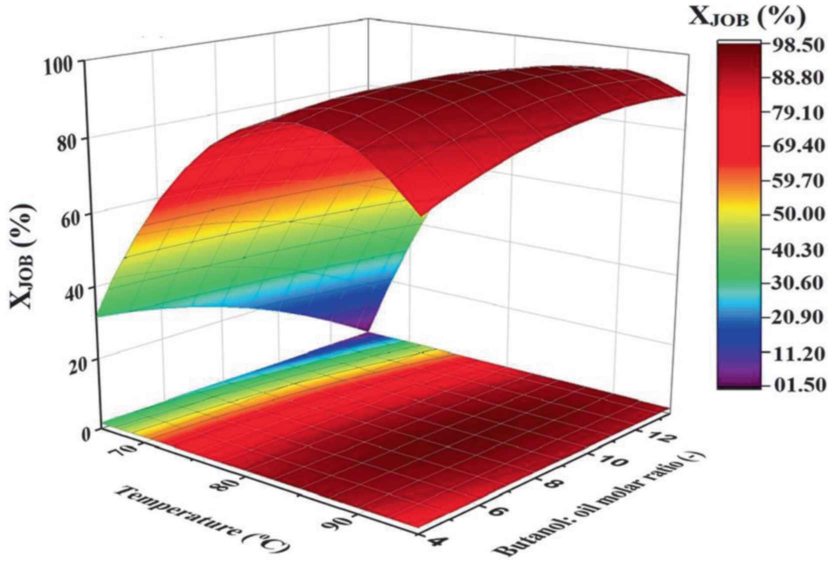

Fig. 1. Response surface 3D plot indicating the influence of temperature and butanol: oil molar ratio on the X_{JOB} at the catalyst amount 15%, 15% glycerol, stirring speed of 200 rpm (temperature and butanol: oil molar ratio refer to the actual values).

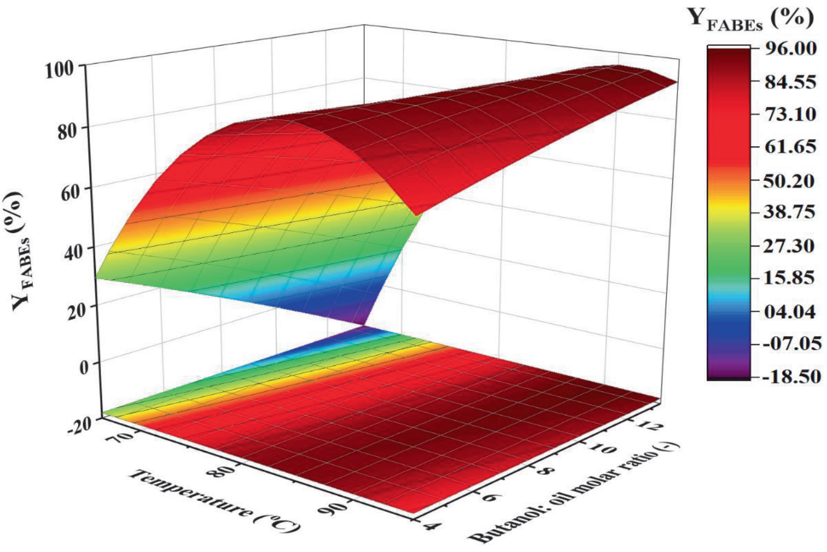

Fig. 2. Response surface 3D plot indicating the influence of temperature and butanol: oil molar ratio on the Y_{FABEs} at the catalyst amount 15%, 15% glycerol, stirring speed of 200 rpm (temperature and butanol: oil molar ratio refer to the actual values).

By using the quadratic model equations produced and the response surface methodology, the maximum X_{JOB} of 98.16% was predicted to be obtained at the optimum temperature and butanol: oil molar ration of 87.35 °C and 9.13:1, respectively. The maximum Y_{FABEs} of 95.79 % was also estimated to be found at the optimum temperature of 90.48 °C and butanol: oil molar ratio of 13.24:1 (Table 4). Moreover, after the prediction of the optimum conditions for both responses, two experiments were carried out at the optimum conditions predicted for Y_{FABEs} (temperature of 90.48°C and butanol: oil molar ratio of 13.24:1) to compare the average of the experimentally obtained responses with that of the predicted values. The optimum conditions predicted for Y_{FABEs} were selected to perform the experiments as the R^2 and R^2-adjusted for Y_{FABEs} were larger than those of X_{JOB} (Table 3). Accordingly, the average experimental Y_{FABEs} of 95.64% was obtained, and this is in excellent agreement with the predicted optimum Y_{FABEs} (95.79 %).

Table 4

Optimum conditions predicted for maximum X_{JOB} and Y_{FABEs} and the optimum responses.

Factors	Conversion		Yield	
	Optimum factors	Optimum response (%)	Optimum factors	Optimum response (%)
Temperature (°C)	87.35		90.48	
Molar ratio (-)	9.13	98.16	13.24	95.79

The maximum Y_{FABEs} (95.64%) found in the current study was in line with the fatty acid butyl ester yield (97%) that was obtained by Navas et al. [2] from the transesterification of castor oil with butanol using MgO/ γ-Al_2O_3 as catalyst by applying 5% catalyst, alcohol: oil molar ratio of 6:1, reaction temperature of 80°C and reaction time of 6 h. However, the maximum Y_{FABEs} of the present work was larger than the fatty acid butyl ester yield (85%) that was found by Navas et al. [2] in the same study using ZnO/ γ-Al_2O_3 as catalyst at the previously mentioned reaction conditions.

Fig. 3 a and b show the plot of the predicted values and experimental results of X_{JOB} and Y_{FABEs}, respectively. As it can be seen from the graphical presentation, the predicted X_{JOB} and Y_{FABEs} generally banded around the predicted straight line and this shows the better correlation of the predicted values with the experimental results.

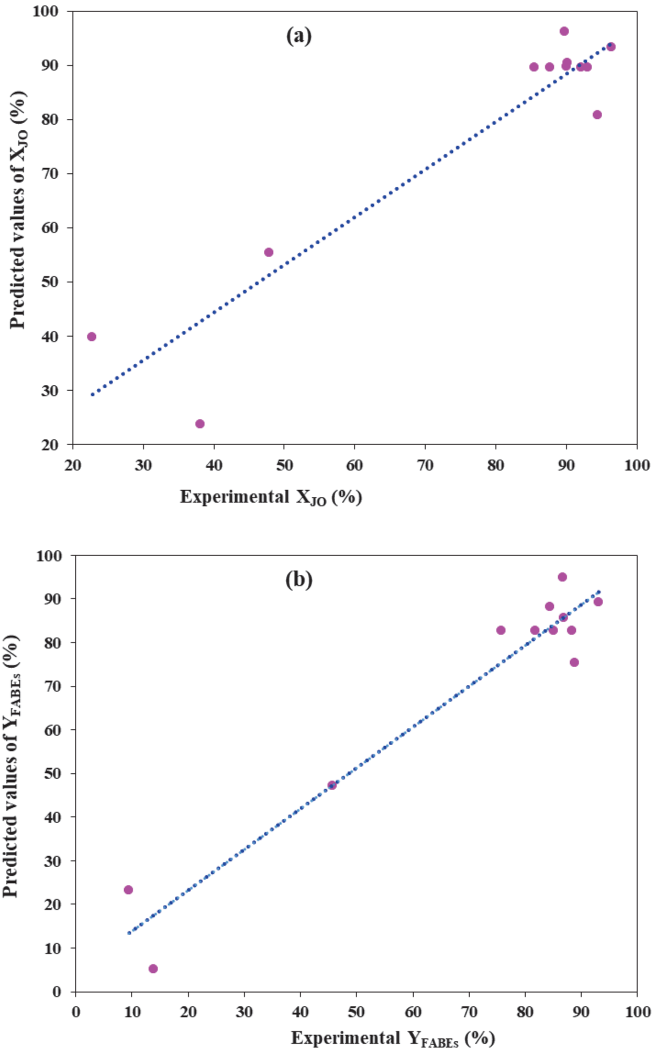

Fig.3. Predicted versus experimental values of (a) X_{JOB} and (b) Y_{FABEs}, respectively.

4. Conclusion

The present study was carried out to investigate the catalytic butanolysis of Jatropha oil using glycerol enriched non-calcined CaO to determine the influences of reaction temperature and butanol: oil molar ratio on X_{JOB} and Y_{FABEs}, and to optimize the responses. Central composite design (CCD) that involved two factors and two levels full factorial (2^2) was used to determine the effects of the factors and to optimize the process. From the main factors and their interaction, temperature was found to highly affect both the X_{JOB} and Y_{FABEs}. Since curvatures are statistically significant ($p \leq 0.05$), quadratic regression models were found to be more suitable for the optimization process. As R^2 and R^2-adjusted of the selected quadratic models for X_{JOB} and Y_{FABEs} were found to be 88.37 and 78.68 % and 93.54 and 88.16%, respectively, both models were suggested to fit adequately to the respective experimental responses to satisfactorily optimize the butanolysis process. Using the models and the response surface methodology, the maximum X_{JOB} (98.16%) and Y_{FABEs} (95.79%) were predicted to be found at the optimum temperatures of 87.35 and 90.48 °C and butanol: oil molar ratios of 9.13:1 and 13.24:1, respectively. Moreover, the maximum Y_{FABEs} of 95.64% was experimentally obtained at the optimum temperature (90.48°C) and alcohol: oil molar ratio (13.24:1), and this was in good agreement with the predicted optimum Y_{FABEs} (95.79%). Based on the results obtained for the experimental ranges used in this experiment, it was suggested that glycerol enriched non-calcined calcium oxide can be used as good alternative catalyst for biodiesel production using butanol. More future studies are also suggested for upscaling the reaction process of the current experiments by using more integrated reaction factors.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

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