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Lignocellulosic Biobutanol Production via ABE Fermentation and Syngas-Based Mixed Alcohol Synthesis: A Technological and Economic Comparison

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Miljøfysikk og fornybar energi

PREFACE

A lifelong fascination for the nature of the world, its manifold facets and phenomena, has gently steered me, I believe, towards physics. The collective efforts of thinking men and women through the ages have sought to meticulously deconstruct the nature of things, in an attempt to understand them, and to manipulate them to the benefit of mankind. The product of these efforts, by its very nature, is never a rigid entity, but subject to constant appraisal, prodding and pondering. In my late adolescence, there came a time when I found such academic deconstruction obtrusive and disenchanting. My schoolbooks on maths, physics and chemistry ended up in the bin. For a long time, my former fascination with these subjects lay dormant.

The nature of the world never lost its allure, however, and, although somewhat reluctantly, I ended up embarking on a degree in Environmental Physics, spurred on by concerns over climate change and the prospect of societal disruption with the end of fossil energy. Now, at the end of my years as a student at the Norwegian University of Life Sciences (NMBU), I have learned to appreciate the aforementioned deconstruction of the nature of things, and the way it fuels a continuous, remarkable conversation of discovery. This thesis, I hope, can serve as a miniscule contribution to this conversation.

My work on this thesis has been interesting and rewarding, reinforcing my impression that anything becomes more interesting when one delves into it properly. It has also reassured me somewhat – the sheer amount of research on renewable energy is a promising start in the efforts to reduce fossil fuel usage and greenhouse gas emissions, the necessity of which becomes ever more pressing, as evidenced in the body of research presented by the Intergovernmental Panel on Climate Change (IPCC) [1].

I have enjoyed taking part in such research myself, and have come to appreciate the subjects of biobutanol and biofuels in general rather more than I envisioned at the outset. In this thesis, I have attempted to gather and concisely present information on two biobutanol production pathways: ABE fermentation and syngas-based alcohol synthesis. While the ever-looming spectre of monetary value hampers the current industrial viability of these pathways to varying degrees, the technologies they encompass are intriguing, and may well become important in the future. And that, I think, is a suitably pragmatic and mildly optimistic note on which to conclude my studies.

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ABSTRACT

The phasing-out and eventual replacement of petrochemical fuels and chemicals with renewable alternatives poses several challenges. Currently, biofuels are largely based on food crops, laying claim to valuable arable land and possibly also contributing to increased food prices. This is not a sustainable practice in the long term, and the question arises about what feedstocks should be used instead.

An achievable answer to this question is lignocellulosic biomass. Widely available and abundant, lignocellulose is a main constituent in all plants, and may be converted into fuels and useful chemicals by a several methods.

Butanol, the four-carbon alcohol, has a variety of applications in chemical industry, and is also being touted by several researchers as a promising biofuel. For a long time prior to the introduction of petrochemical butanol, Acetone-Butanol-Ethanol (ABE) fermentation was the number one method for butanol production, utilizing starch and sugar feedstocks. After dwindling due to unfavourable process economics, this production method has regained some of its relevance due to concerns about the environment and finite fossil fuel resources.

There are two primary pathways for biobutanol production. One is biochemical, utilizing microorganisms to ferment biomass and convert it into products. The ABE process is chief among these. The other pathway is thermochemical processing. Arguably, a main alternative among the technologies of this pathway is syngas-based mixed alcohol synthesis.

The scope of this thesis is to scrutinize these alternatives – the ABE process and the syngas-based mixed alcohol synthesis process – and to compare their technical and economic viabilities. To this end, an extensive literature review has been conducted.

Through the literature review, it was found that lignocellulosic ABE fermentation is a viable technology for production of biobutanol as a bulk chemical, though not yet for biofuel purposes. In particular, process economics are hampered by the fermentation bacterias' sensitivity to inhibitory compounds from essential lignocellulose pretreatment, and by the toxicity of butanol. Mitigative measures include genetic and metabolic engineering of fermentation bacteria to enhance tolerance of inhibitors and butanol, development of novel product recovery techniques, improved reactor designs and upstream processing regimes tailored to each feedstock and fermentation bacteria.

For the thermochemical process, it was found that conversion of biomass to syngas via gasification is potentially easier and considerably faster than the upstream processing of the ABE fermentation. However, optimization of the process for biomass utilization is still underway, and much research is needed in the area of syngas purification to provide a sufficiently clean substrate for mixed alcohol synthesis. Mixed alcohol synthesis is not commercially proven, and needs extensive research and development to achieve commercialization. Key categories of improvement include catalyst selectivity and reactor design.

SAMMENDRAG

Utfasingen og den eventuelle erstatningen av petrokjemiske brensler og kjemikalier med fornybare alternativer byr på flere utfordringer. I skrivende stund er biodrivstoff i hovedsak basert på jordbruk i konkurranse med mat, som legger beslag på dyrebar matjord og kanskje også bidrar til økte matvarepriser. Dette er ingen bærekraftig løsning på sikt, og spørsmålet melder seg om hvilke råmaterialer som kan brukes i stedet.

Et nærliggende svar på dette spørsmålet er lignocelluloseholdig biomasse. Lignocellulose er hovedbestanddel i alt plantemateriale, og er dermed bredt tilgjengelig. Biomassen kan omdannes til brensler og nyttige kjemikalier på mange måter.

Butanol, alkoholen med fire karbonatomer, er bredt anvendt i kjemisk industri, og løftes også frem av mange forskere som et lovende biobrensel. Lenge før petrokjemisk butanol ble standarden utgjorde ABE-fermentering av stivelses- og sukkerholdige råstoffer den foretrukne metoden for butanolproduksjon. Etter å ha mistet sin posisjon grunnet prosessøkonomiske svakheter har metoden nå gjenvunnet noe av sin relevans grunnet klimahensyn og bekymringer angående krympende reserver av fossil energi.

Innen produksjonsmetoder for biobutanol finnes to hovedkategorier. Den ene er biokjemisk, og bruker mikroorganismer til fermentering av biomasse som omdannes til produkter. ABE-prosessen er den fremste blant disse. Den andre kategorien er termokjemisk prosessering. Hovedalternativet blant disse er trolig syngas-basert alkoholsyntese.

Målet med denne oppgaven er å studere disse alternativene – ABE-prosessen og prosessen med alkoholsyntese basert på syngas – og å sammenligne deres tekniske og økonomiske gjennomførbarhet. Med dette mål for øyet har en omfattende litteraturstudie blitt utført.

Litteraturstudien viste at ABE-fermentering av lignocellulose er egnet for produksjon av biobutanol til bruk i kjemisk industri, men at prosessen foreløpig ikke er økonomisk egnet til biobrenselformål. Særlige prosessøkonomiske hindre er fermenteringsbakterienes ømtålighet overfor skadelige stoffer som oppstår under den nødvendige forbehandlingen av biomassen, samt overfor den giftige butanolen. Mulige tiltak er genmanipulering av fermenterings-bakterier for å øke deres motstandsdyktighet, utvikling av nye teknikker for utvinning av butanol fra fermenteringsbrygget, bedre reaktordesign samt forbehandling tilpasset hvert enkelt råmateriale og hver enkelt art av fermenteringsbakterie.

Den termokjemiske prosessens omdanning av biomasse til syngas via gassifisering er potensielt enklere og raskere enn all den nødvendige forbehandlingen for ABE-fermenteringen. Denne metoden for biomassekonvertering er imidlertid fortsatt under utvikling, og mye forskning trengs innen rensing av syngas før man får et tilstrekkelig rent råstoff til bruk i alkoholsyntese. Syntese av blandede alkoholer er ikke kommersielt utviklet, og trenger omfattende forskning og utvikling for å bli det. Sentrale aspekter som må forbedres inkluderer katalysatorens selektivitet, samt reaktordesign.

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GLOSSARY AND ABBREVIATIONS

NMBU	Norwegian University of Life Sciences
IPCC	Intergovernmental Panel on Climate Change
IEA	International Energy Agency
ABE	Acetone-Butanol-Ethanol
ISPR	In-Situ Product Recovery
SSF	Simultaneous Saccharification and Fermentation
LLE	Liquid-Liquid Extraction
BFW	Butanol Fermentation Wastewater
CV	Calorific Value
LHV	Lower Heating Value

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1 INTRODUCTION

At the time of writing, climate change is a subject of much debate and concern, and has been for quite some time. According to IPCC, recent greenhouse gas emissions are the highest on record, contributing to warming of the climate [1]. The International Energy Agency (IEA) states that "biofuels […] can play an important role in reducing CO_2 emissions in the transport sector […]", more specifically by "[…] replacing liquid fossil fuels suitable for planes, marine vessels and other heavy transport modes that cannot be electrified" [2].

Dwindling fossil hydrocarbon resources is another current topic of debate and concern. A staple of human endeavours during the past century, the petrochemical industry has provided raw materials for a great number of products with wide fields of application. As the world's oil supplies diminish over time, the industry faces concerns of volatile oil prices and a need to utilize other raw materials, if possible, to manufacture its products.

One such product is butanol. Since the middle of the 20th century, virtually all butanol has been produced petrochemically, and that still holds true today [3]. Throughout the past century, this alcohol has found widespread industrial application as a bulk chemical. Currently, researchers also contemplate its possible use as a biofuel [4].

In light of the above, efforts to facilitate the production of butanol by means of renewable raw materials seem quite essential. Fortunately, research and development efforts are under way, but significant technological and economical hurdles are yet to be cleared. The available techniques for butanol production fall into two main categories: biochemical and thermochemical. Both can utilize biomass as feedstock.

The major biochemical method of butanol production was developed more than a century ago: Acetone-Butanol-Ethanol (ABE) fermentation was the number one method of butanol production until the petrochemical industry claimed that position by the 1950s. After worldwide decline and discontinuation of the ABE process during the latter half of the 20th century, interest in ABE fermentation has been renewed during the past decade, and it is currently the subject of much research [5].

Previously, ABE fermentation was based on fermentable sugars produced from food crops such as corn and sugarcane [6]. Today more than ever, such feedstocks are in direct conflict with worldwide food production. As a result, much attention has been directed at the utilization of lignocellulosic feedstocks, which do not interfere with food production, and are readily available at generally lower costs than food crops [3]. The use of lignocellulosic feedstocks in ABE fermentation is far from trivial, however, and introduces new challenges to an already demanding production process.

The primary method of the thermochemical butanol production category is based on gasification of biomass, producing syngas which is subsequently cleaned before being converted to alcohols over a catalyst [7]. The gasification process technology is mature, and

has been applied with coal as its chief feedstock for over half a century. Optimisation for lignocellulosic biomass processing is underway. The subsequent process step of synthesis of butanol from syngas, meanwhile, is not an industrially established method. Along with its own set of disadvantages, thermochemical biobutanol production has a few distinct advantages that makes it an interesting alternative to the ABE process.

1.1 Thesis goal

This thesis will evaluate the technical and economic viability of biobutanol production from lignocellulosic feedstocks through ABE fermentation and thermochemical syngas-based alcohol synthesis, comparing the two. To that end, a literature review will be conducted.

2 GENERAL THEORY

2.1 Butanol

Butanol (C_4H_9OH), the four-carbon alcohol, has four structural isomers: n-butanol (alternatively 1-butanol or butyl alcohol), iso-butanol (alternatively 2-methyl-1-propanol or isobutyl alcohol), sec-butanol and tert-butanol [8]. They are depicted schematically in Figure 1. When produced from biomass, butanol is often termed biobutanol. The differences between the isomers in terms of energy content and combustion characteristics are rather modest. Manufacturing them, on the other hand, requires different approaches. No biological process is known to produce tert-butanol, which is exclusively produced petrochemically [9].

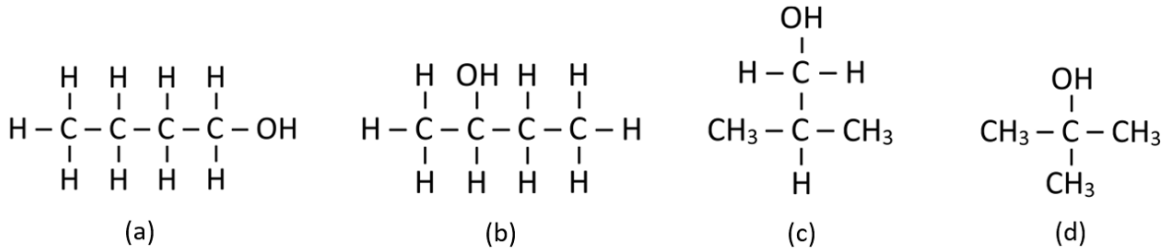

Figure 1: *The four butanol isomers:* (a) *n-butanol (1-butanol),* (b) *sec-butanol (2-butanol),* (c) *iso-butanol (2-methyl-1-propanol),* (d) *tert-butanol (2-methyl-2-propanol) [8].*

All isomers except tert-butanol are considered for fuel applications, most notably n-butanol and isobutanol [8]. These are the two isomers produced by the processes considered in this thesis. Isobutanol has the advantage of being less toxic than n-butanol [10], but aside from that, their qualities are quite similar. Some relevant specifications of the two are listed in Table 1, along with comparable data for ethanol and gasoline.

	n-Butanol	Isobutanol	Ethanol	Gasoline
Lower heating value (MJ/L)	26.9	26.6	21.4	30 – 33
Research octane number	96	106	110	88 – 98
Motor octane number	84	90	90	80 – 88
Density (g/mL) at 20˚C	0.81	0.80	0.79	0.72 – 0.78
Boiling point (˚C)	117.7	107.9	78	27 – 225
Solubility in water at 20˚C (wt%)	7.7	8.7	Miscible	Negligible
Water solubility in oxygenate at 20˚C (wt%)	20.1	20	Miscible	Negligible
Reid vapour pressure (kPa)	2.2	3.3	16	54 – 103
Kinematic viscosity at 20˚C (mm^2/s)	3.6	8.3	1.5	0.37 – 0.44

Table 1: *Properties relevant for fuel application of n- and isobutanol compared to those of ethanol and gasoline [8, 11-13].*

The virtues of n-butanol for biofuel application constitute several advantages when compared to ethanol, and most of these advantages apply to isobutanol as well [4, 12]. Both n-butanol and isobutanol can be used directly or in gasoline blends, and will require little or no engine modification. The fact that both butanol isomers are non-hygroscopic could simplify storage and distribution – blending with gasoline can take place at the refinery, whereas ethanol blending must be postponed until shortly before use. Both n-butanol and isobutanol are safer to handle, due to their low vapour pressures. This may also reduce emissions from fuel evaporation in warm conditions. Both butanol isomers are less corrosive than ethanol, which may facilitate the use of existing pipelines, tanks and related infrastructure. Some corrosion has been observed after engine testing with n-butanol in cold conditions, however, indicating that further studies on this matter are necessary. Butanol has twice the number of carbon atoms in its molecular structure compared to ethanol, resulting in a higher energy content. n-Butanol also has an octane number comparable to that of gasoline, as can be seen from Table 1. While the octane number of isobutanol is considerably higher, it is still lower than that of ethanol.

Butanol is an important bulk chemical in a variety of industrial applications, with frequent utilization as solvent in production of paints, plastics and polymers [8, 14]. n-Butanol is by some distance the most commercially dominant butanol isomer, and the 2.8 million tonnes traded worldwide in 2008 had an estimated global market value of US$5 billion, expected to grow 3.2% annually [10]. In a recent report by Grand View Research [15], the global market

value of isobutanol was expected to grow by about 6% annually from 2014 to 2022, reaching a value of US$1.18 billion by the end of that period. It should be noted that isobutanol "cannot substitute for 1-butanol in the chemical market" [10].

Lastly, it should be mentioned that 1-butene, an easily produced n-butanol derivative, can be quite effectively catalysed into aviation fuel [16].

2.2 Lignocellulosic biomass

The main constituent of plant cell walls is lignocellulose. In other words, lignocellulosic biomass is an abundant resource that can be acquired from a wide variety of sources. Agricultural byproducts and residues in particular – including corn stover, wheat straw, rice straw, etc. – have received considerable attention from researchers examining possible future feedstocks for ABE fermentation. Other notable sources of biomass are dedicated energy crops, such as switchgrass, as well as surpluses from forestry.

The chief components of lignocellulosic biomass are cellulose, hemicellulose and lignin, in addition to minor amounts of other materials. Cellulose and hemicellulose consist primarily of hexose and pentose monosaccharides, respectively. The ratios of lignocellulose components vary between different plants [17]. 30-60% cellulose, 20-40% hemicellulose and 15-25% lignin are typical content percentages on a moisture-free basis [18, 19]. Examples are provided in Table 2.

Material	Cellulose %	Hemicellulose %	Lignin %	Ash %
Barley straw	42	28	7	11
Corn stover	38	26	23	6
Switchgrass	37	29	19	-
Wheat straw	38	29	24	6
Softwood	35 – 40	25 – 30	27 – 30	1[a]
Hardwood	45 – 50	20 – 25	20 – 25	1[a]

Table 2: *Examples of lignocellulosic materials and their approximate composition [17, 20].* [a] *An average value for wood biomass.*

Generally, cellulose fibrils are enveloped by hemicelluloses, which in turn are fixed in "a tight composite structure of lignin and hemicelluloses bound to each other by covalent bonds" [21]. This "tight composite structure" and the fact that lignin has properties that makes it very difficult to degrade [22] conspire to make lignocellulosic materials challenging feedstocks to handle in biorefinery processes. Pretreatment is commonly required to facilitate further processing.

3 THE ABE PROCESS

3.1 Overview

3.1.1 History

Butanol production through fermentation by anaerobic bacteria was first reported by Louis Pasteur in 1861, whereupon it became a subject of research up until and following the turn of the century. Between 1912 and 1914, chemist Chaim Weizmann successfully isolated the bacterial culture later to be named Clostridium acetobutylicum, which was found to produce butanol and acetone from various starchy materials. This culture formed the basis of the Weizmann process, which was the precursor of the ABE fermentation process. The industrial prevalence of the process grew on the grim backdrop of World War 1, during which acetone was in high demand due to its application in Cordite (smokeless gun powder) production. At the time, butanol lacked immediate fields of application, but after the war butanol demand soared largely due to its use in car lacquers. The ABE fermentation process subsequently rose in prominence to become the second-most important industrial fermentation process in the world, next only to ethanol fermentation [6]. During the 50s and 60s, petrochemical production became the economically preferable alternative when producing butanol. Industrial ABE process activity declined worldwide up until the 1980s, when production virtually ceased. Only in China could one find ABE plants in operation after this, but at long last all production ended in 2004. In recent years, however, interest and investment in the process are on the rise [5].

3.1.2 Process steps

The process of ABE production, from lignocellulosic raw material to biobutanol, can be divided into several distinct steps. Depending on the choice of feedstock, treatment methods and fermentation technique, the precise organisation of these steps may vary – for instance, combined hydrolysis and fermentation may take place inside the fermentation reactor. Every step ahead of the actual fermentation is commonly termed “upstream”, while the steps taking place after the fermentation are “downstream”. They can be summed up as follows, illustrated in Figure 2:

Lignocellulosic raw materials from various sources must undergo pretreatment appropriate for each substance. The primary purpose of pretreatment is to prepare the biomass for effective hydrolysis. Pretreated biomass subsequently undergoes hydrolysis to produce fermentable sugars that can be utilized by the fermentation bacteria. In addition, detoxification of the hydrolysate may be required to prevent inhibitory substances formed during upstream processing from hindering fermentation. The hydrolysate – a slurry usually referred to as fermentation substrate – forms the basis for the actual ABE fermentation. For some

lignocellulosic substrates, pretreatment induces sufficient hydrolysis to avoid a dedicated hydrolysis step [5]. When the fermentation has run for a sufficient time, various techniques can be deployed to recover and purify butanol from the fermentation broth. Additionally, the byproducts and residual effluent can generate revenue through purification and processing, thus contributing to improved overall process economics.

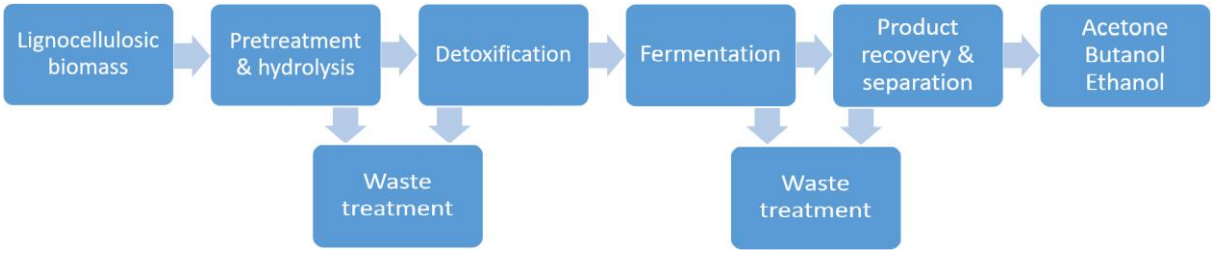

Figure 2: *Schematic overview of the lignocellulosic ABE process, from raw material to product.*

3.2 Upstream processing

As butanol-producing bacteria are unable to hydrolyse lignocellulosic feedstocks, pretreatment is necessary to facilitate hydrolysis of the biomass prior to fermentation [23, 24]. Various fermentation inhibitors can be generated during these processes, with variety and severity depending on both the feedstock being treated as well as the techniques involved [9, 24, 25]. The ABE fermentation is particularly sensitive to inhibitors, which often necessitates some form of detoxification treatment of the hydrolysate ahead of fermentation [26, 27]. Due to their frequently incompatible process conditions, pretreatment and hydrolysis are conducted in separate vessels [23]. In ABE research literature, pretreatment, hydrolysis and detoxification are often sorted under the collective term upstream processing.

In short, the available pretreatment techniques are physical or chemical, or a combination of the two. Additionally, biological methods are being researched, but have yet to come to fruition in terms of economics. The general characteristics of these techniques will be outlined in this section, in addition to brief descriptions of hydrolysis and detoxification.

3.2.1 Pretreatment

The primary obstacle in any biochemical refinery process aiming to use lignocellulosic feedstocks is the issue of pretreatment and saccharification [28, 29]. As this is a general issue in biorefinery processing, considerable amounts of research have been conducted in this field. Some of the aspects relevant to lignocellulosic ABE fermentation will be treated here.

The fundamental purpose of biomass pretreatment is to depolymerize the building blocks of lignocellulose, and to provide surface area for hydrolysis [22, 30]. This process usually takes a couple of hours [5]. As stated in section 2.2, lignocellulosic materials consist of cellulose, hemicellulose and lignin. The cellulase – hydrolytic enzymes involved in cellulose and hemicellulose degradation during enzymatic hydrolysis – are prevented access to the cellulose by lignin, both through physical obstruction and through lignin binding to the cellulase, which reduces enzyme activity [31]. Thus, pretreatment generally strives to reduce lignin content. A reduction in the partly crystalline structure of cellulose is also beneficial for the subsequent hydrolysis, and can be achieved through pretreatment. It should be noted that the ability to remove hemicellulose is often regarded as an advantage in a pretreatment technique, as the anaerobic digestion process used to produce ethanol is unable to utilize the pentose sugars resulting from hemicellulose degradation [32]. However, this is not the case with the fermentative bacteria used in the ABE process, which are fully capable of fermenting pentose as well as hexose sugars [24]. Thus, for the purposes discussed here, hemicellulose removal is not particularly necessary, although techniques with this ability may be used without the hemicellulose actually being removed from the pretreatment reactor.

The various available pretreatment methods have different effects on the lignocellulosic components. All methods have inherent advantages and disadvantages, and are at varying stages of maturity. Some involve severe process conditions (high temperatures, use of chemicals etc.), while others demand special attention to process equipment (e.g. due to corrosive acids).

Physical pretreatment includes various grinding and milling methods, amongst others. None of these methods involve the addition of any chemical compounds to the biomass. The primary effect of physical pretreatment is particle size reduction, which increases the biomass surface area for subsequent enzymatic hydrolysis. High energy requirements render milling economically unfavourable, however [22].

The most prominent chemical pretreatments are dilute acid, alkali and organosolv. So-called organosolv pretreatment uses ethanol and water in partial hydrolysis of lignin to remove it from the feedstock. This normally involves the use a strong inorganic acid catalyst, like sulfuric acid. Lignin is a valuable byproduct, and its separation also reduces waste treatment requirements. Additionally, detoxification is allegedly unnecessary following organosolv pretreatment [27]. Dilute acid pretreatment is very similar to dilute acid hydrolysis, described in section 3.2.2. The main distinction between pretreatment and hydrolysis, in this case, is a matter of when the process is applied during the upstream processing. This method is frequently used in research, and while efficient, it causes the formation of several inhibitory compounds. Alkaline pretreatment using chemicals like ammonia or alkaline peroxide have also been used for the ABE process. These methods have also proved their efficiency, but the formation of inhibitory compounds such as salts pose a problem in their application [25].

Steam explosion is a quite commonly used example of a physico-chemical pretreatment method, and involves rapid heating using high-pressure steam, before an abrupt pressure drop causes explosive decompression of the biomass. Its primary effects on lignocellulose are frequently ascribed to hemicellulose removal alongside an increase of surface area, which aid

subsequent enzymatic hydrolysis through easier access to the cellulose [33]. Steam explosion may be conducted with or without the use of a catalyst, and in the latter case it could be regarded as a physical pretreatment.

Biological pretreatment using rot fungi for lignin degradation is an interesting concept that deserves mention, considering its potentially low costs and energy requirements in addition to high yields and little to no pollution. For the time being, however, treatment rates are too slow for it to compete with the alternatives [28].

3.2.2 Hydrolysis

The two primary hydrolysis processes available for lignocellulose treatment use either dilute acid or enzymes.

Dilute acid hydrolysis uses mineral acids like H_2SO_4 or HCl in concentrations around 2-5wt% [34], with temperature and pressure of approximately 160˚C and 1 MPa, respectively. On the one hand, this method is effective, resulting in high pentose sugar yields from hemicellulose, disruption of lignin structure and better access to cellulose. On the other, inhibitory sugar and lignin degradation products are formed, along with other toxic compounds. Also, process equipment must withstand corrosion [32, 35]. These disadvantages count against the use of acid hydrolysis in the ABE process.

Enzymatic hydrolysis, as the name suggests, involves the use of specific enzymes to promote saccharification of the lignocellulosic polymers. This technique is highly dependent upon pretreatment, more so than acid hydrolysis [27]. On the other hand, its advantages compared to the alternative are numerous. Biomass-to-sugar yields are high, byproduct formation is low, process conditions are gentler and less energy-intensive, and waste processing is less complex [32, 36]. One clear disadvantage is the cost, primarily due to expensive enzymes. Enzymatic hydrolysis is the most frequently used hydrolysis option for ABE research [5], and although its cost makes its industrial deployment “problematic”, improved enzyme cocktails optimized for use in the ABE process may mitigate this [10].

3.2.3 Detoxification

Detoxification methods for ABE fermentation have been investigated by several researchers. Again, there are physical and chemical methods, and combinations of the two, as well as biological detoxification.

Vacuum evaporation is an example of a physical detoxification method. This method concentrates the hydrolysate, removing volatile toxic compounds. On the other hand, some non-

volatile ones may also be concentrated in the process [35]. Another example is electrodialysis, which e.g. removes salts formed after alkaline pretreatment [25].

A widely used form of chemical detoxification is pH adjustment, for instance using acid to lower pH sufficiently to provoke inhibitor ionization and precipitation of certain toxic compounds, before raising the pH again afterwards. Overliming (using $Ca(OH)_2$) is an example of this, and is often used after dilute acid pretreatment. Adsorption of toxic compounds from liquid phase substrate by activated charcoal or ion-exchange resins is also common. The latter is rather costly compared to the alternatives [35].

Biological detoxification includes use of particular enzymes (such as laccase or peroxides) to reduce the amount of acids and phenolic compounds in the hydrolysate, as well as microorganisms that selectively remove inhibitors [35].

Possible problems associated with detoxification include sugar loss, e.g. in the case of overliming, as well as formation of hazardous compounds in the wastewater stream [30].

3.3 ABE Fermentation

The bacterial species of genus *Clostridium* forms the basis of the ABE fermentation. Biosynthesis of butanol only occurs in this group of anaerobic, endospore-forming bacteria [37]. Many strains and variations on these have been isolated and/or genetically engineered, but the four strains most commonly utilized in industry and research are Clostridium Acetobutylicum, Clostridium Beijerinckii, Clostridium Saccharobutylicum and Clostridium Saccharoperbutylacetonicum [5], with emphasis on the first two.

The bacteria can ferment several pentose and hexose monosaccharides, as well as some polysaccharides. Additional nutrient requirements are predominantly limited to sources of nitrogen, to ensure bacterial growth and satisfactory solvent production [24].

A central concept in the area of fermentation is that of sugar yield, which signifies the fraction of fermentable sugars converted to products. This should not be confused with “yield”, another important parameter for fermentation efficiency, which normally signifies grams of product produced per gram of feedstock consumed in the process. Butanol titre, meanwhile, is given in grams per litre fermentation broth. On a glucose basis, the maximum stoichiometric butanol yield is 0.411g/g [34]. On lab-scale, the higher yields achieved to date are in the area of 0.3g/g, while the higher butanol titres are about 0.3g/L [5]. Fermentation productivity is usually given in grams per litre per hour, and values seldom exceed 0.5g/L/h [34].

Fermentation is typically performed at 25˚C to 37˚C and at atmospheric pressure, in an anaerobic environment [38]. Batch fermentation takes 2-6 days, depending on fermentation conditions and feedstock [24].

Normally, a single bacterial strain is used in fermentation. However, a few studies have been conducted on coculture fermentation, using two or more bacterial strains with slightly different metabolism characteristics that complement each other to increase butanol production, yield and volumetric productivity in the fermentation [39].

Industrial fermentation has traditionally been conducted in batch reactors, but disadvantages like mandatory process interruptions for cleaning, sterilization and refilling of fermentation broth make batch fermentation an inferior alternative – fed-batch, semi-continuous and continuous reactors are preferable due to longer production periods [40]. Inoculation – the addition of bacterial culture to the fermentation substrate slurry – must also be repeated after each batch interruption [20]. Due to simplicity of operation, batch fermentation is widely used in research.

During fed-batch fermentation, the reactor is initially operated in batch mode, and normally filled to less than half its maximum volume using low-concentration substrate. Substrate is gradually metabolised by the bacteria, and high-concentration substrate is added at a rate that retains concentrations at non-inhibitory levels. Product recovery (see section 3.4.1) is required to maintain non-toxic butanol concentrations. Fermentation broth volume is slowly increased until about three-quarters of the reactor is filled, at which point the bacterial culture is harvested. This procedure increases cell growth through lower product inhibition and substrate reduction, resulting in higher productivity for the reactor [41].

Continuous culture reactors are also initiated in batch mode, whereupon bacterial cell growth is maintained at the exponential growth stage (see section 3.3.1). Substrate is added and products removed from the reactor simultaneously at a steady rate, sustaining a constant fermentation broth volume. Reactor productivity is improved, and fermentation periods are lengthened. Unstable and eventually declining solvent production is an issue, which contributes to making single-stage continuous reactors unfeasible at the time of writing. Mitigating this, multistage reactors are used, where bacterial cell growth, acid- and solvent production (see section 3.3.1) take place in separate reactor vessels [41].

Use of free cell fermentation – to let bacterial cells move freely within the reactor with the help of mechanical agitation – has been the standard mode of operation for ABE fermentation. This allows some flexibility in terms of combination with saccharification or recovery techniques, but generally involves lower productivity than the alternatives [42]. Strong reactor design candidates for future industrial application include immobilized cell continuous reactors, as well as membrane cell recycle reactors [24].

Immobilized cell continuous reactors are based on bacterial cell adsorption onto apt substrates. Feedstock is added to the bottom of a tubular reactor, while solvent products can be recovered from the top. As no mixing takes place, contact between cells and solvent products is limited, thus reducing product inhibition considerably [41]. Due to this and the lack of mechanical agitation, cell survival time in the broth increases [20]. Longer cell survival times contribute to a butanol yield increase of up to 20%. Certain challenges need to be overcome before the stability of large-scale continuous operation can be guaranteed, most notably the matter of

nutrient supply to the cells, which needs meticulous regulation to avoid excessive cell growth and formation of cell layers, rendering the lower layers unproductive [42].

In membrane cell recycle reactors, the design basis is very much like a free cell continuous fermentation [20], but the fermentation broth is filtered through a membrane while cell growth is still at the exponential stage (see section 3.3.1). Bacterial cells are thus captured by the membrane and cells are recycled to the reactor, while the remaining broth passes through. Feedstock is added and products removed simultaneously, sustaining a constant fermentation volume. Very high cell concentrations (>100g/L) are achievable in this way, but too high concentrations have an adverse effect on the fermentation. Therefore, cell bleeding – removal of excess cells – must be performed to maintain productive cell concentrations [41, 42].

Another notable reactor configuration concept is simultaneous saccharification and fermentation (SSF). During SSF, enzymes and bacteria are added to the same reactor to perform hydrolysis and fermentation, respectively [23]. This setup can also be combined with product recovery such as vacuum fermentation (described in section 3.4), effectively bringing three process steps together in one process unit, which can contribute to reduced costs [43]. Results using these configurations are good, fully on par with or even better than those from experiments based on glucose feedstock.

3.3.1 Fermentation characteristics

The fermentation itself takes place in two phases. First, in the acidogenic phase, exponential bacterial cell growth occurs, primarily producing butyrate and acetate, alongside hydrogen and carbon dioxide. At the end of this phase, the bacteria undergo a metabolic shift, to which there are probably several contributing factors. One likely factor is cellular response to the dangerously low pH in the fermentation broth, which descends to levels associated with cell death. The shift initiates the solventogenic phase, where cell growth is stationary. The acids previously produced are now assimilated by the bacteria and used in production of acetone, butanol and ethanol. This takes place parallel to continued carbohydrate consumption [6]. A simple overview of the metabolic pathways is provided in Figure 3. The final product ratio of acetone, butanol and ethanol, respectively, is typically around 3:6:1 [5, 14]. However, this ratio is subject to variation, primarily depending on the fermentation strain involved. Genetic modification and metabolic engineering, briefly treated in section 3.3.3, actively pursue better butanol selectivity in the fermentation. For instance, the genetically modified strain Clostridium beijerinckii BA101, often touted as a “hyper-butanol-producing strain”, produces approximately 80% butanol, with most of the remainder being acetone [44]. There are also strains that produce isopropanol in place of acetone [24].

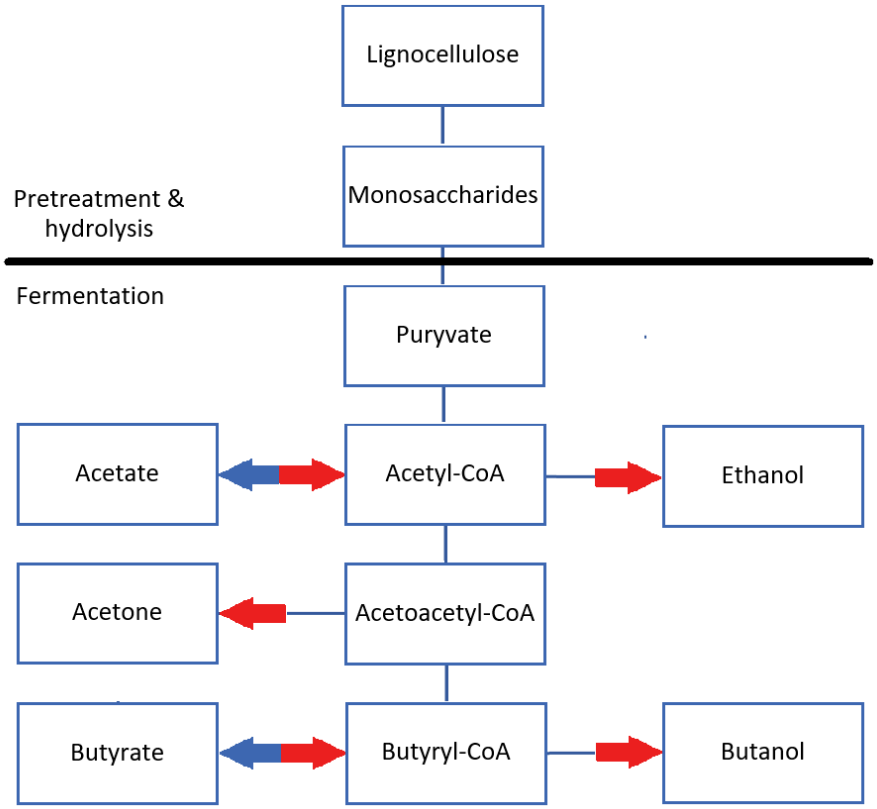

Figure 3: *Simplified overview of metabolic pathways during ABE fermentation. The process pathway goes downwards. Blue arrows indicate reactions dominating during the acidogenic phase of fermentation, while red arrows designate reactions dominating during the solventogenic phase. Adapted from [5].*

A topic that must be touched upon regarding ABE fermentation is infection from bacteriophages. These are viruses that infect the fermentation bacteria, with severely adverse effects on the fermentation process. This has been a recurring problem throughout historical industrial operation of the ABE process [6], necessitating costly and time-consuming sterilization regimes for process equipment. Avoiding phage infection is a challenge to this day, but is mitigated by various means, notably by engineering infection-resistant bacterial strains. Preventing contamination is vital, as infection usually causes a total loss of a fermentation batch [45].

Another detrimental scenario that is known to occur during fermentation is the so-called ‘acid crash’, which signifies a failure of the fermentation bacteria to move on from the acidogenic to the solventogenic phase. It occurs mainly in batch cultures lacking sufficient pH control, but has also happened during continuous culture fermentations [46]. The reason behind the phenomenon remained elusive until 2011, when a study identified accumulation of formic acid in the fermentation broth as the probable root cause [47].

3.3.2 Product toxicity

Several products of the ABE process are toxic, including acetone and ethanol, but the solvent concentration at which butanol becomes toxic is much lower than the others' [6, 48]. Therefore, only butanol is an issue in ABE research concerning product toxicity. Below concentrations between 4 and 4.8 grams per litre fermentation broth, butanol does not affect the cell growth of the fermentative Clostridia, whereas concentrations approaching 16 grams per litre fermentation broth inhibit fermentation to such a degree that it will cease [48, 49]. This is one of the chief disadvantages of the ABE process: Butanol titre must remain low, resulting in a rather meagre process yield.

To address this problem, most ABE research over the past two decades has followed two avenues of approach. One concerns the development of new fermentative bacterial strains through genetics research and metabolic engineering, with an aim to increase the butanol tolerance of the microbes. The other regards novel product recovery techniques that maintain a lower butanol content in the broth [50]. The former is briefly addressed in the next section, while the latter is covered in section 3.4.

3.3.3 Metabolic engineering and genetics

Modification of bacterial strains for optimization of the fermentation process and the related microbiological characteristics are considered beyond the primary scope of this text. Still, it should be noted that this is a crucial field of research on the topic of ABE fermentation, and several researchers regard it as the one that possesses the greater potential for improvement of the process yield (and thereby economics). However, significant positive results have yet to emerge from these efforts. Most research in this field concerns improved tolerance to product solvents, and the scientific consensus seems to expect improvements on this in the future [24].

These subjects have recently been extensively and thoroughly reviewed elsewhere, e.g. [51-53].

3.4 Downstream processing

3.4.1 Product recovery, separation and purification

There is a considerable variety of techniques for product recovery in the ABE process, each with its own equipment requirements, alongside variations in equipment sequencing during product separation and purification. For this reason, downstream processing is widely studied in research literature.

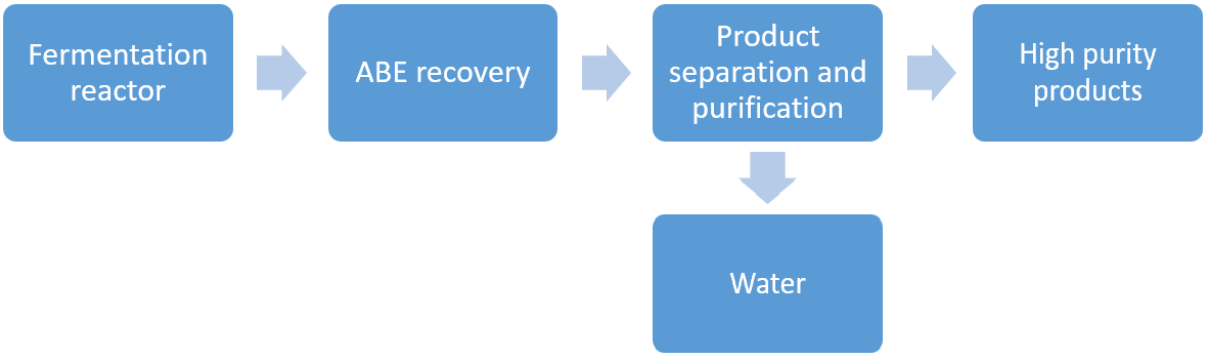

Figure 4: *Schematic overview of the downstream processing sequence. ABE recovery may take place within the fermentation reactor itself, as described in the main text.*

As indicated in Figure 4, the solvent products are first extracted and recovered from the fermentation broth, before subsequent product separation and purification. Product separation and purification is largely based on use of distillation columns, and the order of distillation follows the increasing boiling points of the products: acetone, ethanol and butanol, with boiling points at 56.5˚C, 78.4˚C and 117.7˚C, respectively [54]. Acetone is separated at high purity, whereas ethanol requires further purification after distillation to meet industry standards. For this purpose, molecular sieve adsorption is often employed [12]. A somewhat recent improvement in separation technology is the inclusion of a decanter unit to ease the separation of water and butanol [12]. This separation regime produces product solvents of sufficient purity (>99%) for application in industry or as fuel (additive). Water is frequently recycled for use in prior process steps.

The main point of contention in ABE downstream processing, and the one with the greater room for improvement both in technical terms and regarding its influence on overall process economics, is the aforementioned extraction and recovery of products from the fermentation broth.

Traditionally, direct distillation has been employed after batch fermentation, and distillation is still used in industry for this purpose [21, 24]. However, the energy consumption of this technique is too high to be economically favourable, partly because the heat of evaporation for butanol is higher than that of water. Consequently, large amounts of water must be evaporated before butanol can be recovered [48]. This contributes to an already unsustainable water usage, and increased expenditures for wastewater treatment. To a certain extent, process water recycling could mitigate this [10].

As noted in section 3.3.2, butanol toxicity becomes an issue during fermentation. Therefore, one of the primary goals of the ABE product recovery techniques studied in recent years has been to retain a low butanol concentration in the fermentation broth through butanol removal during fermentation. This enables increased production from a given fermentation volume and facilitates the use of fed-batch- and continuous fermentation techniques [55].

Several recovery techniques are under scrutiny by researchers. Most of these can be deployed "in situ" – in direct contact with the fermentation broth within the fermentation reactor. The primary virtues of in situ product recovery (often abbreviated ISPR) are twofold: Firstly, it doesn't require significant interruption or complete termination of the fermentation process. Secondly, it contributes to a lower toxicity in the fermentation broth by continuously removing butanol from the broth [24].

In short, so-called evaporative techniques apply energy to remove solvent from the fermentation broth, which usually results in rather low product concentrations after product removal from the broth. This, in turn, translates to higher energy requirements, i.e. removal of larger amounts of water, during subsequent product purification. Other techniques use separating agents to remove solvents from the fermentation broth. Separation agents with low affinity for water result in high product concentrations and much less water to handle during purification, and so energy consumption is reduced [55]. Separating agents must be removed from the products afterwards, however.

Evaporative techniques include pervaporation and gas stripping as well as vacuum and flash fermentation. These are considered to be among the most mature ISPR techniques [56], alongside the non-evaporative techniques liquid-liquid extraction, perstraction and adsorption. As recovery is such a crucial technical step in the ABE process, all these techniques are presented in brief below.

3.4.1.1 Gas stripping

By letting an inert "carrier gas" bubble through the fermentation broth, this gas can capture acetone, butanol and ethanol, which can be collected after subsequent cooling of the gas in a condenser. Gases can be reused for the same purpose until fermentation ceases. This process is termed gas stripping [49]. Nitrogen is often used. An alternative is to use CO_2 and H_2 – the

main gaseous byproducts of the ABE fermentation – which can be separated from the fermentation broth.

A disadvantage of gas stripping is its relatively high energy requirements compared to other ISPR techniques, largely due to energy-intensive condensation of product solvents. The technique has several advantages, though, and it boasts some of the most promising production results among all researched recovery techniques [5]. It is a simple technology, easy in operation and relatively uncomplicated to scale up, and will contribute to reduced energy and water consumption during operation compared to traditional ABE process techniques [5, 57]. Acids are not removed from the reactor during gas stripping, which promotes greater acid conversion into product solvents [58].

Gas stripping can be performed within the reactor or in a separate vessel, the latter by circulating the fermentation broth between the two.

3.4.1.2 Liquid-liquid extraction

Liquid-liquid (or solvent) extraction (LLE) can be performed either after fermentation is complete, or *in situ* during fermentation, usually by mixing in a water-insoluble organic extractant inside the fermenter [57, 59]. The basic principle behind this technique is the fact that butanol is "more soluble in the organic (extractant) phase than in the aqueous (fermentation broth) phase; therefore, butanol selectively concentrates in the organic phase" [59]. The organic phase substances can be extracted from the broth, whereupon butanol can be removed in a distillation column more effectively than would be the case by means of direct distillation. Using an extractant that is immiscible with water facilitates its separation from the fermentation broth, and subsequent recycling for further use in the fermenter. The organic phase tends to accumulate atop the aqueous phase inside the fermentation reactor [60]. This allows substrates, water and nutrients to remain in the broth while butanol is recovered.

However, LLE has its disadvantages. Extractant solvents can be toxic to fermentation organisms in the case of prolonged exposure, incomplete phase separation causes loss of extractant, emulsion formation may occur, and a rag layer – accumulation and inactivation of microbial cells at the extractant-broth interface – may form [57, 59, 61].

The energy requirements for heating and cooling associated with LLE are an order of magnitude higher than for other techniques [55].

Variations on LLE have been proposed. Notably, a dual extraction system with solvent regeneration has been modelled [48]. Here, acetone-butanol-ethanol is recovered in one step using extractant solvents that are more toxic to the fermentation microbes, but concurrently more effective at product extraction. In a second step, the remaining fermentation broth is cleansed of toxic extractant using a second, non-toxic extractant, before being recycled through the fermenter. The results from this modelling indicate considerably lower energy requirements compared to standard LLE.

3.4.1.3 Perstraction

Addressing some of the problematic aspects of LLE, perstraction (or membrane solvent extraction) introduces a membrane to separate the extractant from the fermentation broth. This provides a surface through which butanol can be transferred between the immiscible organic and aqueous phases, due to the difference in vapour pressure between the two membrane sides. Note that this does not constitute a phase change from liquid to vapour – perstraction, like LLE, takes place entirely in the liquid phase. Product solvents are immediately dissolved in the extractant after diffusion through the membrane. Through separation of the phases, issues such as extractant toxicity and emulsion and rag layer formation (microbial cells at interface) are reduced considerably. The primary disadvantage of this technique is that the membrane represents an obstacle for the butanol exchange rate, through which product solvent flux is limited [59, 61]. Also, membrane fouling or clogging is always an issue.

3.4.1.4 Pervaporation

Pervaporation introduces a membrane for selective removal of volatile or organic components from the fermentation broth. A phase change from liquid to vapour occurs as the compounds in question selectively diffuse across the membrane as a vapour [59].

Due to its many advantages, some regard pervaporation as the most promising separation technology. Its ease of operation, not to mention its high efficiency both in terms of product separation and energy usage, count among its chief benefits. The lack of extractant components added to the fermentation broth also means no harm done to the fermenting bacteria [57]. Several membrane varieties have been considered, and polymethylsiloxane membranes are widely considered as the most promising for ABE application, due to high solvent selectivity [62].

3.4.1.5 Adsorption

Adsorption can take place in situ or ex situ. The latter alternative has gained some attention recently, for reasons stated below. The difference between these two techniques is quite straightforward: In situ means the process takes place where the fermentation itself takes place, within the fermentation reactor. Ex situ techniques involve the circulation of fermentation broth out of the reactor and through a separate adsorption column, where product solvent extraction takes place before the remaining broth is circulated back into the reactor [63].

The concept of adsorption revolves around use of compounds to which product solvents become bound, facilitating their removal from the remaining fermentation broth. Subsequent desorption is often performed using steam, but alternatives exist, e.g. vacuum evaporation or methanol [50].

Of the several adsorbent candidates that have been studied, silicate, charcoal and polyvinylpyridine are reported to be the most effective. Silicate "appears to be the more attractive as it can be used to concentrate butanol from dilute solutions (5 to 790-810 g/L) and results in complete desorption of butanol (or ABE)" [64]. Also, heat treatment can be utilized for silicate regeneration.

Sequential heating of silicate after adsorption removes water in a first step, before removing butanol at a higher temperature afterwards. Failure to remove microbial cells from the fermentation broth before application of adsorbent may cause adsorbent fouling. This can be mitigated through the use of a filtration membrane, or by centrifuging cells before treating the cleared broth with adsorbents [64].

Poor biocompatibility with fermentation microbes and non-selective adsorption of byproducts alongside butanol counts among the chief shortcomings of adsorption recovery, and have limited its application. These problems may be alleviated by way of ex situ recovery, which has gained attention in recent years [50]. This approach could allow such improvements as periodic replacement of the adsorption column when adsorbents are saturated, although this has yet to be experimentally verified [65].

3.4.1.6 Flash and vacuum

Flash fermentation and vacuum fermentation are very similar techniques, designed for continuous fermentation. The main difference is that flash is carried out in an external vessel, while vacuum takes place within the fermentation reactor. The latter reportedly has lesser energy requirements and superior separation ability. Cost may become an issue with vacuum fermentation, however, as the reactor must be able to withstand roughly 6.5kPa vacuum [55].

During flash fermentation, circulation of fermentation broth takes place between the fermentation reactor and a vacuum chamber. Atmospheric pressure is maintained in the reactor. In the vacuum chamber, boiling takes place at 37˚C whereupon the evaporated ABE is condensed. Vacuum is maintained using compressors, the operation of which constitutes practically all the energy consumption of this process [66].

Vacuum fermentation is based on maintaining vacuum pressure in the fermentation reactor, which causes the fermentation broth to boil at low temperatures. Vacuum recovery was once considered to be unsuitable for butanol production, since butanol has a higher boiling point than water. However, when maintained at certain levels of concentration, the liquid heteroazeotropic mixture formed by butanol and water can boil at temperatures below the boiling point of both butanol and water, and the vapours produced will contain more butanol than the boiling liquid,

resulting in higher butanol concentrations in the recovered stream than in the fermentation broth [67].

3.4.2 Byproduct processing and waste treatment

Byproducts and waste are generated throughout the ABE process. Upstream processing generates waste, some of which may be utilized. The primary example is lignin, which, if separated and purified, may be utilized in other value-added products, or it could simply undergo combustion to generate electrical power [68]. ABE fermentation produces gases, liquid solvents, and an effluent slurry that can be separated into solids and liquid wastewater. Everything aside from butanol is regarded either as byproducts or as waste. Proper utilization of these will contribute favourably to the process economics.

Acetone is the primary byproduct, and can, as previously stated, be utilized in chemical industry with little or no purification beyond distillation. Ethanol, meanwhile, tends to require further purification measures after distillation to meet industry standards, and the investments needed to achieve that may in some cases exceed the potential revenue generated [69].

In terms of mass, ABE fermentation produces slightly more gases than solvents. Almost all the gas is carbon dioxide or hydrogen, in roughly equimolar amounts. Historically, these have been separated by selective adsorption or through use of membranes and utilized in various ways [6]. As previously stated, one of the applications currently being considered is gas stripping (see section 3.4.1.1).

Treated and dried solid effluent from ABE fermentation is rich in proteins and vitamins, and has frequently found application as animal feed [6, 9]. Depending on the quality of the solids, an attractive alternative is combustion of the solids to generate electric power [69]. Several current industrial ABE process plants already utilize anaerobic digestion of waste effluent, producing biogas which can be used for generation of heat and power [10].

Large amounts of butanol fermentation wastewater (BFW) are produced during ABE fermentation, and its contents include residual solvents, which makes it a problem for the environment, not to mention toxic to humans [70].

In recent years, a few studies have been conducted that specifically address treatment of BFW, and contemplate its conversion into profitable compounds. One such profitable compound is bacterial cellulose, with potential use in food and biomedicine, amongst others. By use of Gluconacetobacter xylinus, BFW was recently fermented into bacterial cellulose, without use of pretreatment or nutrient additives [71]. In another line of approach, two separate studies have considered fermentation of BFW using oleaginous yeast for production of microbial oil, which has recently gained attention due to its potentially valuable fields of application, one of which is as feedstock in biodiesel production [72, 73]. Both demonstrated that this utilization was possible without any form of BFW pretreatment, and the amount of organic pollutants in the BFW was substantially reduced in the process. One significant disadvantage of this process,

however, is the lengthy five-day fermentation time. In another study, an anaerobic baffled reactor was used for BFW treatment, producing methane [70]. This, too, proved to be a promising line of investigation, resulting in a profitable product as well as great reduction of BFW pollution levels. A "major problem" with this technique, according to [74], is acidification phenomena in the anaerobic baffled reactor, leading to reduced methanation rates. In fact, Lin et al. [74] suggest it may be more prudent to pretreat the BFW using an adsorbent, before using the treated BFW as feedstock in another session of ABE fermentation using Clostridia.

3.5 Industrial and economic state of ABE fermentation

During the last decade, ABE process plants have started production in China and Brazil, and several companies around the world have expressed an interest in butanol fermentation, including non-ABE technologies [5]. Researchers particularly cite butanol's biofuel proficiency as a primary motivation for the resurgent interest in the ABE process. The bulk of recent industrial activity based on the ABE process has taken place in China, mostly utilizing corn as feedstock [3]. Examples outside of China include UK-based Green Biologics, which specifically emphasises development of lignocellulosic ABE fermentation [75]. Establishing sustainable industrial businesses in this market is a challenge, however, as exemplified by Cobalt Technologies. This US-based company also endeavoured to use lignocellulose in the ABE process, but filed for bankruptcy in late 2015 despite being deemed a promising venture only a few years ago [5, 76].

The majority of industrial ABE plants are operated semi-continuously, using as many as eight fermentation tanks with fermentation lasting up to three weeks at a time, with periodic addition of feedstock and fermentation bacteria. After fermentation, product solvents are recovered by distillation. Cost reduction is achieved through co-location with ethanol plants, with shared waste treatment [10].

Fermentative butanol production for bulk chemical purposes is already economically competitive, chiefly using conventional starch and sugar feedstocks. For biofuel purposes, butanol fermentation is not currently competitive. Most of the production costs stem from high feedstock prices, with distillation-based product recovery and energy usage contributing about a fifth of total expenditures on average. The economic sustainability of industrial ABE fermentation is very sensitive to price fluctuations, both for feedstocks and for butanol – perhaps predominantly the latter, which is dictated by petrochemical butanol prices and therefore closely related to the price of crude oil [10].

Butanol fermentation of lignocellulosic feedstocks can benefit from lower feedstock prices, but as for any biorefinery process, the high costs associated with lignocellulose pretreatment and hydrolysis are an issue. Still, utilization of agricultural residues, for instance, would represent markedly reduced costs for ABE fermentation [10].

Product recovery and purification costs can make up as much as 40% of current ABE process costs [9]. This high percentage is caused by the low product concentrations in the fermentation broth. Higher concentrations would mean lower energy requirements for downstream processing, and thus lower costs.

4 THE THERMOCHEMICAL PROCESS

4.1 Overview

4.1.1 History

The overall process of thermochemical butanol production, as outlined in the next sections, has yet to be commercially realized. However, the principal process steps involved are well-established in industry and research in other fields of application.

Gasification converts carbon rich materials into synthetic gases (syngas). It has found substantial industrial application since the 1940s in combination with Fischer-Tropsch synthesis for production of liquid fuels, with coal as the primary feedstock. Recent research in this field has chiefly been concerned with utilization of biomass feedstocks, and several process pathways have been developed [77].

Alcohol synthesis by reacting syngas over catalysts has been known since the 1920s. The oil embargo of the 1970s saw a resurgence of interest in the field, particularly with an aim to produce higher alcohols for fuel applications. When oil prices dropped again, interest waned, and since then research has largely been environmentally motivated [78]. Notably, though, during the 1980s, research into heavy-alkali-promoted, low-temperature, copper-based, zinc oxide-containing catalysts established the knowledge that these were considerably more active and selective towards higher alcohols, with prominent selectivity towards isobutanol.

Alcohol synthesis on an industrial scale has largely been confined to methanol, using syngas from steam reforming of methane. However, development of selective catalysts for formation of higher alcohols – isobutanol in particular – from syngas has gained interest among researchers for the past three decades [79-81].

4.1.2 Process steps

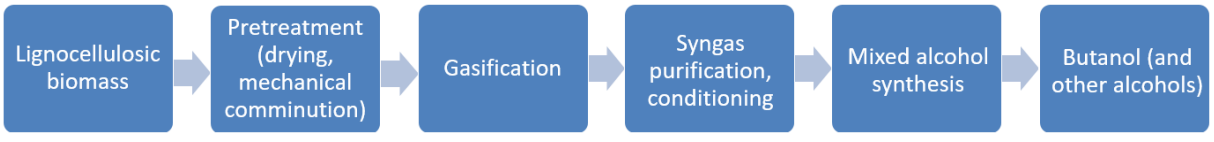

Figure 5: *Overview of process steps involved in thermochemical butanol production via syngas [7].*

Figure 5 summarises the process outlined in the following. Lignocellulosic biomass is pretreated before gasification. Gasification produces syngas, which subsequently goes through purification and conditioning processes with an aim to remove undesirable components before

the syngas serves as feedstock in mixed alcohol synthesis. The final product of the process is a mixture of alcohols, where isobutanol constitutes a prominent fraction. Synthesis of n-butanol is also possible, but selectivity is much better for isobutanol. Thus, isobutanol is the desired isomer in thermochemical butanol processing.

As will become evident in the following sections, gasification and alcohol synthesis are high temperature exothermic processes, and heat regeneration through e.g. a conventional steam cycle for direct process use or for electricity generation should be included in the process design.

4.2 Pretreatment

A thermochemical process such as gasification is capable of efficient conversion of a wide range of lignocellulosic materials, including lignin. Some pretreatment is strictly required, however, to reduce biomass particle size and to reduce moisture content, which greatly facilitates subsequent gasification. Particle size reduction, usually to around 20-80mm, is achieved through mechanical comminution [82]. For the gasification process to produce fuel gas with high heating values, which is desirable for the purposes discussed here, biomass moisture content is usually reduced to 10-20% [83]. The significance of low moisture content will become clear in the following section.

4.3 Gasification

Lignocellulosic biomass can be converted into a gaseous fuel by gasification, which involves thermal decomposition through partial oxidation in a suitable oxidation medium, converting the energy in the carbon bonds of the biomass into combustible gas. This conversion process is very fast, usually taking place in less than 10 minutes [83]. Possible oxidation media include O_2, CO_2, supercritical steam etc. Typical process temperatures range from 800˚C to 1500˚C [77, 78]. The product gas can be used as engine fuel or in gas turbines, or as liquid fuel feedstock, as considered here.

The following is a general summary of the chemical reactions in a gasifier:

$$Partial\ oxidation \quad C + \frac{1}{2}O_2 \leftrightarrow CO \quad (\Delta H = -268\ MJ/kg\ mole) \quad (1)$$

$$Complete\ oxidation \quad C + O_2 \leftrightarrow CO_2 \quad (\Delta H = -406\ MJ/kg\ mole) \quad (2)$$

$$Water\ gas\ reaction \quad C + H_2O \leftrightarrow CO + H_2 \quad (\Delta H = +118\ MJ/kg\ mole) \quad (3)$$

CO, H_2 and H_2O can partake in further reactions:

$$Water\ gas\ shift \quad CO + H_2O \leftrightarrow CO_2 + H_2 \quad (\Delta H = -42\ MJ/kg\ mole) \quad (4)$$

$$Methane\ formation \quad CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad (\Delta H = -88\ MJ/kg\ mole) \quad (5)$$

Notably, these are all equilibrium reactions, their directions depending on conditions such as temperature, pressure and reactant concentrations. As indicated by these reactions, gasification produces a gaseous mixture of CO_2, CO, CH_4, H_2 and H_2O [82].

Variations in processing conditions and methods as well as oxidation media influence the quality of the product gas, commonly quantified by heating value or calorific value (CV), in units of MJ/Nm^3. Gas CV of 4-6 is considered low, and usually produced with air, possibly in combination with steam. Gas with a CV of 12-18 is deemed medium quality, and is produced using steam and oxygen. With oxygen, CV values in the high 20s are possible. Using hydrogen as oxygenation medium, a high CV of about 40 can be achieved. Chemical synthesis requires medium or high CV gas [82, 83].

As emphasised in section 4.2, feedstock moisture content must be kept low. Feedstock moisture above 30% hinders ignition and reduces CV. Higher moisture and carbon monoxide levels give more hydrogen by the water gas shift reaction, which in turn increases methane production. This is undesirable. Also, high biomass ash content (above about 5%) can impede gasification and cause slagging – melting of ash in the gasifier hearth – and resulting feed blockage [82].

A range of gasifier reactor designs are available [83], but the designs demonstrated with biomass are entrained flow, fixed bed and fluidised bed, of which the latter two are most commonly used. Fixed bed is the traditional industry standard, with operating temperatures around 1000˚C and various air-and-feed flow configurations. The so-called downdraft fixed bed reactor, in which biomass is fed into the top of the reactor and undergoes gradual conversion to syngas which is extracted from the bottom of the reactor, is the most popular variety for biomass conversion. Its simple design is an advantage, along with the low tar content of the product gas, but the product gas also has relatively low CV. Fluidised bed gasifiers, meanwhile, feature uniform temperature distribution in a bed of fine-grained material which is "fluidised" by air injection. The major challenge of this design is avoiding bed material slagging due to biomass ash [82, 84].

Impurities in the product gas can include particles, tars, and nitrogen-, sulphur- or alkali-compounds. These can largely be removed through purification and conditioning, i.e. gas clean-up. The degree of required purification is dictated by the prospective application of the product gas.

4.4 Syngas purification and conditioning

Raw syngas usually contains impurities and contaminants that can poison catalysts employed in subsequent syngas upgrading. These include particles, tars, hydrogen sulphide, carbon dioxide etc. that require removal through several costly cleaning processes [85, 86]. The exact methods deployed depend on the intended application of the syngas.

Butanol synthesis, which is described in section 4.5, involves the use of modified methanol catalysts. For mixed alcohol synthesis using these catalysts, certain cleanliness requirements must be met. Some notable points of interest will be mentioned here: Syngas content of sulphur should ideally be kept below 0.1ppm, as it acts as a potent site-blocking poison, particularly on Cu catalysts. Water vapour at higher partial pressures will also inhibit the alcohol synthesis, and should be reduced. Other possible syngas components that should be avoided include Cl, as well as Ni and Fe carbonyls. Cl will contribute to sintering of Cu catalysts, while Ni and Fe carbonyls cause active catalyst site blockage [87].

A very wide variety of syngas purification and conditioning technologies are available, and detailed descriptions can be found elsewhere, such as [88]. The aim is to refine the raw syngas to a product consisting almost entirely of CO and H_2. In short, the different methods are commonly categorized as hot gas (temperature > 300˚C), warm gas and cold gas (temperature < 100˚C) clean-up. A disadvantage of the latter alternative is the temperature regulation requirement to cool down and heat up the gas before and after clean-up, whereas the former alternative presents challenges in the form of severe process conditions. Hot gas clean-up includes mature technology such as cyclones and filters for particle removal, alongside thermal and catalytic cracking to remove tars. Sulphur removal at high temperatures is performed by adsorption. Cold gas clean-up includes mature and very effective technologies that usually involve water or liquid absorption. Wet scrubbers fall into this category, and are commonly employed for chlorine removal, in addition to efficiently removing most other impurities [88].

4.5 Mixed alcohol synthesis

Topics concerning the development of or in-depth specifics regarding catalysts are beyond the scope of this thesis. However, mixed alcohol synthesis takes place over inorganic catalysts, so a brief treatment of some relevant issues is necessary. Some terms need to be clarified first: Catalyst productivity indicates the amount of product produced per amount of catalyst per time, normally given in g/kg/h. Occasionally, “yield” – liquid product concentration per unit time, with units g/L/h – is also used to describe productivity. Selectivity, in the following, signifies the molar fraction of carbon monoxide, CO, converted to a specific product [78].

“Mixed alcohols” usually refers to the C_2-C_6 range of higher alcohols [78]. Two types of catalyst are currently used for isobutanol production from syngas: modified methanol catalysts and zirconia-based catalysts [89]. Modified high- and low-pressure methanol catalysts result primarily in a mixture of branched alcohols, among which isobutanol is a thermodynamically favoured product [7, 78, 81]. Various catalysts based on Zirconia (ZrO_2) have also demonstrated a notable isobutanol productivity and selectivity [79, 89]. Several of these require very high reaction temperature and pressure, although some recent efforts have been made to synthesise isobutanol with Zirconia catalysts at less demanding conditions, with noteworthy results.

Developing catalysts with high selectivity is among the main challenges of mixed alcohol synthesis, particularly when the need to achieve a high fraction of alcohols among the process

products is taken into account. Modified methanol catalysts is arguably the most promising alternative in terms of selectivity [90]. In light of this, the main emphasis in this text will be on modified methanol catalysts.

Methanol catalysts are "modified" by adding an alkali promoter and other active elements, which encourages the formation of higher alcohols at the expense of methanol. These catalysts are termed high-pressure or low-pressure, occasionally interchanged with high- or low temperature, respectively. Typical active components are Zinc or Chromium oxides for high-pressure methanol catalysts, while the low-pressure catalysts use Copper [78]. The typical process conditions for the two varieties are listed in Table 3.

	Modified high-pressure methanol catalyst	Modified low-pressure methanol catalyst
Catalyst components	ZnO/Cr_2O_3	$Cu/ZnO(Al_2O_3)$
Temperature (˚C)	300 – 425	275 – 310
Pressure (MPa)	12.5 – 30	5 – 10
H_2/CO ratio	1	1 – 1.2

Table 3: *Typical components and process conditions for modified methanol catalysts [78, 87].*

The mechanism by which higher alcohol synthesis takes place is known as oxygen retention reversal aldol condensation, and involves carbon-chain growth with addition of β-carbon (the carbon next to the alcohol oxygen) [79].

The overall stoichiometric reaction for higher alcohol synthesis may be summarised as follows, where *n* ranges from 1 to 8 [87, 91]:

$$nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O \qquad (6)$$

The reaction is exothermic, and higher n means more exothermic reactions. The above reaction can quite adequately describe higher alcohol synthesis, when coupled with the water gas shift reaction:

$$Water\ gas\ shift \qquad CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (\Delta H = -42\ MJ/kg\ mole) \qquad (4)$$

As can be seen in the above reactions, hydrogenation of CO leads to alcohol formation, but other reactions also occur, such as CO_2 hydrogenation. The side reactions involved and the specific products generated depend on the catalyst used. Most studies on alcohol synthesis catalysts focus on CO hydrogenation, however, and CO conversion percentage – usually signifying the molar amount of CO converted to products [78] – is an important parameter in discussion of catalyst efficiency. Of the modified methanol catalysts, the high-pressure ones have the higher reported CO conversions, but these are achieved at very high pressure and temperature. Low-pressure catalysts typically have CO conversions below 10% [7, 79, 80].

For modified low-temperature methanol catalysts, methanol makes up about 80% of the products. For high-temperature methanol catalysts, the reported methanol fractions are in the

approximate range of 30-50%, depending on the reactor configuration [79, 87]. Isobutanol is generally the most abundant product next to methanol, but is limited to a fraction of about 20% for high-temperature methanol catalysts.

The influence of pressure on higher alcohol synthesis has been afforded limited attention by researchers. Nevertheless, several points of interest have been elucidated. Alcohol formation reactions are volume contracting, and thus increased pressure generally leads to greater product equilibrium concentration, meaning greater alcohol formation. To some extent, the catalyst also dictates the influence of the pressure on reaction kinetics [92]. High pressures and high temperatures in combination tend to increase higher alcohol synthesis at the expense of methanol formation [87]. Also, notably, reaction pressure has significant influence on process expenses [91].

High CO_2 concentrations inhibit formation of higher alcohols on modified methanol catalysts [80, 87]. Syngas based on lignocellulosic biomass may contain as much as 25% CO_2 [92]. This can be regulated after gasification by means of the water gas shift reaction.

Reactor configurations influence the alcohol production efficiency. For instance, the use of a double bed reactor system has been shown to significantly improve CO conversion and selectivity of higher alcohols in general, including butanol [81]. In this process, there are two catalyst beds within the reactor – one lower in the reactor, and one toward the top. These operate at different temperatures and use different catalysts to cater to different synthesis reaction steps. The first, lower-temperature bed emphasizes methanol formation, while the second bed achieves improved isobutanol formation [79]. A variation on the same concept can be accomplished using two reactors in series. One significant advantage of this reactor type is that considerable isobutanol productivity can be achieved at relatively modest reaction pressures, e.g. 7.6 MPa [93].

The high process temperatures and heat generation of the synthesis reactions pose a challenge in alcohol synthesis reactor design. CO hydrogenation involves highly exothermic reactions, making diligent reactor temperature control a necessity – the consequence would otherwise be reduced yields and catalyst deactivation by sintering [87, 92]. This is particularly true for fixed bed reactors. Reactor modifications necessitate extra equipment cost and further complication of operation [91]. One proposed reactor design that potentially mitigates this is the slurry phase reactor, in which fine-grained catalyst is mixed into a “slurry liquid” (e.g. mineral oil, wax), whereupon syngas is bubbled up through the slurry from the bottom to produce products subsequently collected in vapour phase [94, 95]. Advantages of this design include high heat transfer capacity and good temperature control due to the presence of the slurry liquid, as well as the prospect of on-line catalyst replacement and recycling. To date, slurry reactors have only found commercial-scale application in Fischer-Tropsch synthesis [96]. If applied to isobutanol synthesis, the slurry phase reactor could prove beneficial for high-temperature processes based on Zirconia catalysts, and has been deemed “ideal” for processes using modified methanol catalysts [97].

Other techniques to improve isobutanol yield have been proposed, aside from improved reactor designs, and the most notable among these is injection of lower alcohols (methanol, ethanol and

propanol) into the reactor, which has been tested at pilot-scale with promising results. The lower alcohols are part of the alcohol mix produced, and can be recycled to increase the higher alcohol yield [78, 87].

After synthesis the alcohols and unconverted syngas are cooled before separation by distillation. The alcohol stream is depressurised ahead of dehydration and separation. Dehydrated alcohols are sent through alcohol separation columns [78, 87].

4.6 Byproduct processing and waste treatment

As previously mentioned, and as indicated by the name of the process, mixed alcohol synthesis generates several product alcohols. The major byproduct of isobutanol synthesis is methanol, which can be recycled, as described earlier, or sold separately after distillation. The same applies to other alcohols, although only lower alcohols are recycled, as previously noted [87].

Considerable amounts of wastewater may be generated during syngas purification and conditioning processes, depending on the technology deployed, and will require wastewater treatment [82, 85]. An example of this tar removal by wet scrubbing [88].

4.7 Current industrial and economic state of thermochemical butanol production

As indicated in section 4.1.1, mixed alcohols synthesis has been known for about a century. Despite this, unfavourable selectivity and yield has hindered its commercial application, with industrial alcohol synthesis being restricted to methanol synthesis. A few companies designed pilot-scale plants for mixed alcohol synthesis during the 1980s and 1990s, but no commercial plants have been built subsequently, and activity in this field of research remains rather low. Improvements in the areas of reactor temperature control, catalyst activity and selectivity are considered vital to make the process commercially viable [78, 87].

Also, lignocellulose-based gasification is commercially hampered by the need for complex and costly purification and conditioning processes to refine the raw syngas, which is currently not of sufficient quality for further processing such as higher alcohol synthesis [85].

5 PROCESS ECONOMICS

At the time of writing, rather few in-depth studies have been conducted concerning the economic viability of the ABE process using lignocellulosic feedstocks. Two techno-economic analyses are available, as well as two other studies on process economics. All these are listed in Table 4 below. These are recent publications, based on different assumptions about production plant capacity, feedstock, process steps, etc. Note the wide variety in ABE process feedstock costs in Table 4, even among those studies using the same feedstock. Also, note the concomitant butanol production cost. Along with the four studies concerning ABE, a single techno-economic study on thermochemical butanol production via mixed alcohol synthesis is listed. To the best of this author's knowledge, it is the only available study of its kind.

Process path	Feed-stock	Feedstock cost (US$/t)	Capital investment (US$/L butanol)	Butanol production cost (US$/L)	Butanol yield (L/t dry feedstock)	Annual production capacity (million L)	Reference
ABE	CS	110.5	3.61	1.46	156	113.4	[69]
	CS	64.3	4.69	0.88	135	94.5	[42]
	CS	33	0.83[a]	0.48	316	12.3	[54]
	WS	24	1.05[a]	0.84	159	119.6	[98]
Thermo-chemical	PW	75	3.57	0.83	152[b]	100.1	[7]

Table 4: *Key figures from techno-economic analyses of lignocellulose-based butanol production. t is metric tons. CS = Corn Stover; WS = Wheat Straw; PW = Pine Wood.* [a] *This number is based on fixed capital costs, whereas the corresponding numbers from the other studies are total capital costs.* [b] *This figure is included for the sake of comparison, but it should be noted that it doesn't adhere to the definition of "yield" normally used when discussing alcohol synthesis.*

The most recent techno-economic analysis of the ABE process was conducted by Baral & Shah [69], and published in 2016. Corn stover feedstock was used, with dilute sulfuric acid pretreatment preceding simultaneous saccharification and vacuum fermentation. Using SuperPro Designer as modelling software for process modelling and economic analysis, the study considers a cellulosic biorefinery with a butanol production capacity of 113.4 million L/year, requiring more than 900000 tonnes of untreated feedstock per year. The total capital investment is calculated to be about US$410 million. A 30-year lifespan is assumed for the production plant. The estimated butanol production cost was US$1.8/L, which was offset by US$0.3/L through byproduct revenue, giving a butanol cost of US$1.5/L. The authors claim that process optimization could reduce costs further, achieving a highly competitive butanol production cost of US$0.6/L [69].

In their 2014 study, Tao et al. [42] use Aspen Plus for simulation of a biobutanol plant with a processing capacity of 2000 dry metric tons per day of corn stover feedstock [42]. The plant includes dilute acid and steam explosion pretreatment, ion exchange columns for inhibitor

removal, enzymatic hydrolysis and vacuum fermentation. After recovery, the product solvents are separated through distillation. Solids from distillation and biogas from anaerobic treatment of wastewater are burned in a combustor for electricity production. Total capital investment is estimated to US$443 million. The plant is operational 350 days per year. Production plant lifespan is assumed to be 30 years. Annual production is estimated to 94.5 million litres of butanol. A sober acetone-butanol-ethanol ratio of 3:6:1 is assumed, along with a rather optimistic – by the researchers' own admission – assumption of 85% sugar yield (a value that has yet to be achieved even on lab scale). This gives a minimum butanol selling price of US$0.88/L. The sugar yield and product solvent ratio both influence the minimum butanol selling price. Also, feedstock price contributed about 25% of the cost, while byproduct revenue offset the selling price by 28%.

Basing calculations and simulations for cost estimation on MATLAB, Kumar et. al. [54] consider a biorefinery with an annual production capacity of 10 000 tonnes of n-butanol, with 330 operational days per year. The process includes wet grinding pretreatment, acid or enzyme hydrolysis, dilute acid or alkaline inhibitor treatment, batch fermentation and product solvent recovery and separation by distillation. Various lignocellulosic feedstocks are considered, at varying cost. No adjustments to operational specifications of the plant are mentioned for the different feedstocks. Total capital costs for the plant are not provided, only fixed capital costs of roughly US$10.3 million are given. A butanol yield of 0.39g/g was assumed for all feedstocks. This gave a production cost of between 0.59 and 0.75 US$/L butanol for the different lignocellulosic feedstocks. The estimated price of corn stover-based n-butanol is US$0.59/L, and is listed in Table 4.

The last ABE study included in Table 4 is one from 2013 by Qureshi et al. [98]. This is a cost estimation study of biobutanol production through ABE processing of wheat straw biomass. SuperPro Designer was used to design and simulate a plant with a butanol production capacity of about 150000 tonnes per year, operational for 330 days per year. The process included dilute acid pretreatment, enzymatic hydrolysis, batch fermentation and recovery and separation by pervaporation and distillation, respectively. Again, total capital costs were not given, but fixed capital investment was estimated to US$193 million. The resulting butanol production cost was US$0.84/L [98].

Another notable study on ABE fermentation is that of Pfromm et al. [45] from 2010, where iThink modelling software is used to make "a technical and economic assessment" of fermentative production of n-butanol and ethanol for biofuel use, comparing the two. Corn and switchgrass are used as feedstocks, supplied at 1689 tonnes per day. The authors refrain from estimating actual economic figures in the switchgrass case, due to a lack of data to back up assumptions: "Large scale industrial experience of switchgrass production, harvest, transport, storage and conversion to biofuel via fermentation on a thousand tonne per day facility scale is lacking at this time." This is why the study is excluded from Table 4. Instead, the study provides liquid fuel production figures in terms of the lower heating value (LHV) of the products. For the case of switchgrass, a LHV of 11.1TJ/day for ethanol from yeast fermentation and a combined LHV of 6.2TJ/day for both butanol and ethanol from ABE fermentation are calculated. With about half the calculated LHV yield of ethanol fermentation, on top of

considerably more complex process requirements, fermentative production of n-butanol is deemed severely uncompetitive in this study [45].

To provide some context for the ABE fermentation LHV of 6.2TJ/day reported by Pfromm et al. [45], a rough calculation of the corresponding LHV from Tao et al. [42] can be made (as this study features the production capacity closest to the average of the ABE studies in Table 4). Using the LHV of n-butanol from Table 1, the above mentioned 94.5 million litres per year and 350 annual operational days reported by Tao et al. [42] correspond to an LHV of about 7.3 TJ/day. Tao et al. [42] also assume a feedstock supply of 2000 t/day. Scaling this supply down to the 1689 t/day feedstock supply assumed by Pfromm et al. [45] results in an LHV of about 6.2 TJ/day. Note that this approximated LHV/day value stems entirely from n-butanol, which is not the case for the corresponding number from Pfromm et al. [45] – however, the numbers are the same.

The only available techno-economic analysis on syngas-based alcohol synthesis of biobutanol is by Okoli and Adams [7]. In this study, Aspen Plus is used for modelling a complete production process, including pretreatment, gasifier, gas clean-up and mixed alcohol synthesis in two fixed-bed reactors in series. Plant life is assumed to be 30 years, with ~330 operational days per year. A daily feedstock supply of 2000 tonnes of pine wood at US$75/t is used. An "n-th plant assumption" is used, meaning that the learning curve associated with plant construction and operation is surmounted. The catalyst chosen in this study is not the one with the best reported CO conversion (this catalyst's conversion is 8.5%), but it was chosen because it's reportedly the only one with sufficient yield data for modelling purposes. CO conversions of 18.5% have been reported for some catalysts. However: "For this work, a futuristic CO conversion of 40% is assumed". The study reports a total project investment of US$351 million. A minimum butanol selling price of US$0.83/L is calculated. Last but not least, it should be noted that a sensitivity analysis of the impact of CO conversion suggests that one could reduce the assumed 40% conversion to 18% and still retain a butanol production price around US$1/L.

6 DISCUSSION: COMPARISON OF PRODUCTION PATHWAYS

6.1 Process conditions and technology

In this section, the technical pros and cons of the two butanol production pathways presented in previous sections will be summarised and compared.

The central processing steps of the two butanol production pathways considered here are fermentation and alcohol synthesis, respectively. To convert lignocellulosic biomass into suitable substrates for these two processes, the two pathways have very different requirements for preceding processing.

The pretreatment regime of the thermochemical pathway only involves grinding and drying, and is less complex and considerably less time-consuming than that of the ABE pathway. Still, it is no less crucial to the subsequent processing.

For the ABE pathway, pretreatment is normally followed by hydrolysis, and frequently also detoxification. There are various possible configurations regarding the order of the process steps involved, and they should preferably be tailored to suit both feedstock and fermentative bacterial culture. This tailoring will require considerable research efforts, but is quite necessary to ensure a reliable and stable fermentation process. All this fermentation substrate processing is time consuming and requires diligent process control in order to minimize formation of compounds that may inhibit subsequent fermentation.

The thermochemical pathway uses gasification followed by gas purification and conditioning to convert the pretreated biomass into sufficiently clean syngas for the alcohol synthesis. The operative term here is process control. These processes are energy-intensive, at least partly proceeding at high temperatures and requiring careful temperature monitoring and regulation. The purification and conditioning are crucial process steps with a wide selection of possible methods, all with their own process control requirements. However, many of these methods will need further research and development ahead of industrial application. At the time of writing, gasification and subsequent purification and conditioning have yet to produce syngas of sufficient quality to serve as substrate for catalytic mixed alcohol synthesis. Fortunately, research in this area is likely to receive quite a lot of attention, as biomass gasification and syngas purification concern other, commercially established technologies as well.

ABE fermentation is hampered by low productivity and product yield. Various proposed reactor designs represent modest improvements in this regard, most notably in the form of simultaneous saccharification and fermentation. Nevertheless, the major potential for improvement arguably lies in metabolic engineering and genetics.

While metabolic engineering and genetics are not directly treated in-depth in this text, a brief elaboration on their importance should be made. In short, the low butanol tolerance of the microbes in the fermentation reactor is the key issue of the ABE process. Improved recovery

techniques will allow more energy-effective and biocompatible maintenance of sustainable butanol levels in the fermentation broth, which allows more complete utilization of costly feedstock. However, the rate of production will still be limited, due to the low butanol fraction in the broth. If bacterial butanol tolerance was increased significantly, the ABE process would more than likely become economically sustainable – with improved butanol titre and yield, feedstock requirements, and thereby costs, would be considerably reduced.

Reactor design has significant potential for development in mixed alcohol synthesis, too. The proposed improvements have their own distinct advantages and disadvantages. Pending further development of the slurry reactor concept, the double bed or double reactor configuration seems to be the simpler avenue of approach. Development of catalysts for mixed alcohol synthesis is rather slow, as research efforts are limited, despite increasing interest in recent years. This is a pivotal aspect of mixed alcohol synthesis, much like fermentation bacteria in the case of the ABE process, but is beyond the scope of this text.

Product recovery and purification after completion of the main butanol production processes are more complex for the ABE pathway than for the thermochemical pathway. Virtually no other alternatives to distillation have been considered so far for the latter pathway, and the lack of less desirable byproducts warrants its use. Downstream processing in general plays a more significant part in the overall ABE process economics than it does for the thermochemical pathway. The aforementioned low yield of the ABE fermentation inflates the energy requirements for product recovery and separation, rendering distillation less viable. There is extensive research in this area, and several promising candidate technologies are emerging. However, comparison of experiments cited in literature is rather challenging, due to the wide variety of experimental setups and methods used. At any rate, application of ISPR technology on a commercial scale should be able to help the ABE process gain a proper foothold in the industry chemicals market.

A possible issue with ABE research is the prevalence of simplistic experimental setups, frequently utilizing batch fermentation with various feedstocks. While a broad understanding of the base topics is undeniably valuable, significant process improvement may require more research directed at continuous processes. Compared to mixed alcohol synthesis of syngas, however, there is at least a considerable amount of research being done.

Refineries that combine use of thermochemical and biochemical techniques for more effective and complete utilization of lignocellulosic biomass may constitute viable avenues of approach in the future. In particular, the ability of thermochemical processes to utilize lignin set them apart from biochemical processes.

Finally, the issue of process time should be addressed. The ABE process is exceedingly time-consuming, including several days of upstream processing before fermentation itself. By comparison, the pretreatment regime of the thermochemical pathway is quicker, and gasification of dry biomass to syngas takes mere minutes. Alcohol synthesis takes hours, as opposed to several days for ABE fermentation. This is an advantage for the thermochemical pathway.

6.2 Economics

In this section, the process economics of both pathways will be discussed, with particular emphasis on the studies reviewed in section 5.

First, a few comments on the comparison of the corn stover ABE fermentation studies included in Table 4: The study by Kumar et al. [54] assumes far and away the lowest feedstock costs, in addition to a very ambitious (and futuristic, at best) butanol yield. Judging from the usual fraction of total capital investment made up of fixed capital costs, the total capital investment of this study is also likely to be markedly lower than the others'. In this context, fixed capital costs consist of equipment expenditures during plant construction, while total capital investments also include costs for engineering, construction etc., which add up to a larger sum. The fraction of total capital investment made up by fixed capital costs varies. For the other two studies, note that despite having the higher assumed butanol yield and lower total capital investment of the two, the study by Baral & Shah [69] ends up with the higher butanol production cost. This suggests that feedstock cost is a more decisive parameter. However, the study by Qureshi et al. [98] diverts somewhat from the vague pattern of the other studies. Compared to the results of Tao et al. [42], this study assumes lower capital investments, considerably lower feedstock costs, higher yield and higher production capacity, and yet ends up with almost the same butanol production cost. Barring some oversight on this author's part, there are several possible causes for this discrepancy beyond the parameters shown in Table 4, including differing assumptions in process design and the difference in simulation software.

Regarding the comparison of the calculated n-butanol production in the form of LHV in the studies by Pfromm et al. [45] and Tao et al. [42]: The calculated LHV for both studies is 6.2 TJ/day, but as previously noted, Pfromm et al. [45] include the LHV of both n-butanol and ethanol in this value, while Tao et al. [42] only include n-butanol. Thus, the LHV is somewhat lower for Pfromm et al. [45], but the discrepancy is too small for the results of Tao et al. [42] to escape the conclusions of Pfromm et al. [45] about n-butanol fermentation falling economically short of ethanol fermentation, probably even when differences in feedstock choice and process design are taken into account. Comparison of ethanol and butanol production is not the main purpose of this text, but it is an important concern, and the conclusions of Pfromm et al. [45] clearly illustrate the challenge of establishing biobutanol as a viable alternative in the biofuels market.

More research is needed before substantiated estimates can be made regarding the commercial feasibility of isobutanol production via alcohol synthesis using syngas. Interestingly, though, the single in-depth techno-economic study available suggests that this pathway could compete with production via the biochemical pathway, even based on assumptions of research progress which seem reasonably attainable in the near term – the suggestion that a butanol production cost of US$1/L is obtainable with a CO conversion of 18% is particularly noteworthy, and if corroborated by future techno-economic studies on the subject, this could be a key argument for more research and pilot-scale testing of this production process.

The commercial feasibility of both production pathways seems limited at the time of writing. On a starch- and glucose-basis, the ABE process is well-established in the industry, and persists even to this day on a very limited scale. However, it requires some restructuring – particularly concerning upstream processing – to effectively utilize lignocellulosic biomass. Application of ISPR technology on a commercial scale should be able to help ABE fermentation to gain a proper foothold in the industry chemicals market. The fundamental problems of the ABE process still concern low yield and productivity, which are likely to persist unless a substantial improvement in the field of metabolic engineering should come to pass.

As previously noted, syngas-based isobutanol synthesis still lacks pilot plant-scale testing, not to mention much of the necessary research and development to get that far. Improvements on relevant alcohol catalysts alongside syngas purification and conditioning appear to be of particular importance for the prospective success of this process pathway.

A considerable obstacle for commercial biobutanol production regardless of production pathway is the total capital investment, which are US$410 million and US$443 million for the two studies providing these figures for the ABE process, and US$351 million for the one concerning the alcohol synthesis process. Research and development should be stimulated to reduce these figures.

7 CONCLUSIONS

In this thesis, an attempt was made to compare the technical and economic viability of two biobutanol production pathways: the ABE process and the thermochemical process based on gasification and alcohol synthesis. Both technologies seem promising, but with limited commercial viability for the time being. The primary products of the two process pathways are different butanol isomers, and notably, one will not be able to substitute for the other in chemical industry applications. Thus, the two processes would not be in direct competition with one another on that front. The n-butanol-producing ABE process has the advantage of being considerably more established in research and industry, but until fundamental problems such as low yield and productivity are addressed, it still struggles to regain its footing in the fiercely competitive biochemical market. To a certain extent, application of novel ISPR technologies could mitigate this in the near term. The isobutanol-producing thermochemical process has a longer way to go to become viable on an industrial scale. Research activity on this topic, particularly regarding alcohol synthesis, would require a substantial increase to make thermochemical biobutanol production a worthwhile alternative within the next couple of decades. In the current market, where isobutanol is in less demand compared to n-butanol, there seems to be limited incentive for this.

While current techno-economic studies suggest that butanol might struggle to compete with ethanol in the biofuels market in the foreseeable future, the prospect of biobutanol in fuel applications is intriguing. Even so, based on this review of the limited techno-economic literature on the topic, fuel application of biobutanol seems likely to require copious amounts of research and development to become a reality, and perhaps also incentives brought on by other relevant concerns such as oil price fluctuations, government policies and climate impact, which are beyond the scope of this thesis.

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