Diese Arbeit wurde vorgelegt am Lehrstuhl für Systemverfahrenstechnik

The present work was submitted to Chair of System Process Engineering

Simulation und Optimierung von Herstellungsverfahren für Biobutanol der zweiten Generation

Process Simulation and Optimization for Production of Second-generation Biobutanol

Masterarbeit

Master’s Thesis

presented by

Wang, Hong

Student ID no.: 341671

Prof. Ph. D. Alexander Mitsos

Dr.-Ing. Adel Mhamdi

Aachen, May 2, 2017

Abstract

In this thesis, a promising process design for butanol fuel production using lignocellulosic biomass through thermochemical route has been carried out and developed. The process design is based on an extensive literature survey and analysis for the potentials of variable feedstocks including energy crops as well as residual and waste materials of biomass, possible production routes and the state of corresponding technologies. The designed process is simulated using Aspen Plus and consists of the following 5 major steps: biomass drying, autothermal gasification with entrained flow gasifier, gas cleanup and conditioning, higher alcohol synthesis over a modified methanol catalyst and alcohol separation. To enhance the product yields, a portion of the generated methane and other hydrocarbons is reformed through autothermal reforming to produce additional syngas and recycled together with unreacted syngas. Through the process optimization, a final product yield of 6232.5 kg/h of butanol fuel is obtained, which contains 88.2 wt.% of isobutanol and 10.7 wt.% of propanol. A heat integration based on pinch analysis is carried out and an optimized heat exchanger network has been developed, resulting in an energy-efficient process which requires no external hot utilities and only small part of power from grid. An overall plant efficiency of 60.9% is achieved. Based on the simulation results from Aspen Plus, an economic evaluation is carried out to estimate the net production costs of butanol fuel, which turns out to have a specific net production cost (NPC) of 2.25 €/l. Still the NPC is much higher than the acceptable market fuel price. A sensitivity analysis is conducted, finding out that the variation of investment cost of entrained flow gasifier, cost of raw biomass and cost of maintenance labor has the most significant impact on the net production costs. The expected future targets in terms of technology development, simulation improvement as well as costs reduction potentials are briefly discussed at the end of this thesis.

Master’s Thesis
of
Hong Wang

Process Simulation and Optimization for Production of Alternative Liquid Fuel.

Aufgabenstellung

For this thesis, a process design for production of biobutanol as alternative liquid fuel should be carried out. A further economic evaluation is supplemented to analysis the economic feasibility of the designed process. An extensive literature review is firstly carried out to define the state of the relevant technologies for the production of butanol fuel from renewable feedstocks. Different routes will be compared and among them a most promising one will be chosen for the process design, which will be later in detail simulated. The production process is going to be built up with the chosen technologies and reasonable process parameters.

The production process will be detailed simulated with sufficient literature data through Aspen Plus. After process simulation, an energetic optimization based on pinch analysis and heat integration for the designed process should be conducted.

At the end, an economic evaluation based on the simulation results is carried out to estimate the net production costs using the in-house software TEPET by DLR. Further sensitivity analysis is expected as well.

Supervisor: Friedemann Georg Albrecht, M. Sc.

Dr.-Ing. Fatemeh Ebrahimi

Submission date: 02. Mai 2017

Eidesstattliche Versicherung

Name, Vorname

Matrikelnummer (Angabe freiwillig)

Hiermit versichere ich an Eides Statt, dass ich die vorliegende Arbeit selbstständig und ohne unzulässige fremde Hilfe angefertigt habe. Ich habe keine außer den angegebenen Quellen und Hilfsmittel verwendet. Wörtliche wie inhaltliche Zitate habe ich vollständig als solche kenntlich gemacht. Die Arbeit hat in gleicher oder ähnlicher Form noch keiner Prüfungsbehörde vorgelegen.

Ich erkläre mich hiermit einverstanden, dass die vorliegende Arbeit in der Lehrstuhlbibliothek aufbewahrt wird und kopiert werden darf. Für den Fall, dass die Arbeit zusätzlich auf einem Datenträger eingereicht wird, erkläre ich, dass die schriftliche und die elektronische Form vollständig übereinstimmen.

Ich bin damit einverstanden, dass die RWTH Aachen folgende Daten zu meiner Person im Internet veröffentlicht: Name, Vorname, Titel der Arbeit.

Mir ist bekannt, dass ich diese Einwilligung jederzeit schriftlich mit Wirkung für die Zukunft widerrufen kann und meine elektronisch gespeicherten Daten unverzüglich gelöscht werden müssen und die Aachener Verfahrenstechnik bei Widerruf meiner Einwilligung verpflichtet ist, mein Werk aus der Bibliothek des Instituts/Lehrstuhls zu entfernen.

Ort, Datum

Unterschrift

Belehrung:

§ 156 StGB: Falsche Versicherung an Eides Statt

Wer vor einer zur Abnahme einer Versicherung an Eides Statt zuständigen Behörde eine solche Versicherung falsch abgibt oder unter Berufung auf eine solche Versicherung falsch aussagt, wird mit Freiheitsstrafe bis zu drei Jahren oder mit Geldstrafe bestraft.

§ 161 StGB: Fahrlässiger Falscheid; fahrlässige falsche Versicherung an Eides Statt

(1) Wenn eine der in den §§ 154 bis 156 bezeichneten Handlungen aus Fahrlässigkeit begangen worden ist, so tritt Freiheitsstrafe bis zu einem Jahr oder Geldstrafe ein.

(2) Straflosigkeit tritt ein, wenn der Täter die falsche Angabe rechtzeitig berichtigt. Die Vorschriften des § 158 Abs. 2 und 3 gelten entsprechend.

Erklärung

Ich erkläre mich hiermit einverstanden, dass die vorliegende Arbeit in der Lehstuhlbibliothek aufbewahrt wird und kopiert werden darf und habe keine Einwände gegen eine Veröffentlichung der gesamten Arbeit oder von einzelnen Teilen daraus.

Ich bin damit einverstanden, dass die RWTH Aachen folgende Daten zu meiner Person im Internet veröffentlicht: Wang, Hong, Process Simulation and Optimization for Production of Second-generation Biobutanol.

Mir ist bekannt,

> dass ich diese Einwilligung jederzeit schriftlich mit Wirkung für die Zukunft widerrufen kann und meine elektronisch gespeicherten Daten unverzüglich gelöscht werden müssen und
>
> die Aachener Verfahrenstechnik bei Widerruf meiner Einwilligung verpflichtet ist, mein Werk aus der Bibliothek des Instituts/Lehrstuhls zu entfernen.

Ort, Datum

Unterschrift

Contents

1 Introduction

According to the Federal Emissions Protection Act (Bundes-Immissionsschutzgesetz), it is obligated in Germany to achieve a greenhouse gas (GHG) emission reduction of 4% compared to the reference value (83.8 kg CO_2-eq./GJ) from 2017 through the petrol and diesel fuel in transport sector. This target will be raised to 6% from 2020 (Bundestag 2009). As one of the most attractive and promising options to reduce the GHG emission, biofuels from biomass have been intensely studied and some of them have been already successfully brought to the market over the past years. In 2015, the share of biofuels among the total fuel consumption in Germany accounted to be 4.8% (energetically), in which the most consumed biofuels are biodiesel and bioethanol, which are alternative fuels to fossil diesel and petrol, respectively. Among the total renewable energy consumption in transport sector, the share of renewable electricity accounted to be only 11% (Fachagentur Nachwachsende Rohstoffe e.V.). Renewable electricity is only predominant in electricity supply for train by now. Compared with electricity, liquid fuels remain a higher energy density and it is easier to handle with or store for usage of transportation. Therefore, biofuels will still certainly play an irreplaceable and more important role for transportation in the future and should be further developed to meet the stricter requirements for environment protection.

1.1 Second-generation biofuels

Traditionally, biofuels are produced from cultivated energy crops such as wheat, corn, sugar cane, rapeseed etc. These are the so-called first-generation biofuels. Nowadays the production of most biofuels uses those energy crops as feedstock. It certainly has advantages like an easy pretreatment of feedstocks and the availability of already well-developed conventional technologies of extraction or fermentation process for final products. But obviously, the cultivation of energy crops competes directly with food crops cultivation because of the limited agricultural land area. It is widely discussed that an intensive cultivation of energy crops could have pushed up the price of food crops to a higher level, thus threatening the food supply. Besides, considering the GHG emissions at the cultivation process, the first-generation biofuels are not necessarily much better than fossil petrol and diesel fuel regarding to the environmental impacts on life cycle.

A prospective solution to this “Food vs. Fuel” dilemma is the usage of residual and waste materials from agriculture and forest industry, such as straw and forest residues, as feedstocks for bioenergy usage, which are then the so-called “second-generation”. These kinds of raw materials require no additional area for cultivation and the utilization of it even helps to recycle the waste into valuable energy carrier. In 2009, the Biofuel Sustainability Ordinance (Biokraftstoff-Nachhaltigkeitsverordnung) was issued, aiming for a sustainable utilization of biomass for biofuels production and taking consideration of the GHG emission at the entire production chain. The key criteria of sustainable biomass utilization are defined. Firstly, land with high carbon content or high biodiversity are not allowed to be used for cultivation. Secondly, the GHG emission in the entire production chain, including cultivation, transportation and processing, must be reduced by at least 35% compared to fossil fuel from 2011. The requirement on the minimum reduction is raised to 50% from 2017 and will be further increased to 60% from 2018, if the production plant is put into operation after 31.12.2016 (Bundestag 2009). The produced fuels cannot be admitted as biofuels if the aforementioned requirements are not fulfilled and will not benefit from the Renewable Energy Act (EEG) or other political and financial supports for bioenergy.

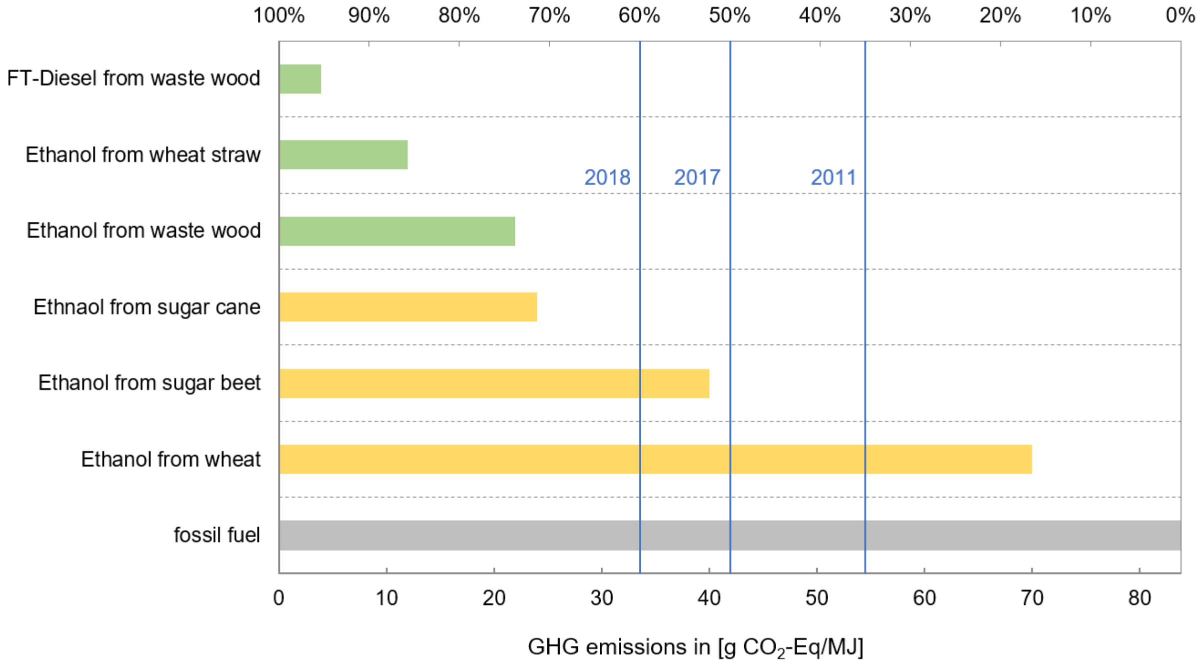


Figure 1-1: Standard GHG emissions of different biofuels

Figure 1.1 shows the standard GHG emissions of a series of biofuels from different feedstocks. Biofuels from residual and waste materials have much higher potential on GHG emission reduction. A required 50% GHG emission reduction means a maximal GHG emission of 41.9 g CO_2-eq./GJ from 2017 (Bundestag 2009). Some first-generation biofuels have even already exceeded the maximum. The utilization of cultivated energy crops will be strictly limited in the future, development and application of next generation biofuels is strongly necessary.

Another possible raw material is algae. Fuel from algae, or called algal biofuel, is then the third-generation biofuel. Cultivation of algae requests much less area than energy crops. Algae grows also much faster and can be grown with minimal impacts on fresh water resources. It is claimed to have 10 to 100 times higher fuel productivity per unit area from algae than other biofuels crops (Greenwell et al. 2010). This technology is still at an early stage of research and development. Therefore, it will not be further discussed in this thesis.

1.2 Potential of residual and waste materials of biomass

Figure 1.2 shows the technical potentials of energy crops and lignocellulose biomass in 2015, aside it is a forecast potential for these two raw materials in 2025-2035 in Germany. Despite a slight decrease, the potential of lignocellulose biomass is still more than twice of that for energy crops in the future, i.e. 889 PJ/a as opposed of 425 PJ/a (Kaltschmitt et al. 2016).

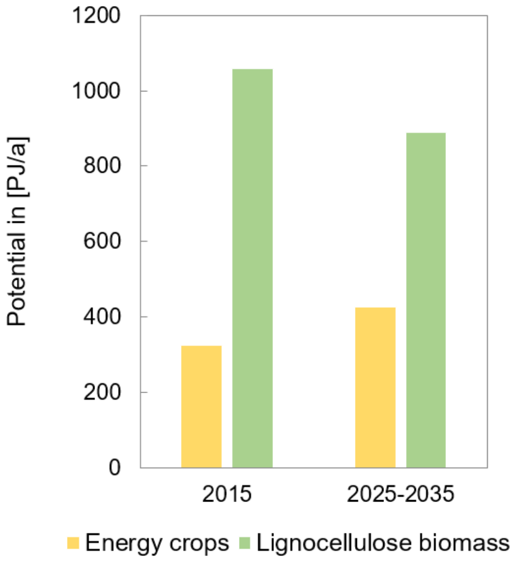


Figure 1-2: Biomass potentials in Germany

Figure 1.3 shows the unused biomass potential of residual and waste materials in 2015 in Germany. A total of 359 PJ/a residual forest wood and straw are available for further energetic usage (Brosowski et al. 2016).

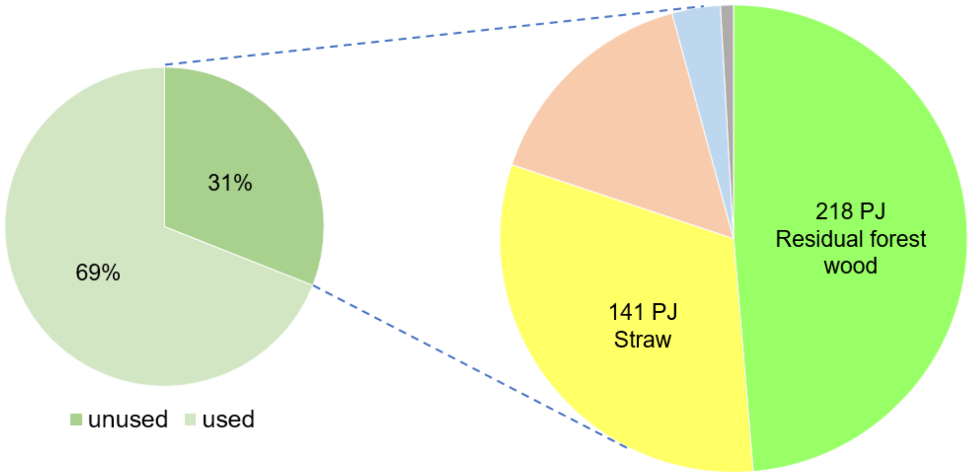


Figure 1-3: Unused potential of lignocellulosic biomass in Germany in 2015

A study by DLR, DBFZ and IFEU considered different scenarios for biomass development and utilization and analyzed the technical biofuel potentials under two scenarios – Business as usual (BAU) and Environment (E). The “Business as usual” scenario represents the extrapolation of the short and medium-term trends and developments. “Environment” scenario depicts a model environment, in which the importance of environmental protection and sustainability is emphasized (Kreyenberg et al. 2015). In Table 1.1 are some relevant results from this study.

Table 1-1: Biofuel potentials in different scenarios

Year	2020		2025		2030	
Scenarios	BAU	U	BAU	U	BAU	U
Biofuel potential in PJ/a (without biogas potential)	148.47	128.63	174.10	146.91	186.21	154.56

In 2005, the total energy consumption in transport sector was 2586 PJ. The target is to decrease this energy consumption by 10% in 2020 to 2327 PJ (Umweltbundesamt 2015). Assuming a 100% utilization of biogas potential in transport sector, the total biofuel potential can amount to 446 PJ and 365 PJ for scenario “Business as usual” and “Environment”, respectively (Kreyenberg et al. 2015). Therefore, a share from 5.53% to 19.2% of the energy consumption for transport sector in 2020 could be covered through biofuels.

1.3 Ethanol fuel vs. butanol fuel

Even 9000 years ago, our ancestors already knew how to produce alcoholic beverage with fruit juice and liquid honey through fermentation. Alcohol production with high purity became possible since the distillation technology was discovered. As one of the most consumed beverage in the world, the usage of alcohol as fuel for cars has also been found and developed for over 100 years. Currently in the fuel market there are several kinds of ethanol blended petrol available such as E5, E10, E85. Compared to regular petrol, pure ethanol contains approx. 35% less energy per unit volume, results in lower mileage. The enthalpy of vaporization of ethanol is more than twice of petrol, which means more heat/work is needed to evaporate the fuel in compression process and this could be problematic for cold start of engine especially in cold winter. Acting as a blend stock, ethanol will easily separate from petrol phase into the water phase when petrol meets water because of the high polarity of ethanol molecule. Besides, ethanol could be corrosive to materials of some parts of engine under the operation conditions. Thus, the conventional engine must be specifically modified, before those petrol with more than 5% blended ethanol being used.

Because of those drawbacks of ethanol by the usage as motor fuel, researchers has tried to find an advanced biofuel as alternative. Butanol as fuel has received much attention in the last few years. Traditionally, butanol is used as industrial intermediate to produce butyl esters or as solvent for paints, coatings and chemical extractant in production of some organic components. In Table 1.2 a few relevant thermochemical properties of butanol and those of ethanol and petrol are listed.

Table 1-2: Comparison of fuel properties between petrol, butanol and ethanol

Parameters	Petrol	Butanol	Ethanol
Lower heating value [MJ/L]	32.4	26.8	21.2
Octane number (RON)	95	94	104
Enthalpy of evaporation [kJ/kg]	420	578	910
Vapor pressure (50°C) [hPa]	700-900	45.4	293

It is clear to see that butanol has a more similar fuel property as petrol than ethanol when considering heating value, octane number and enthalpy of evaporation. With a better blending performance than ethanol, butanol can be blended with petrol theoretically in any ratio without modifying the conventional combustion engines. Still a regulatory limit of 12.5% was announced in the United States and a 16% blended isobutanol fuel has also been approved by Underwriter Laboratories to be used with no need for any equipment modification . Unlike a full miscibility with water of ethanol, butanol is much less hydroscopic and has only 8.5% water solubility, which means a longer storage time without quality decrease and phase separation resulted from water imbibition and easier transport with existed petrol pipeline. Furthermore, butanol is less corrosive for engine and distribution equipment. Tests for stress corrosion cracking (SCC) and elastomeric compatibility issues have been down by Det Norske Veritas on both ethanol-blended petrol and butanol-blended petrol. It is approved that no SCC was noted for carbon steel in isobutanol-blended petrol at concentration of 12.5% and 50%, nor even with neat isobutanol (Ryan et al. 2011). Besides, a lower enthalpy of evaporation provides a better cold start performance and a lower vapor pressure could be beneficial because of less leakage or emission at storage and refueling. Hence butanol should be more suitable than ethanol to serve as a clean fuel additive or a neat alternative fuel.

Table 1-3: Physical and chemical properties of butanol isomers

$C_4H_{10}O$	1-butanol	2-butanol	isobutanol	tert-butanol
Octane number (RON)	94	106	105	109
Melting point [°C]	-89	-115	-108	26
Boiling point [°C]	118	99	108	83
Vapor pressure (20 °C) [hPa]	6.67	16.5	11.8	41.2
Ignition temperature [°C]	325	390	430	470
Water solubility (20 °C) [g/l]	77	350	85	complete
Possible applications	Solvents, fuels, feedstocks	Feedstocks of chem. industry	Solvents, fuels	Anti-knock agent

Butanol has 4 isomers: n-butanol, 2-butanol, isobutanol and tert-butanol. Several physical and chemical properties of them are given in Table 1.3.

Except tert-butanol, which could be solid under atmosphere conditions and are fully miscible with water, the other three isomers could be directly used as motor fuel. While 2-butanol has a relatively high water solubility, 1-butanol and isobutanol are the 2 most promising and preferred isomers of butanol in the usage of motor fuel. With a relatively higher octane number, tert-butanol could also act as petrol octane booster to improve the anti-knock performance of petrol.

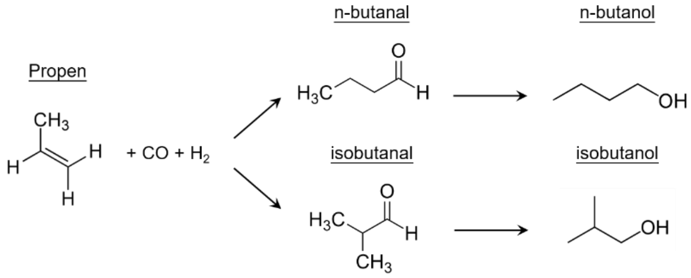
1.4 Objectives

In this thesis, a process design for butanol fuel production using lignocellulosic biomass as feedstocks is to be carried out. The technical and economic feasibilities of butanol fuel production are expected to be studied. Through an extensive literature review, the state of relevant technologies should be identified. Among them the promising options will be selected for the further process design. With sufficient process data from literatures, the designed process will be in detail simulated using the commercial simulation software Aspen Plus®. From simulation results, the productivity of butanol fuel and the efficiencies of the production process are expected to be obtained. Process optimization in terms of process design and energy utilization will be addressed and conducted as well. Based on the simulation results of optimized process, an economic evaluation through the in-house software TEPET of German Aerospace Center (DLR) is to be carried out and the net production costs of the designed process is expected to be calculated. A sensitivity analysis should be carried out to find the influence factors which have significant impact on the net production costs, so that the targets of future development on costs reduction can be identified.

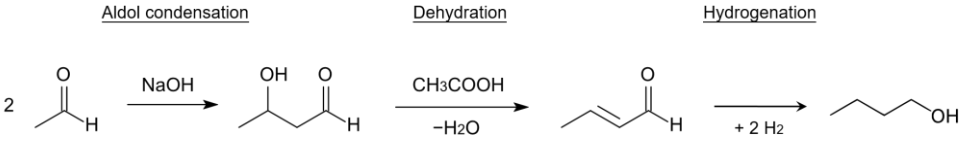
2 Literature review

Currently the most common method to produce butyl alcohol is through hydroformylation reaction (also called oxo process) in petrochemical industry using fossil resources. Propene reacts with hydrogen and carbon monoxide under a temperature from 80 to 200 °C and a pressure from 1.8 MPa to 30 MPa, depending on the employed catalysts in process, to form n-butyraldehyde and isobutyraldehyde, which are further reduced with hydrogen to n-butanol and isobutanol, respectively (Spivey 2014).

Another possible petrochemical production method is through crotonaldehyde hydrogenation. 2 molecules acetaldehyde are put through aldol condensation reaction to form crotonaldehyde, which is then reduced with hydrogen to n-butanol as the only product. Figure 2.1 shows the main chemical reactions of the two petrochemical routes (Spivey 2014).



a) Oxo synthesis



b) Crotonaldehyde hydrogenation

Figure 2-1: Petrochemical routes for butanol production

Petrochemical routes for butanol production use mostly fossil resources like byproducts from petroleum refining as feedstocks, thus it will not be further discussed in this thesis.

2.1 Overview of possible production methods

To produce butanol from renewable resources, the available processes can be categorized mainly as biochemical, thermochemical and photosynthesis routes.

Biochemical route involves the fermentation of feedstocks by specific bacteria. Like ethanol can be produced through fermentation of sugars by yeast, some particular bacteria can also transfer sugars into butanol and other products. Fermentation process was once a commercialized method in industry for butanol production until the Second World War. After that, fermentation method was gradually replaced by petroleum chemical method since the specific raw material cost is cheaper from petroleum and yield of petrochemical methods is higher than fermentation as well (Green 2011).

In thermochemical route the key substance is syngas. Syngas is a gas mixture consisting primarily of hydrogen and carbon monoxide. Considering only renewable feedstocks, syngas can be produced through gasification of biomass or through reverse water-gas-shift reaction using hydrogen and carbon dioxide as reactants, which can be obtained from electrolysis of water with surplus renewable electricity like wind or solar power and industry off gas, respectively. Syngas with required H_2:CO ratio is then through catalytic conversion under high pressure and temperature to be transferred into different fuel products, in this case, into mixed alcohols.

Photosynthesis route involves a direct biocatalytic conversion of CO_2 into chemical products. Genetically engineered microorganisms consume CO_2, water, sunlight and/or electricity and produce desired advanced biofuels. This option is still at an early research stage, the mechanism of biocatalytic pathway in particular microbes should be further studied and the yield is still far away from industrial scale. Hence this route will not in details discussed in this thesis.

Figure 2.2 shows an overview of above mentioned production routes for butanol.

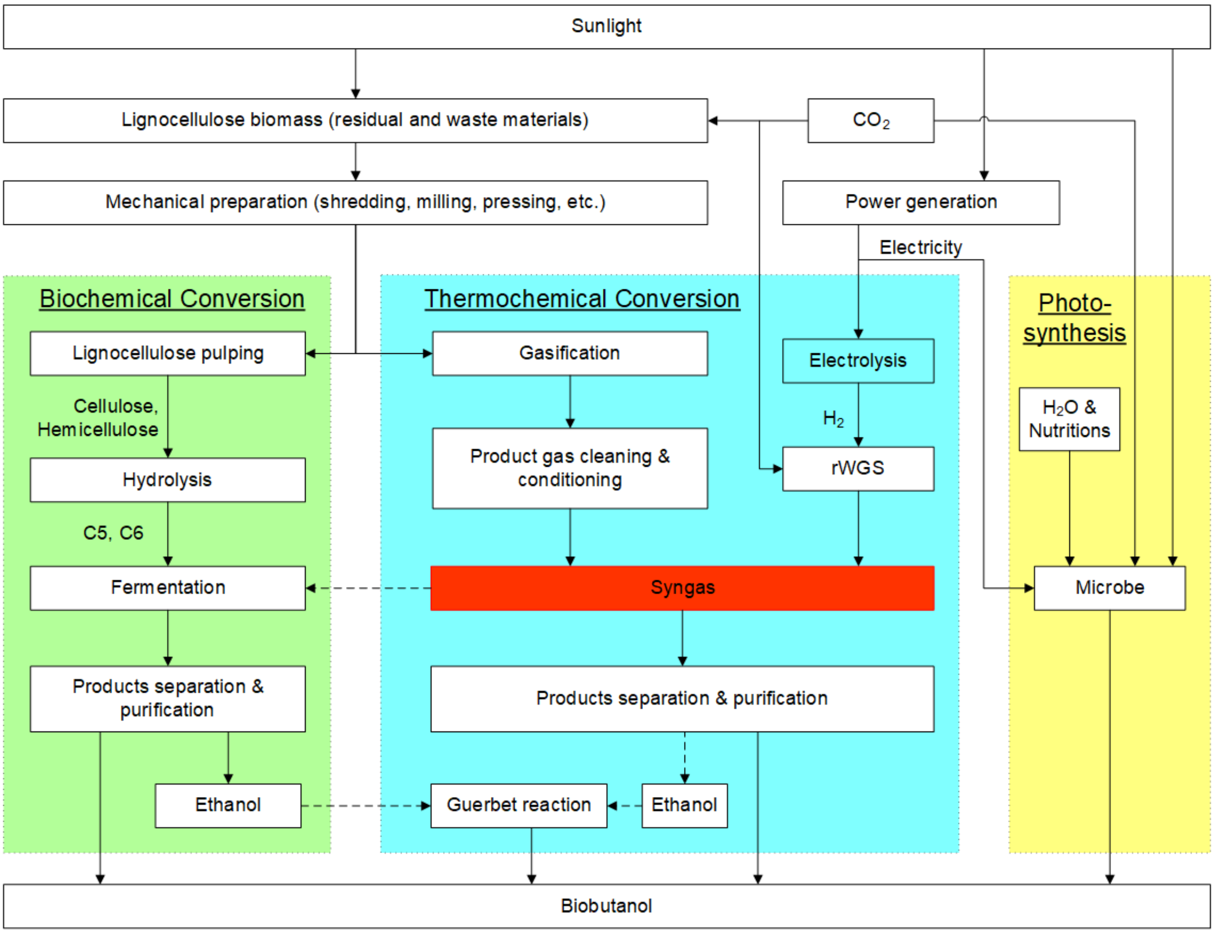


Figure 2-2: Overview of possible butanol production routes from renewable resources

2.2 Biochemical methods

According to the different feedstocks supplied in fermentation process, there are two major biochemical routes for butanol production: alcoholic fermentation and syngas fermentation.

2.2.1 ABE fermentation

Butanol as a natural product of anaerobic bacteria was first discovered in 1862. The Acetone-butanol-ethanol (ABE) fermentation process was then developed in the UK in 1912 by Chaim Weizmann, a biochemist and the first President of Israel. During the First World War ABE fermentation was brought to industrial scale to produce acetone for ammunitions and later to produce butanol for paint lacquers. Until 1950s, about two thirds of the world’s butanol supply derived from fermentation. Due to the increased substrate prices and increased supply of cheap crude oil, butanol production shifted gradually from biological routes to petrochemical routes. The strongly fluctuated oil prices in the last decades and aroused interest in biobutanol as a possible substitution of fossil fuel make fermentation process attractive again for butanol production. Figure 2.3 shows a simplified flowsheet of ABE fermentation.

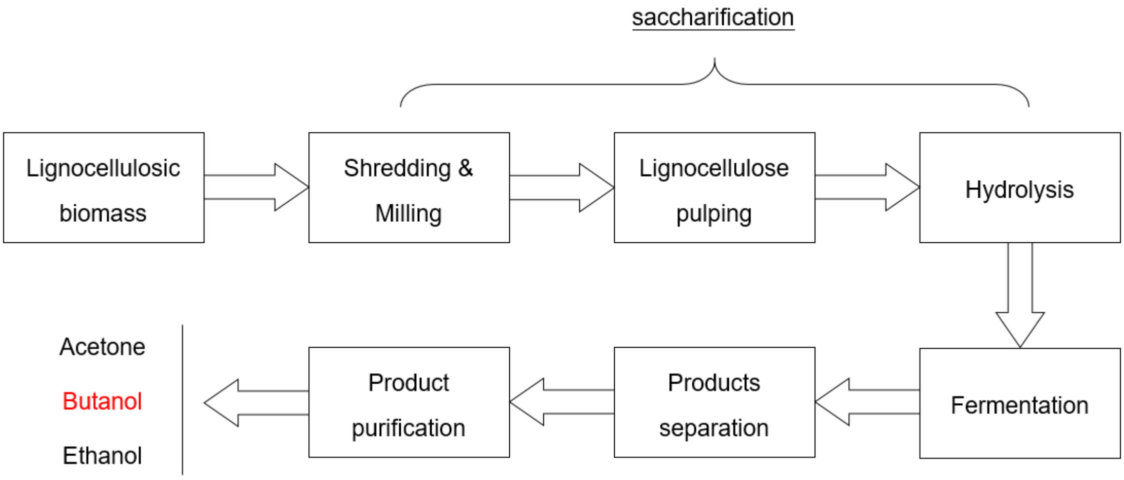


Figure 2-3: Simplified flowsheet of ABE fermentation

Strains of bacteria from the Class Clostridia are usually employed in ABE fermentation. C6 sugars (e.g. glucose) and C5 sugars (e.g. xylose) can be directly fermented under strictly anaerobic condition. A typical products ratio of acetone, butanol and ethanol in the solvent is 3:6:1. It is also reported that using particular species of Clostridia a product mixture with only alcohols (isopropanol, butanol and/or ethanol) was obtained (Qureshi, Ezeji 2008). The developed IBE or IB fermentation process could be dominant taking account of alcohol fuels production.

2.2.1.1 Saccharification of lignocellulosic biomass

Straws and forest residues are lignocellulosic biomass, which cannot be directly fermented by Clostridium. Lignocellulose is composed of cellulose, hemicellulose and lignin. Cellulose and hemicellulose are polysaccharide consisting of different sugar monomers (C6 and C5 sugars), which are then fermentable. Therefore, saccharification of lignocellulose is necessary before fermentation.

In saccharification of lignocellulose the key process is hydrolysis. There are two methods to hydrolyte these carbohydrate polymers: enzymatic hydrolysis and acid catalyzed hydrolysis.

Enzymatic hydrolysis refers to the conversion of cellulose and hemicellulose into sugar monomers by means of enzyme. Because of the resistance resulted from hydrogen bonds between the three components in lignocellulose, a pretreatment process is required, aiming at decomposing the complicated bonds among them by chemicals, mechanical or thermal energy, so that enzymes can quickly and easily hydrolyze the polysaccharides. Table 2.1 gives a brief overview of possible methods of pretreatment (Kaltschmitt et al. 2016).

Table 2-1: Pretreatment methods for enzymatic hydrolysis

Methods	Chemicals	Temperature /°C	remarks
Hot water hydrolysis	Water	160 - 220	Autohydrolysis
Steam explosion	Steam	180 - 220	Autohydrolysis, physical destruction
Acid catalyzed pretreatment	Diluted acid	120 - 160	Suspension with 5-10% solid concentration
Organosolv process	Organic solvent	155 - 205	Liquid phase with dissolved lignin and hemicelluloselime
Alkali pretreatment	Lime Oxidant Ammonia	85 - 150 180 - 200 65 - 90	Ammonia pretreatment requires pressure of 17 to 20 bar

After pretreatment, a group of different enzymes is applied for the different hydrogen and chemical bonds between and inside of those polysaccharides.

In acid catalyzed hydrolysis, lignocellulose is treated either with concentrated acids at atmosphere temperature or with diluted acids at around 200 °C (Kaltschmitt et al. 2016).

Chemical byproducts such as furfural, glucuronic, acetic could be produced in hydrolytic process. These byproducts could inhibit microbe growth and subsequent fermentation process. To enhance butanol production, novel bacterial strains with higher tolerance or methods to reduce harmful byproducts should be further developed.

2.2.1.2 Fermentation through bacteria and development

A normal butanol fermentation process can be considered in two phases. In the acid fermentation phase bacteria grow exponential and convert substrate into acetic and butyric acids. In the solvent fermentation phase substrate and acids are converted into solvents (ABE). CO_2, hydrogen and small amount of lactic and propionic acid are also produced during fermentation. The most common strains employed for butanol production are Clostridium acetobutylicum and Clostridium beijerinckii. However, high toxicity and inhibition of butanol to microorganisms limit its concentration in fermentation broth, since fermentation is normally batch process, yields of butanol are traditionally limited up to 20 g/L. Figure 2.4 shows a simplified typical metabolic pathway of Clostridium to produce ABE (Ezeji et al. 2007).

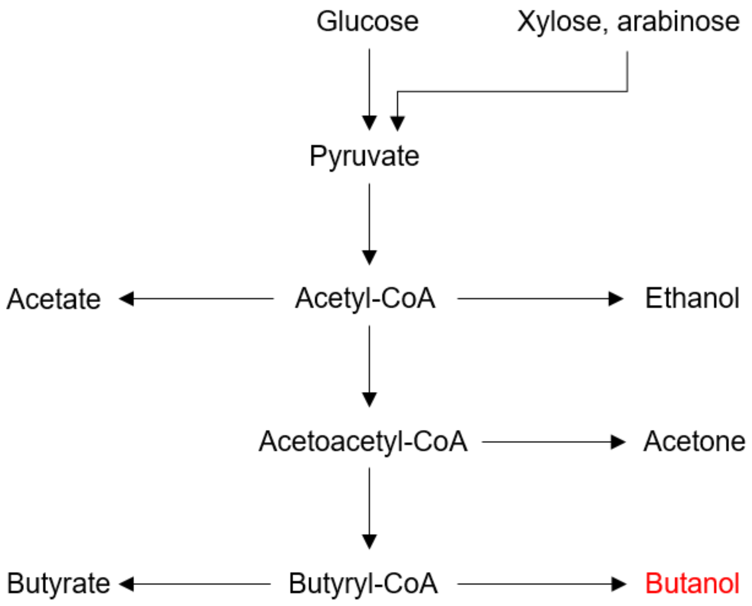


Figure 2-4: Simplified metabolic pathway of Clostridium for ABE solvents production

Therefore, strains which can utilize a wide range of carbon sources, are more tolerant to butanol and achieve higher butanol titer are desired. A better understanding of genes which affect the microbial metabolism makes it possible to improve butanol production by genetically modifying strains. Effort on genetic technology has been done through insertion of heterogenetic genes or knocking out relative endogenous genes of Clostridium and yeast. Gevo has successfully employed genetically modified yeast to produce isobutanol and achieved an annual production of 440,000 gallons (around 1.67 mio. liters) in 2016 (Gevo 2016). Modifications in the strains can also focus on breaking the pathway in which unwanted products are synthesized so that single butanol product could be obtained or changing the pathway for formation of acetate and butyrate (Durre 2011). Table 2.2 summarized some strains applied for biobutanol production, in which residual and waste materials are used as feedstocks (Visioli et al. 2014).

Table 2-2: Microorganism, substrate and yield reported for butanol production

Microorganism	Substrate	Productivity	Technology
C. acetobutylicum	Cassava Bagasse	76.4 g/l of butanol	Enzymatic hydrolysis, gas stripping
C. acetobutylicum NCIM 2337	Rice straw	13.5 g/l of butanol	Acid treatment
C. beijerinckii P260	Barley straw	26.64 g/l ABE	Dilute sulfuric acid hydrolysis
C. saccharoperbuty-lacetonicum N1-4	Rice straw	6.6 g/l butanol	Enzymatic hydrolysis

Improved fermentation technology benefits biobutanol production as well. Bioreactors can be operated in batch, fed-batch or continuous modes. Batch process is approved for years in industry and traditionally is applied for fermentation. It has certainly advantages such as lower investment costs, more flexible, easily control, higher possible conversion rate and lower infection risk. Still about 20% operating time is unproductive during “charging”, “discharging” and sterilization phases (Kaltschmitt et al. 2016). In fed-batch fermentation not all substrates are fed at the process beginning. A base concentration of medium is firstly fed to maintain initial cell culture. When it consumes the substrate, more substrate is gradually fed to maintain the fermentation process. Feed rate is controlled to keep the substrate concentration at a proper level to prevent depletion or exceeding the inhibitive substrate concentration. Due to a higher complexity of components continuous fermentation is only worthwhile for large-scale plant. Fresh substrate and fermented substrate are fed and lead away at the same time, respectively, pursuing a quasi-stationary state during the whole process. Continuous process shows advantages such as longer productive time, higher volume-specific productivity, constant product quality if operation condition is maintained. Still it is less flexible, has higher product recovery costs due to low concentration of butanol and the substrate quality must stay constant as well.

2.2.1.3 Separation technologies

Due to the high toxicity of butanol to microorganism, a simultaneous removal of fermentation products is necessary. As is seen from Table 2.2, butanol yield can be effectively increased when using advanced separation methods (Kujawska et al. 2015).

Traditionally the fermentation products are recovered by distillation, that is one of the most widely used process in chemical industry for products separation or purification. A special physical property of butanol-water mixture is formation of heteroazeotrope in distillation. Butanol is enriched preferred in the vapor phase. After condensation of vapor a two-phase liquid mixture is formed, in which one phase contains about 80 wt.-% butanol and the water phase has only around 7 wt.-% butanol. Taking advantage of this property a considerably simple two-column system can be applied and a good separation performance in combination with further water stripper is achieved. Still the energy demand is approximately 2.5 times as the energy content of recovered butanol (Kujawska et al. 2015). Most of the energy consumption by distillation is from the evaporation of water which accounts for the majority in the feed. Conventional distillation process could be further improved but novel separation methods should also be developed to reduce the energy consumption as well as the production costs.

Several techniques have been investigated and are possible to be used for butanol recovery: adsorption, gas stripping, liquid-liquid extraction, membrane distillation, perstraction, pervaporation and reverse osmosis. A brief introduction and some relevant features of abovementioned technologies are summarized in Table 2.3 (Kujawska et al. 2015).

Table 2-3: Products recovery methods for ABE fermentation

Methods	Features
Adsorption	High selectivity to n-butanol, difficult desorption
Gas stripping	Selective removal of volatile components, cost-efficient
Liquid-liquid extraction	High capacity and selectivity for n- butanol/water
Membrane distillation	Applying hydrophobic membrane, based on vapor/liquid equilibrium
Perstraction	Membrane extraction

Pervaporation	Separation of binary or multicomponent liquid mixtures
Reverse osmosis	Membrane based technology commonly applied in desalination of water

In combination with proper hydrolysis methods, fermentation technology and separation methods, the productivity and yield of butanol could be enhanced. More efforts should be made for optimization of operating conditions for each unit process and to commercialize the improved technology.

2.2.2 Syngas fermentation

Another possible carbon source for fermentation is syngas. For lignocellulosic biomass is difficult to be degraded into fermentable sugars and inhibitors to enzymes and microorganisms could be produced as byproducts during the hydrolysis process, gasification of lignocellulose into syngas is a considerable solution, since microorganisms that convert syngas to desired organic products are available as well. A typical metabolic pathway called reductive acetyl-CoA pathway from mesophilic or thermophilic bacteria can be used for butanol production through syngas fermentation (Henstra et al. 2007).

Several usually applied microorganisms reported to have butanol generation are listed in Table 2.4 together with their products and operating conditions (Henstra et al. 2007).

Table 2-4: Possible microorganisms and their products from syngas fermentation

Microorganism	Temp. in °C	pH	Products
Clostridium carboxidivorans	38	6,2	Acetate, ethanol, butyrate, butanol
Butyribacterium methylotrophicum	37	6	Acetate, ethanol, butyrate, butanol

Syngas fermentation is combination of a thermochemical and a biochemical biomass conversion. Figure 2.5 describes a simplified typical production concept from syngas fermentation (Kaltschmitt et al. 2016).

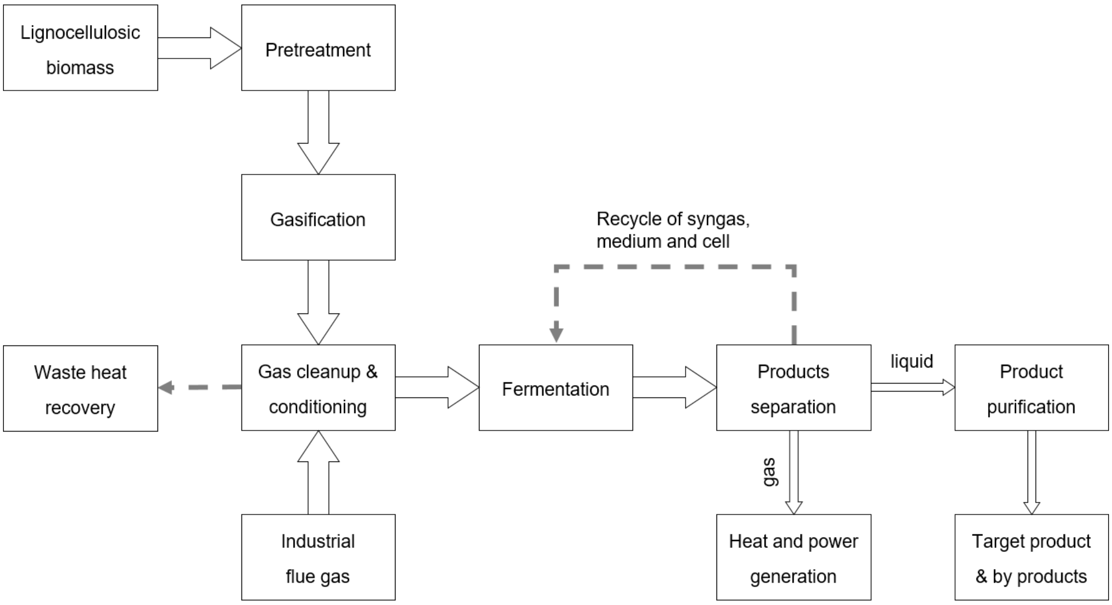


Figure 2-5: Simplified process diagram of syngas fermentation

Through gasification lignocellulosic biomass is converted into valuable syngas with a very high carbon conversion efficiency up to 99% (Kumar et al. 2009). Still a following gas cleanup is necessary but the microorganisms for syngas fermentation have relatively higher tolerance against contamination such as tar, sulfur or chlorine compared to chemical catalysts, which means less costly gas cleanup methods can be employed. However, conversion rates are generally limited by gas-liquid mass transfer, which resulted in lower productivity. Using of increased pressure, solvents with higher gas solubility or continuous stirred tank reactors (CSTR) provide possible solutions. Separation of products is then similar to ABE fermentation (Kumar et al. 2009). Not fermented syngas can be recycled to improve the total products yield. It is worth mentioning that an ethanol production process which combines gasification of biologic waste, syngas fermentation and distillation are already commercialized.

2.3 Thermochemical methods

Thermochemical methods mainly refer to chemically catalytic conversion of feedstocks to desired products. For biobutanol production is usually a catalytic conversion of syngas to mixed alcohols that is called higher alcohol synthesis or mixed alcohol synthesis. Besides, there are possibilities to produce butanol or higher alcohols via condensation or homologation of lower alcohols.

2.3.1 Alcohol synthesis

Direct alcohol synthesis especially synthesis of isobutanol and methanol from syngas has been considered promising to be applied in the production of methyl tert-butyl ether (MTBE) (Spivey 2014), a petrol addictive used to improve the octane number, and has been intensively studied since the 1980s. However, due to its possible contamination to groundwater and toxicity for humans, MTBE has been already phased out as fuel addictive in U.S. Currently with the increased interest in alcohols especially butanol as fuel addictive or neat fuel, higher alcohol synthesis has become the most attractive thermochemical route as an alternative to traditional alcohol fermentation. A process flowsheet including the production of syngas and synthesis of alcohols is given in Figure 2.6.

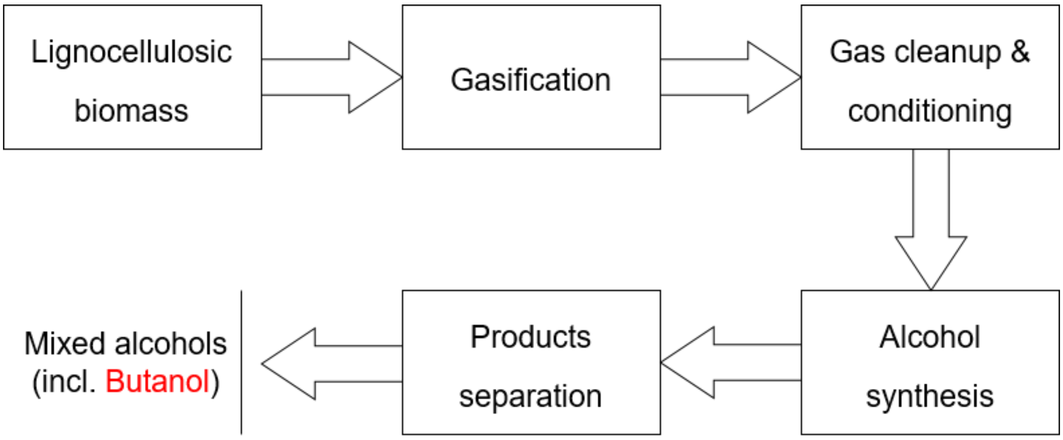


Figure 2-6: Simplified process flowsheet of alcohol synthesis

Gasification is a widely-used technology in industry to produce syngas, which will be further used to generate electricity and heat or to produce transport fuels and chemicals. Raw gas after gasification must be cleaned up to prevent catalyst poisoning. The H_2:CO ratio in syngas affects the conversion rate and products selectivity as well, hence this ratio should be adjusted specifically for desired alcohol product before syngas flows into the synthesis reactor (Herman 2000). Synthesis reactions are operated typically under a pressure from 30 to 300 bar and at a moderate temperature up to 440 °C (Kaltschmitt et al. 2016). Because the alcohol synthesis reactions are strongly exothermic, an effective heat removal and temperature control is important for reactor design. After proper separation, the desired products with required purity can be obtained.

2.3.1.1 Gasification technologies

Gasification is a substoichiometric oxidation process to produce combustible gas products, which can be further utilized. A most general gasification reaction combines all possible reactions in gasification process and without considering stoichiometry can be written as in Equation 2.1 (Kaltschmitt et al. 2016).

$$\begin{aligned} C_xH_yO_z(\text{biomass}) + O_2(21\%\ \ in\ \ air) + H_2O(steam) + CO_2 \\ \rightarrow CH_4 + CO + CO_2 + H_2 + H_2O(rest\ \ steam) + C(coke) + tar \end{aligned} \tag*{2.1)}$$

Using different gasification agents (O_2, H_2O, CO_2) can obtain different product gas composition. Considering the heat demand in the process, gasification can also be classified into autothermal and allothermal gasification. The former means the required heat for the endothermal gasification is supplied via partially combustion of feedstocks while the latter via external heat source.

In general, there are 3 different types of gasifier: fixed bed, fluidized bed and entrained flow gasifier. By far biomass is commercially used rather in small to medium scale plant, thus fluidized and fixed bed gasifiers are usually preferred for biomass gasification. Entrained flow gasifier for biomass is in the research stage and has been successfully applied in the pilot plant. Table 2.5 compares the relevant features of those three gasifiers (Kaltschmitt et al. 2016).

Table 2-5: Comparison between 3 different types of gasifier

Type of gasifier	Fixed bed		Fluidized bed		Entrained flow
	Co-current	Counter	Steady	Circulating	
Input energy content	< 2 MW	100 kW – 10 MW	Some MW to 50 MW	10 – 100 MW	Only for large plant
Particle size In mm	High requirements on lumpiness	20 -200	1 - 70	1 – 50	Dust or pasty form
Flow rate	low		Relatively low	High, bed materials can be discharging	high

Residence time	> 10^3 s		10^2 – 10^3 s		Till few seconds
Water content of input material	< 20%	to 60%	< 50%		n.a.
Temp. of major reaction	> 1000 °C	to 1100 °C	700 – 900 °C		1200 – 2000 °C
Methane content	n.a.	n.a.	Relatively high (9-11 Vol.%)		Low (<1%)
Tar content in g/m^3	0.1 - 6	10 - 150	1 - 23	2 - 30	< 0.1
Particle content in g/m^3	01 - 8	0.1 - 3	1 - 100	8 - 100	< 0.05
Scale-up	good	bad	Very good	Very good	good

Co-current flow fixed bed gasifier can only be applied up to 2 MW thermal output due to the technical limitations, which gives no chance considering the scale of economy for the fuel production in the future. Counter-current flow fixed bed gasifier can be employed up to medium-scale plant and has broad feedstocks spectrum, however the raw gas from it contains much higher tar, which causes problems in the further usage in turbine, gas motor or catalytic synthesis. Hence, a considerable cost-intensive gas cleanup step is inevitable. The relatively long residence time of feedstocks limits the productivity of raw gas as well.

Fluidized bed gasifier operates at relatively moderate temperature but it carries higher amount of particle out and a tar removal step is still needed. Besides the content of methane in raw gas is very high, which is an unwished component for further products synthesis.

Due to the high investment cost of entrained flow gasifier, it is generally considered only feasible for large-scale plant. As the operation temperature is very high (up to 2000 °C), it is possible to produce almost tar-free raw gas which has very low content of methane as well. A short residence time up to just few seconds and possible operation under high pressure allows it to achieve a high productivity with small specific gasifier volume at the same time. However, feedstocks must be pretreated to have extremely fine particle size or to become slurry phase. Torrefaction or pyrolysis methods can be used for biomass pretreatment. Alexander T. and his colleagues compare the performance of entrained flow and fluidized bed biomass gasifiers on different scales (10 MW, 50 MW, 100 MW and 500 MW) based on simulation works (Tremel et al. 2013). With economic evaluation on both gasifiers it points out that entrained flow gasifier could be competitive for biomass gasification on a smaller scale as well but a larger gasifier throughput is favorable considering specific investment costs.

Several pilot plants have been built to demonstrate biofuel production through biomass gasification in Germany. The bioliq® gasification concept includes a regional fast pyrolysis of lignocellulosic biomass, in that an energy-dense bioslurry suitable for economic transport over long distance is produced, and a central pressurized entrained flow gasification of bioslurry, which is operated at >1200 °C and up to 80 bar and uses oxygen as gasification agent (Dahmen et al. 2012).

The Carbo-V® gasification is a two-stage process. In the first stage a fixed bed gasifier is employed and operated at around 450 °C to produce pyrolysis gas and bio coke. In the second stage a fluidized bed gasifier is applied to gasify the produced bio coke at high temperature from 1000 to 1400 °C. Pyrolysis gas is combusted to supply the required heat for the endothermic high temperature gasification in the second stage (the Linde Group. 2014).

Tar-free and methane-lean raw gas can be obtained from the both gasification concepts. According to a manufacturing cost estimation for biofuel from bioliq® process, biomass feedstocks and transport costs amount to about half of the costs. Investment costs for flash pyrolysis, gasification and FT synthesis amount to around 34% (Dahmen et al. 2012).

2.3.1.2 Possible catalysts and development

Catalytic synthesis of alcohols can be seen as a catalytic hydrogenation of CO. Equation 2.2 describes the general formation reaction of alcohols with n carbon atoms from syngas (Kaltschmitt et al. 2016).

$$\mathrm{nCO} + 2\mathrm{n}H_2 \leftrightarrow C_nH_{2n+1}OH + (n-1)H_2O \qquad 2.2)$$

Formation of C_{2+} alcohols and oxygenates from syngas is carried out through the formation of methanol and subsequent chain growth via insertion of CO (Spivey 2014). However, the yield of higher alcohols is usually low due to the limited chain growth. Suitable catalysts with proper promoters and supports should be specifically developed to improve the activity and selectivity towards desired products.

According to Equation 2.2, the optimal H_2:CO ratio in feed gas seems to be 2. Together with alcohol formation several side reactions such as water gas shift (WGS) reaction and methanation reaction could be active as well. Combining the WGS reaction, Equation 2.2 can be rewritten as Equation 2.3. For butanol synthesis, H_2:CO ratio could be 0.714 if applied catalyst is active for WGS reaction (Verkerk et al. 1999).

$$(2n-1)CO+(n+1)H_2 \leftrightarrow C_nH_{2n+1}OH+(n-1)CO_2 \qquad 2.3)$$

Generally, HAS catalysts can be classified into four categories: modified methanol synthesis, modified Fischer-Tropsch synthesis, Molybdenum-based and Rhodium-based catalysts (Luk et al. 2017). To evaluate the performance of applied catalysts, several terms should be defined before a further discussion. Productivity means the amount of produced product per unit time for a certain weight of catalyst loaded. Its unit is typically “g product/kg catalyst/h”. It can be used either for all alcohol products or for a specific alcohol. Sometimes it can be called Yield as well. CO-conversion indicates the amount of CO converted to all products in a single-pass. It is usually calculated by $(CO_{initial}-CO_{final})/CO_{initial}$ on a molar basis (Dutta, Phillips 2009). Sometimes conversions will be presented exclusive of produced CO_2. Selectivity refers to the fraction of CO converted to a specific product on a molar basis. It’s usually presented on a CO_2-exlusive basis in the literatures.

Modified methanol catalysts are obtained with the addition of an alkali promoter and other active elements to methanol catalysts, so that products distribution can be shifted from methanol to higher alcohols. It is found that higher alcohol yields increase with increasing alkali atomic size, in the order Li<Na<K<Rb<Cs. Branched alcohols are thermochemically preferred than their linear isomers, especially isobutanol shows a relatively high selectivity compared with other catalyst groups (Spivey 2014). Ho et al. reviewed all four catalyst groups and summarized the data for conversion, selectivity, yields and reaction conditions etc. They rank the modified FTS catalysts as the best according to the C_{2+} oxygenates yield. Still modified FTS catalysts have relatively high hydrocarbon selectivity and can be very active in the WGS reaction, which leads to a relatively high CO_2 selectivity (10-30%) as well (Luk et al. 2017). The Dow Chemical Company patented a catalyst of molybdenum disulfide doped with alkali and transition metals for HAS. The National Renewable Energy Laboratory in U.S. cooperated with Dow on the improvement of this catalyst to produce ethanol from lignocellulosic biomass through thermochemical route and has built a pilot-scale demonstration plant to validate a

conceptual commercial-scale cellulosic ethanol refinery (Bain et al. 2014). Besides, MoS_2-based catalysts show a unique advantage of higher tolerance to sulfur in syngas. Rh-based catalysts are found highly selective to higher alcohols but its activity is limited, leading to a relatively lower conversion. Some reported data of butanol production from HAS are given in Table 2.6 (Beretta et al. 1996; Burcham et al. 1998; Hoflund et al. 1999).

Table 2-6: Butanol synthesis from HAS

	1	2	3
Catalysts	$Cs/Cu/ZnO/Cr_2O_3$	$Cs/Cu/ZnO/Cr_2O_3$	K/Pd-Zn/Cr/Mn
Temperature in K	598 678	598 613	713
Pressure in MPa	7.6	7.6	10.34
H_2:CO ratio	0.75	0.75	1
Yield in g/kg/h	138.8	202.0	179.0
CO-conversion in %	6.6 (CO_2-free)	8.5 (CO_2-free)	28 (total)

In general, HAS catalysts share some similar problems. A high selectivity to butanol and a high CO-conversion are scarcely to achieve at the same time. Reaction conditions play an important role as well. Beretta et al. developed a double bed synthesis reactor to improve the isobutanol yields. Two beds are operated at different temperature, basing on that lower temperatures in the first bed result in higher methanol selectivity and with increased temperatures in the second bed an enhanced formation of isobutanol is obtained.

Researchers have considered to use a slurry reactor stead of fixed bed reactor, yet significant enhancement on butanol synthesis has not been obtained. However, the advantages of slurry technology such as excellent heat removal, continuous operation on catalyst exchange, better interparticle mass transfer performance due to usage of smaller catalyst particles, makes it still promising. It is tested as well, that recycling of not reacted syngas or injection of lower alcohols into reactor could enhance the higher alcohol yields (Herman 2000).

2.3.2 Guerbet reaction

Another promising method to produce butanol is the direct condensation of lower alcohols to higher alcohols through Guerbet reaction. Equation 2.4 and 2.5 shows the two possible condensation routes from lower alcohols to butanol (Spivey 2014).

$$2C_2H_5O \rightarrow C_4H_9OH + H_2O \quad 2.4)$$

$$\mathrm{MeOH + EtOH \rightarrow n - PrOH} + H_2O \quad 2.5)\ a$$

$$\mathrm{MeOH + n - PrOH \rightarrow i - BuOH} + H_2O \quad 2.5)\ b$$

Promoted zeolites, hydroxyapatites and mixed metal oxide catalysts are usually employed for Guerbet reaction, with different activity and selectivity. Yield of butanol was still lower than 30%. Recent years researchers have tested several different homogeneous catalysts and obtained better results. Table 2.7 gives some examples of experiments data from recent studies (Tseng et al. 2016; Chakraborty et al. 2015; Dowson et al. 2013).

Table 2-7: Reported results on ethanol upgrading to butanol through Guerbet reaction

Catalysts	Conversion in %	Selectivity in %	Yield in %
Rutheniumbis(diphenylphosphanyl)methane	> 20	till 94	> 18.8
N,N,N,-Ru(II) complex	till 50	relatively high	till 38
Bifunctional iridium catalysts with nickel or copper hydroxides	37	> 99	34
	32	> 99	28

Because of the difficulty on chain growth in alcohol synthesis, its product contains usually more lower alcohols. Therefore, Guerbet reaction can be a considerable option to transfer produced lower alcohols from alcohol synthesis further to desired higher alcohols, so that the total yields of higher alcohols can be enhanced.

Furthermore, Equation 2.6 to 2.8 describes a homologation reaction of lower alcohols to promote higher alcohol formation (Spivey 2014).

$$C_nH_{2n+1} + CO + 2H_2 \leftrightarrow CH_3(CH_2)_nOH + H_2O \qquad 2.6)$$

$$CH_3OH + nCO + 2nH_2 \leftrightarrow C_nH_{2n+3}OH + nH_2O \qquad 2.7)$$

$$C_2H_5OH + nCO + 2nH_2 \leftrightarrow C_{n+2}H_{2n+5}OH + nH_2O \qquad 2.8)$$

According to this mechanism, it is possible to improve the higher alcohol production through injection of lower alcohols such as methanol, ethanol or propanol in the alcohol synthesis from syngas. It is reported that yields of C_{3+} products are significant enhanced through injection of C_1 and C_2 alcohols and the same effect is obtained for the yields of C_{4+} products if C_1 and C_3 alcohols are injected. (Spivey 2014)

2.4 Comparison between biochemical and thermochemical routes

ABE fermentation process was once commercialized and the main production route for n-butanol in industry. Due to the price decrease of crude oil, it was not competitive with petroleum route anymore and gradually phased out. With the increasing requirement on environment protection and the possible usage of butanol as transport fuel or fuel additive, ABE fermentation became attractive again. After years of development, the biochemical process remains still some drawbacks such as lower reaction rate, limited yield of butanol production and much energy intensive subsequent product separation process. Further research of gene technology and metabolic engineering on Clostridia or yeast and innovative separation technology should be studied and applied to pursue a commercialized production in the future. As an alternative, thermochemical routes present some promising features such as a broad feedstock spectrum, higher reaction rate and less costly product separation. Still the low selectivity to desired products requires significant advancement on catalysts research and optimization of reaction conditions. Table 2.8 compares these two routes taking into consideration of several relevant factors.

Table 2-8: Comparison between biochemical and thermochemical routes

	Biochemical routes	Thermochemical routes

Feedstock spectrum	Relatively small	Large, integration of renewable electricity possible
Feedstock pretreatment	Costly for lignocellulose	No specific pretreatment
Operation conditions	Room temperature and pressure, but strictly anaerobic for fermentation	High temperature and pressure
Reaction rate	Slow, commonly batch process	High
Conversion	High	Relatively low
selectivity	High, to 90% possible	Low
Product separation	Energy intensive and costly	relatively less costly

Butanol production through biochemical methods has been intensively studied in the recent years. Detailed process design for production of second-generation biobutanol through promising thermochemical route has not yet been presented that much. Thus, this thesis is going to focus on the production process design based on a thermochemical method and trying to analysis the potential of biobutanol production via thermochemical route by means of techno-economic evaluation.

3 Process description and simulation

Process simulation helps to analysis, develop or optimize a technical process or system before actually constructing or modifying the process. In this thesis, a detailed design of butanol production process via thermochemical route using lignocellulosic biomass as feedstock is accomplished and simulated through the commercial simulation software Aspen Plus® V8.2. The required process data are mostly from relevant literatures and studies. Through the simulation, following results are expected to be obtained:

- the yield of butanol product and possible byproducts and
- the overall efficiency and the carbon efficiency of this process.

Besides, the potential of a further optimization by means of heat integration and improved process design will be addressed as well. Simulation results are then used to complete the techno-economic evaluation through the in-house software TEPET.

3.1 Overview of the production process

Because of the existence of all three phases of matter (solid, liquid and gas) and both conventional and unconventional components (biomass, bioslurry and ash) in the system, no single property method in Aspen Plus is sufficient for the whole process. For steam cycle, cooling water system and the units, in that only water exits, IAPWS-95 steam table is recommended by Aspen Plus, as it is the current standard for properties of water and steam. For alcohol separation and quench system in biomass gasification, the non-random two-liquid (NRTL) activity coefficient model with the Redlich-Kwong equation of state for vapor phase is chosen, as it can handle any combination of polar and non-polar compounds up to strong nonideality. The Peng Robinson cubic equation of state with the Boston-Mathias alpha function (PR-BM) is used for the rest units in the process simulation, as it is recommended for applications such as gas processing, refinery and petrochemical processes (Okoli, Adams 2014).

Figure 3.1 presents the simplified process flow diagram with the key processing units.

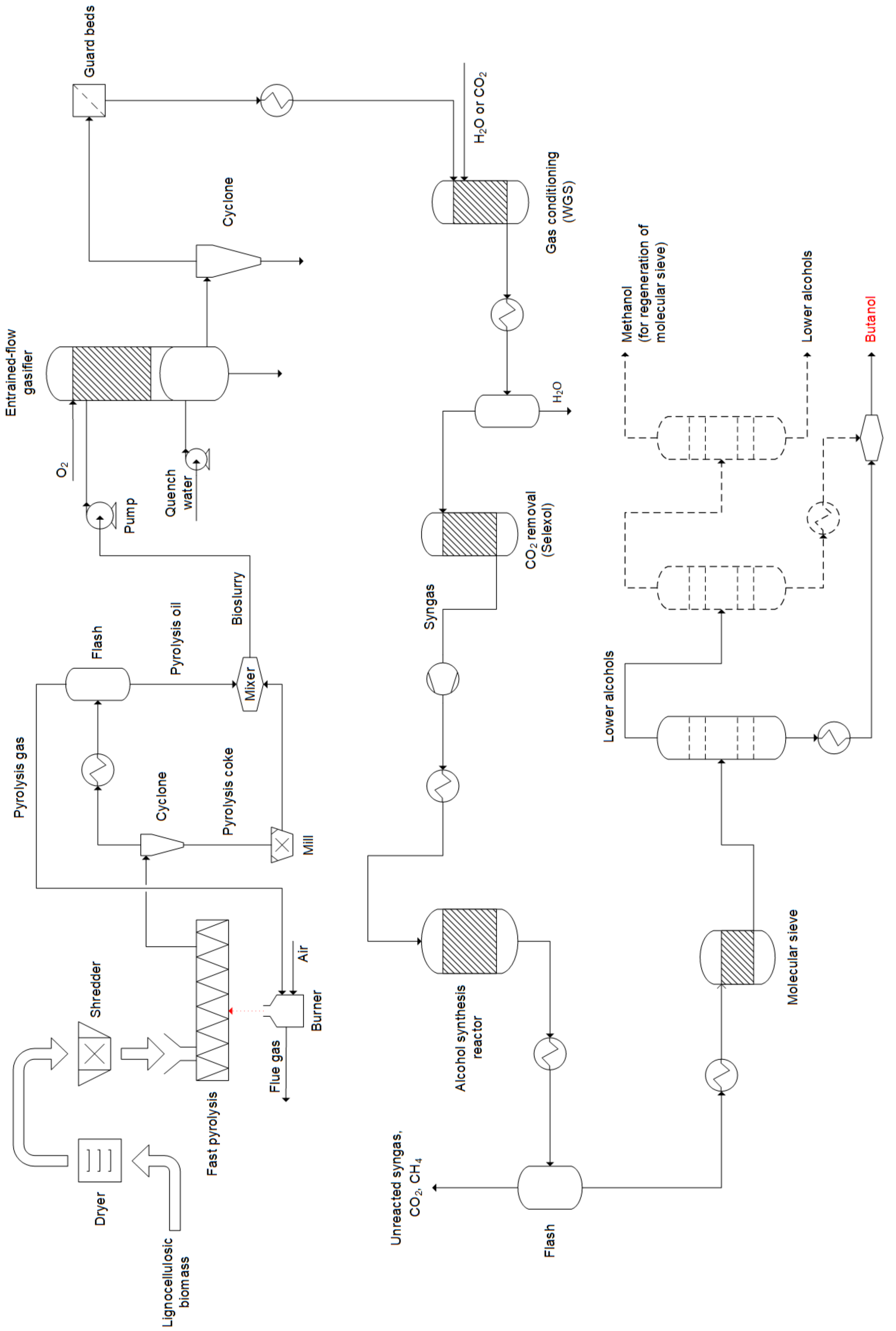


Figure 3-1: Simplified process flow diagram for biobutanol production

The production process can be generally considered in 3 main steps. The first step is the production of syngas. From forest or farmland collected lignocellulosic biomass such as straws or forest residues usually contains relatively high amount of moisture, thus the biomass should be firstly dried before it is grinded into small particles, as the energy required for particle size diminution is reduced at lower moisture. In this case,

the biomass is dried to a 10 wt.% moisture. The grinded dry biomass is converted into pyrolysis gas, biooil and biochar through a fast pyrolysis process at atmosphere pressure and at temperature of around 500 °C. The heat required for fast pyrolysis is supplied by combustion of produced pyrolysis gas. Biooil and biochar powder will be mixed to generate a dense slurry, that is subsequently gasified in an entrained flow gasifier at 1200 °C using oxygen as gasification agent. Due to the very high temperature in gasification, almost tar-free raw gas can be produced. Other contaminations such as tiny particles, sulfur and nitrogen components in raw gas after gasification must be removed to prevent the catalysts poisoning. The desired H_2:CO ratio can be conditioned through WGS reaction. CO_2 should be removed from raw gas as well. The second step is the catalytically synthesis of alcohols. The cleaned syngas is compressed to ca. 70 bar and converted into mixed alcohols and other byproducts in the synthesis reactor at 440 °C (Hoflund et al. 1999). The last step is products separation. Gas mixture from synthesis reactor will be cooled down, so that the alcohols and water can be condensed, while the not reacted syngas and other low hydrocarbon stay in gas phase. Alcohol-water mixture is dried with a molecular sieve, which could be possible to reduce the energy demand in the distillation process. After distillation, the desired alcohol product that contains mainly butanol is obtained. Further purification of butanol can be carried out depending on the different applications.

3.2 Feed handling and preparation

The capacity of biomass to butanol plant depends on the available biomass potential in the region where the plant is constructed. Considering an increased transport costs with increasing distance, it is assumed that lignocellulosic biomass is collected in a radius of r=50 km around the plant (Albrecht et al. 2017). The total available biomass potential of straws and forest residues per unit area is derived from a simplified calculation, which considers the percentage of land utilization in forestry and agriculture in Germany and the typical specific mass yields of those biomass. The amount of available lignocellulosic biomass can be estimated as 300.61

t/km^2 per year. (Fachagentur Nachwachsende Rohstoffe e.V.)The usage of biomass for liquid fuel production in 2014 amount to ca. 17.8% of the total used biomass, according to a prediction for 2020/2030, this percentage stays in a range from 12.8% to 18.4% (Kaltschmitt et al. 2016). Hence it makes sense to assume that 15% of the total available lignocellulosic biomass in the circle can be used for the butanol production. Giving a reasonable yearly full load hours of 8260 h, the mass flow of input biomass is around 42874 kg/h.

According to the element analysis of different lignocellulose, the elementary C, H, O composition in dry, ash- and heteroatom-free basis among them are quite similar and can be represented in a chemical formula with integer atom number as $C_6H_9O_4$ (Dahmen et al. 2012). The relevant property analysis is shown in Table 3.1 (Kaltschmitt et al. 2016).

Table 3-1: Property analysis of lignocellulosic biomass

Components	Content (wt.%, in dry basis)	Components	Content (wt.%, in dry basis)
Carbon	46.87	Fixed carbon	17.6
Hydrogen	5.90	Volatile mass	76.8
Oxygen	41.63	Ash	5.6
Ash	5.6	Total	100
Total	100	Lower heating value	18.03 MJ/kg

It is assumed that the collected fresh lignocellulosic biomass contains an average moisture of 25 wt.% and should be dried to 10 wt. % moisture content. With a moisture below ca. 15 wt.% the lignocellulosic biomass can be stored without biological degradation. Through a sensitivity analysis from Philipps et al. it is pointed out that drying to a very low moisture content of biomass don’t increase the products yield correspondingly. Therefore, drying the biomass to 10 wt.% moisture is a conservative but sufficient choice (Okoli, Adams 2014).

In Aspen Plus, biomass is treated as an unconventional component. Coal enthalpy model (HCOALGEN) and coal density model (DCOALIGT) are chosen for property models of biomass. Required component attribute data to define biomass are from Table 3.1.

The biomass is dried using flue gas from the pyrolysis process and the power generation section, where the purge gas is combusted to produce steam for steam cycle. Biomass is preheated to 105 °C at the same time as well. The temperature of flue gas from power generation section is determined through a Design-Spec module in Aspen Plus so that the required heat duty for biomass drying can be met. Exhaust gas from dryer is further used to preheat the air for the combustion of pyrolysis gas.

To simulate the drying process in Aspen Plus, a stoichiometric reactor and a two-outlet flash are selected. A calculator block is used to compute the water amount that should be removed from wet biomass during drying. The calculated total heat duty for biomass drying is 6966 kW. After drying the mass flow of biomass is reduced to 35728.3 kg/h. Dried lignocellulosic biomass is grinded into small particles in the size of < 3 mm (Dahmen et al. 2012). The grinding process is not simulated in Aspen Plus and is only considered in the techno-economic evaluation.

3.3 Biomass gasification

To avoid the contamination or poisoning of catalysts used in the fuel synthesis process, the requirements on raw gas cleanup are extremely high compared with other utilization of product gas from gasification. Entrained flow gasifier can produce raw gas with the least contamination among the three types of gasifier. Besides, the energy input of biomass is around 161 MW and the entrained flow gasifier is especially suitable for large-scale plants. Although it requires more complex biomass pretreatment, entrained flow gasifier could still be a beneficial choice considering the less costly raw gas cleanup and the scale of economy.

Gasification process with entrained flow gasifier can be generally divided into two parts. A fast pyrolysis process in which a slurry phase mixture is produced and a gasification process in which the produced slurry is converted into product gas. A detailed flow diagram is presented in Figure 3.2.

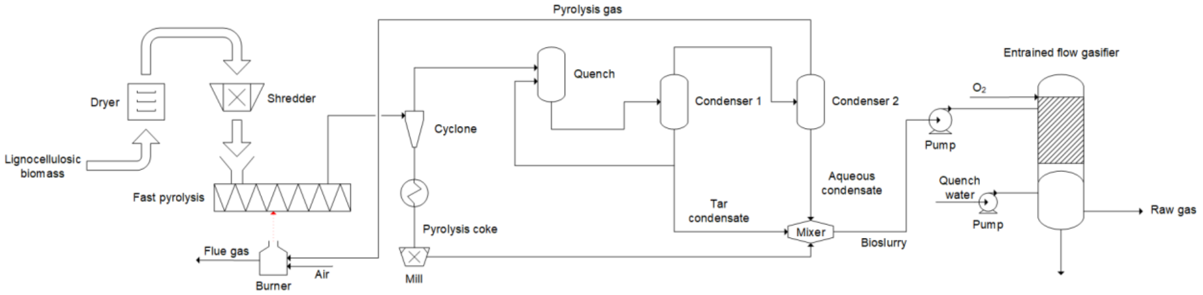


Figure 3-2: Detailed biomass gasification flow diagram with entrained flow gasifier

Dried, grinded biomass particles are mixed with an excess of a hot, grainy heat carrier such as sand or stainless steel balls and thermally decomposed within few seconds at atmosphere pressure and at temperature of around 500 °C under exclusion of air in pyrolysis reactor. Solid char is separated from products and can be easily pulverized into highly porous powders. Organic tar vapor and other condensable compositions are condensed to around room temperature and separated with gas phase (Dahmen et al. 2012). A quench system is applied which uses the condensate to cool down the hot product vapor directly from pyrolysis reactor. Pyrolysis gas is composed mainly of CO, CO_2 and with a small amount of hydrogen, methane and short-chain hydrocarbons. The required heat duty of pyrolysis process is 9432 kW and is expected to be supplied by the combustion of produced pyrolysis gas. Sand as heat carrier is heated by the combustion and transported simultaneously by the exhaust gas to the pyrolysis reactor. Produced char and condensate (biooil) are then mixed to form a bioslurry.

In Aspen Plus, pyrolysis process is simulated using a yield reactor. An assumed stoichiometric chemical equation derived from experimental data can be written as in Equation 3.1 (exclusive of ash, heteroatoms and moisture content) (Dahmen et al. 2012).

$$C_6H_9O_4 + ash \rightarrow \underbrace{\underset{\text{char + ash}}{(C_{2.25}H_{2.2}O_{0.36} + ash)} + \underset{\text{organic liquid}}{C_{2.76}H_{3.2}O_{0.76}} + \underset{\text{reaction water}}{1.5\,(H_2O)_l}}_{\text{“bioslurry”}} + \underset{\text{gas}}{C_1H_{0.6}O_{1.35}} \qquad 3.1)$$

Bioslurry contains all the char, ash, organic liquids, reaction water and moisture from feedstocks. It is treated as unconventional component in simulation as well. The estimated property analysis of slurry in dry basis is given in Table 3.2.

Table 3-2: Property analysis of slurry (in dry basis)

Components	Content (wt.%, dry basis)	Components	Content (wt.%, dry basis)
Carbon	65.49	Fixed carbon	29.51
Hydrogen	5.93	Volatile mass	61.10
Oxygen	19.19	Ash	9.39

The yield distribution of pyrolysis products is derived from experimental data in literature and calculated by means of atom balance based on Equation 3.1. The results are presented in Table 3.3.

Table 3-3: Products distribution from pyrolysis process

Components	Yields (in wt.%)
Dry slurry	53.68
H_2O	26.35
CO_2	12.75
CO	5.90
CH_4	0.66
C_2H_4	0.58
C_2H_2	0.04
H_2	0.04

Two-outlet flashes are selected to simulate the separation units for solid-vapor mixture after pyrolysis reactor and liquid-gas mixture after condenser. A stoichiometric reactor is used to simulate the combustion of pyrolysis gas. Air for the combustion should be preheated, the temperature of air after preheating is determined that the required heat duty of pyrolysis reactor can be completely supplied with the combustion heat of pyrolysis gas. A Design-Spec module is imposed to calculate this temperature and it gives a result of 46.8 °C with a preheating duty of 127 kW at an air inlet temperature of 15 °C.

Bioslurry with a mass flow of 28453.2 kg/h is pressurized to 30 bar and heated to 120 °C (Dahmen et al. 2012). The gasification pressure can be up to 80 bar and it is theoretically beneficial to run the gasification under the same pressure as the synthesis unit, since it is much easier to pressurize slurry than to compress gas. However, considering the operation conditions of gas cleanup units between gasification and synthesis, a gasification pressure of 30 bar is chosen. A preheating of slurry can improve the syngas efficiency, but slurry could be thermally unstable if preheated higher to critical temperature, so a preheating to 120 °C is set.

Preheated slurry is then gasified in an entrained flow gasifier under pressure of 30 bar and at temperature of 1200 °C, where the thermodynamic equilibrium is quickly attained. For fuel synthesis, an almost inert gas free syngas is normally desired to prevent a reduced partial pressure and in return to avoid useless work that is used for compression of inert gas. Hence, steam or pure oxygen is ideal as gasification agent. In this case, an autothermal gasification with pure oxygen as gasification agent is chosen. At high temperature above 1200 °C the methane and soot formation is sufficiently limited. Raw gas from gasifier outlet is rapidly quenched to 180 °C via injection of excess water so that the gas composition at high temperature is maintained (Dahmen et al. 2012).

In Aspen Plus, the autothermal gasification process is simulated using two tandem reactors. A yield reactor to simulate the decomposition of slurry to gas products and a subsequent Gibbs reactor to simulate the gas composition in thermodynamic equilibrium at operation condition. Required amount of oxygen in yield reactor and its yield distribution are calculated through mass balance and atom balance. Heat for decomposition of slurry in yield reactor is from the partial oxidation of gas products in Gibbs reactor, the oxygen amount for Gibbs reactor is calculated imposing a Design-Spec module with the target to achieve a completely autothermal gasification. Simulation results from gasification are presented in Table 3.4.

Table 3-4: Product gas components and other relevant results of gasification process

Gas components	Yields (in mol.%)	Gasification performance	
H_2	30.9		
CO	39.0	Total carbon efficiency	83.8 mol.%
CO_2	10.2	Oxygen demand	469.4 kmol/h
H_2O	19.8	Quench water demand	81.1 t/h
CH_4	0.03	H2:CO ratio	0.793

3.4 Gas cleanup and conditioning

A tar-free product gas is produced via biomass gasification using the chosen entrained flow gasifier. Other impurities such as slag and soot particles, sulfur, nitrogen and halogen compounds, alkali salts etc. must be removed to a parts-per-million (ppm) or even parts-perbillion level to prevent catalysts poisoning. The general requirements on syngas cleanup for fuel synthesis are given in Table 3.5 (Kaltschmitt et al. 2016).

Table 3-5: General requirements on syngas cleanup for fuel synthesis

Gas parameters	Requirements
Particle content	< 0.1 mg/m^3
Particle size	n.a.
Tar content	< 0.1 mg/m^3
Alkali content	< 10 ppb
NH_3 content	< 1 ppm
Sulfur content	< 0.1 ppm
Chlorine content	< 0.01 ppm

Different technologies are available for gas cleanup. For example, cyclone is mostly employed as the first step of cleaning to sufficiently remove high amount of particle in the raw gas. In this case, particles can be effectively removed by quench water as well. A treatment unit for waste water is necessary. Amine gas treating system is an industrial process which is usually applied to remove the acid gas such as H_2S and CO_2 based on the chemical reaction between absorbent and acid gas. Rectisol and Selexol process, which based on the physical adsorption phenomenon, are also well-developed for acid gases removal in industry. Besides, methanol in Rectisol process is also a good adsorbent for some trace contaminants like ammonia. The solvents from those processes should be regenerated and recycled. H_2S can be regenerated and converted to elemental sulfur through Claus process or LO-CAT process if needed. Table 3.6 gives an overview of possible technologies for gas cleanup and their key features.

Table 3-6: Features of possible gas cleanup technologies

Cleaning methods	Impurities	Features
Cyclone	Dust	Low pressure loss, low costs
Fabric filter	Dust, tar, alkali	High filtration efficiency, high pressure loss, cooling down necessary
Absorption	Tar, dust, alkali, CO_2, S- and N-components	Commercially applied, cooling required, high pressure loss
Electrical precipitator	Tar, dust, alkali	High filtration efficiency and lower pressure loss
Hot gas filter	Dust, alkaline	Temp. < 900 °C, high pressure loss and costly
Adsorption	S-, Cl- components, organic components, CO, CO_2	High pressure loss, expense for regeneration
Catalytic reduction	Tar, N-components	No waste water, on cooling down but possible deactivation through catalyst poinsoning

Hot gas cleaning system is an alternative option for the conventional scrubber systems. It could consist of ceramic particle filter and a fixed bed for adsorption of acid gases. If organic components are formed, a catalytic reactor is added to decompose it and sulfur or nitrogen compounds as well.

The gas cleaning process is not simulated in Aspen Plus to reduce complexity of the simulation. That's the reason that sulfur, nitrogen and chlorine contents in property analysis for both biomass and bioslurry are neglected and defined as zero. Still the costs on gas cleanup are going to be considered in the techno-economic evaluation later.

The H_2:CO ratio in product gas is about 0.8, which is below the desired ratio of 1 for butanol synthesis. The WGS reaction can be used to convert part of CO into H_2 to adjust the ratio. A part of cleaned product gas is split and mixed with high temperature steam and preheated to the reaction temperature of 230 °C. No extra pressure change needed for the reaction. For the low temperature shift, a typical metal oxides mixture composed of CuO, ZnO and Al_2O_3 are employed for the catalytic conversion. It should be noticed that an excess of steam injection is necessary to reduce the carbon deposition, preventing the deactivation of catalysts. The split friction of product gas for WGS reaction is calculated in Aspen Plus by using a Design-Spec module. Target is to achieve a H_2:CO ratio of 1 after remixing the 2 streams. Then the conditioned gas mixture is cooled down to 40 °C, water is completely condensed and separated with the gas phase.

As seen in the gasification section, CO_2 is one of the main components in the product gas. Due to the generation of CO_2 in WGS reaction, CO_2 removal unit is set after the WGS reactor. The CO_2 tolerance depends on the applied specific catalysts in the synthesis process. Yet it is still not clear, if the existence or up to what content level of CO_2 in syngas has significant influence of yields or distribution of alcohol products. A CO_2 removal down to 5 mol.% content in syngas was suggested in the process design of Phillips et al. In this case (by Indirect 2011). A Selexol process is chosen for CO_2 removal. Cold Selexol solvent adsorbs CO_2 from product gas at relatively high pressure. Solvents are regenerated through pressure reduction and gas stripping. In Aspen Plus, the CO_2 removal unit is simulated using a component separator block. A Design-Spec module is used to calculated the split fraction of CO_2 to ensure the CO_2 content in the inlet stream of alcohol synthesis reactor is 5 mol.%. The power demand for the refrigeration cycle is estimated through an interpolation of reference value according to the CO_2 removal capacity.

3.5 Alcohol synthesis

According to literature review, there were once many research works focused on the catalytic conversion of syngas to isobutanol, that is further utilized with methanol for MTBE synthesis. The modified methanol catalysts are mostly employed for isobutanol synthesis in these studies and are reported to have the highest productivity of isobutanol found by author among the four possible catalysts groups. In the recent years, neither progressive works specifically aimed at chemically catalytic synthesis of butanol nor better results are found. An ideal catalyst for butanol synthesis is expected to have high CO conversion and high selectivity to butanol or higher alcohols. It should be sufficiently active to have high productivity as well. Gar B. Hoflund et al. reported a Cs/Pb promoted Zn/Cr spinel catalyst containing excess ZnO to have the highest isobutanol selectivity and an acceptably high productivity at the same time (Hoflund et al. 1999). Although a low total CO conversion of 19 mol.% was obtained in the study, this particular product distribution was chosen for the analysis in this work, since sufficient yield data are also presented to simulate the alcohol synthesis process. Table 3.7 listed the product distribution used for process simulation. It should be noticed that this catalyst is active to WGS reaction as well, yet the CO_2 selectivity is not given in the literature like in many similar literatures.

Table 3-7: Products distribution of alcohol synthesis process (CO_2-free basis)

Products	Selectivity (CO_2-free basis, mol.%)
Methanol	6.79
Ethanol	0
Isopropanol	1.36
n-propanol	7.8
Isobutanol	62.35
Hydrocarbons	21.70
Total	100

U.S. NREL has set short-term research and development targets for mixed alcohol synthesis in their study on thermochemical production of ethanol. Single-pass CO conversion is supposed to increase to above 50% with the selectivity to total alcohols up to 90%. Chinedu Okoli et al. has assumed a 40% CO conversion (CO_2-free basis) in their study on techno-economic analysis for thermochemical lignocellulosic biomass-to-butanol process (Okoli, Adams 2014). With the high selectivity to isobutanol, a conservative and acceptable minimal single-pass CO conversion (CO_2-free basis) of 30% was assumed.

The cleaned, conditioned syngas is compressed to a high pressure of 70 bar using a three-stage compressor with intercooling and preheated to the reactor operation temperature of 440 °C. In the existence of catalysts, syngas is converted into a gas mixture consisted of mixed alcohols and short-chain hydrogens. Main synthesis reactions are listed in Table 3.8.

Table 3-8: Main reactions of alcohol synthesis

Water gas shift	$CO + H_2O \leftrightarrow CO_2 + H_2$
Methanol	$CO + 2\ H_2 \rightarrow CH_3OH$
Ethanol	$2\ CO + 4\ H_2 \rightarrow C_2H_5OH + H_2O$
Isopropanol	$3\ CO + 6\ H_2 \rightarrow C_3H_7OH + 2\ H_2O$
n-propanol	$3\ CO + 6\ H_2 \rightarrow C_3H_7OH + 2\ H_2O$
Isobutanol	$4\ CO + 8\ H_2 \rightarrow C_4H_9OH + 3\ H_2O$
Methane	$CO + 3\ H_2 \rightarrow CH_4 + H_2O$
Ethane	$2\ CO + 5\ H_2 \rightarrow C_2H_6 + 2\ H_2O$
Propane	$3\ CO + 7\ H_2 \rightarrow C_3H_8 + 3\ H_2O$
butane	$4\ CO + 9\ H_2 \rightarrow C_4H_{10} + 4\ H_2O$

Though the synthesis reactor is simulated with an isothermal operation condition, it must be mentioned that it would be very difficult to maintain a constant temperature in a conventional fixed bed reactor system for such strongly exothermal reactions. Temperature is a significant influence factor for the alcohol selectivity and product distribution. Advanced slurry bed reactor could be more suitable for alcohol synthesis process. These discussions are already beyond the objectives of this thesis, therefore the impact of reactor type on the alcohol synthesis is temporarily neglected for the current work.

In Aspen Plus, the alcohol synthesis reactor is simulated using a stoichiometric reactor and an equilibrium reactor. Stoichiometric reactor is for the formation of alcohols and hydrocarbons, the subsequent equilibrium reactor is for the water gas shift reaction (Guo et al. 2016). A kinetical simulation is not considered in this thesis since no available kinetic information of the chosen catalyst are found in literature. It makes less sense to use a general kinetic model from other catalysts since the kinetic performance is strongly dependent on the specific catalysts, reactor types or operation conditions. To build a convincing kinetic model, which forecasts or explains well the experimental results, more detailed information from experiments should be obtained. Therefore, the product distribution from literature is directly applied to calculate the yields of products.

Fractional conversion of CO to each specific product in the first reactor is calculated with the chosen product distribution from literature and the assumed single-pass CO conversion by defining a calculator block. As mentioned, the selectivity to CO_2 in the reactor is not reported but a water gas shift reaction does occur with the employed catalyst. Hence, an equilibrium reactor is added after the first reactor to simulate the CO_2 formation. Strictly speaking, it is not accurate because the water gas shift reaction occurs simultaneously with the main alcohol formation reactions and the thermodynamic equilibrium is affected by the gas composition and the partial pressure of gas components in the reactor. Yet there might be no better solutions than the combination of a stoichiometric and an equilibrium reactor since no sufficient kinetic information is available. From the simulation results, the CO conversion to CO_2 is around 19 mol.%, which is in the possible range of conversion for CO_2 formation using modified methanol catalysts (Luk et al. 2017).

3.6 Alcohol separation

After synthesis reactor, the gas mixture is cooled down to room temperature to condense the alcohol products. No condensable gas components such as unreacted syngas, generated short chain hydrocarbons and CO_2, also including a small amount of alcohols are separated from the condensate. The gas phase mainly consists of syngas, which can be recycled to alcohol synthesis reactor to improve the total products yields. It is also possible to reform the generated hydrocarbons to syngas, in combination with a recycle of unreacted syngas, the product yields can be further enhanced. Those will be discussed in more details in the next chapter.

To recover as more as possible butanol through condensation, the condensate from the first heat exchanger is further cooled down from room temperature to 10 °C through an active cooling. Around 3% more isobutanol is recovered if the condensation temperature is reduced from 30 °C to 10 °C. A lower condensing temperature didn’t make significant improvement. At 10 °C ca. 99.3% butanol was condensed. Thus, an active cooling to 10 °C is sufficient.

A significant quantity of carbon dioxides and a small amount of syngas and hydrocarbons are dissolved in the liquid alcohol stream, especially under the high system pressure. These dissolved gases are removed by flashing the condensed alcohol mixture from 70 bar to around 4 bar (by Indirect 2011). It is not depressurized to atmosphere pressure because the subsequent molecular sieve dehydrator unit is operated under pressure to adsorb water.

The degassed liquid alcohol mixture is then slightly superheated to 150 °C and dehydrated using a molecular sieve (Dutta, Phillips 2009). Molecular sieve is usually used to dry gas streams in the petroleum industry or to dry solvent in the laboratory. A water removal of below ppm level can be achieved by molecular sieve. It can be also applied as separation or filtration unit. In biochemical production of ethanol, after the ethanol-water mixture is distillate to the azeotropic concentration, the molecular sieve is applied to dry ethanol to a required higher concentration. In the thermochemical process, it is suggested to dry the entire mixed alcohols before it is sent to the distillation column, since the water content in the mixed alcohol stream is much lower than in the biochemical process. In this case, the water content in the inlet stream of molecular sieve is around 11 wt.%. For regeneration of adsorbents in molecular sieve, the recovered methanol vapor from distillation column is flushed as sweep gas in the molecular sieve to desorb the adsorbed water in combination with a depressurization.

Molecular sieve is operated in batch mode, that means two identical columns are needed for a continuous separation. Water is adsorbed from the superheated mixed alcohols in the adsorption phase and removed by flushing of methanol vapor during the desorption phase. In Aspen Plus, the dehydration by molecular sieve is simulated with a component separator block. 99.5% of water is supposed to be removed.

The size of operated molecular sieve is roughly estimated with the adsorption capacity and bulk density of the chosen material in molecular sieve and the dehydration demand. Table 3.9 listed the water adsorption capacity and bulk density of the chosen two microporous materials (Peters et al. 2006).

Table 3-9: Properties of possible microporous materials for molecular sieve

Model	Pore diameter in nm	Bulk density in g/ml	H_2O capture in wt.%
3A	0.3	0.60-0.68	20
4A	0.4	0.60-0.65	23

After dehydration, the dried mixed alcohol vapor is condensed to room temperature and depressurized to atmosphere pressure. Rest of the dissolved CO_2 and hydrocarbons are mostly released and separated with liquid phase. The condensate is then sent to distillation column, which is operated under atmosphere pressure.

A typical distillation column containing trays, overhead condenser and reboiler is applied. In Aspen Plus, a RadFrac single column is selected to simulate the distillation unit. The overhead condenser is set to have vapor distillate only. Operation parameters such as reflux ratio or distillate to feed ratio and column parameters like stage numbers are specified to pursue a maximal recovery of isobutanol in the bottoms liquid and a maximal recovery of methanol in the distillate vapor. Theoretically a higher reflux ratio can improve the separation performance or decrease the number of theoretical stages required. But higher reflux ratio also results in higher energy demand. The select of reflux ratio is rather a trade-off between separation requirements and costs. In industry, the reflux ratio is normally not over 1.5.

Isobutanol is almost completely recovered in the liquid bottoms with the most n-propanol and a small amount of methanol and isopropanol. A nearly 90 wt.% purity of butanol product is obtained after the first distillation column. Looking back to the objectives of this thesis, the production of butanol is for a usage as alternative liquid fuel. Combustion properties of the produced fuel product is more concerned. Table 3.10 listed the composition of the butanol product using only one distillation column. A comparison of lower heating value between this butanol product, pure isobutanol and pure propanol is also presented.

Table 3-10: Product composition and fuel properties

Alcohols	Proportion in wt.%	Lower heating value in MJ/L
Methanol	1.1	15.78
n-propanol	9.9	24.65
Isopropanol	0.7	23.93
Isobutanol	88.2	26.43
Butanol product	100	26.12

In terms of lower heating value, there is almost no difference between produced butanol product and pure butanol. Still the combustion performance and the compatibility of this alcohol mixture with conventional engine should be further confirmed. It was determined that no more extra distillation columns are needed for this butanol fuel production. If a chemical utilization of product is desired, a highly pure butanol product is surely required and further separation units would be necessary.

Distillate vapor from distillation column consists mainly of methanol. This vapor stream is used as sweep gas for the regeneration of molecular sieve. After recovery of water it is possible to recycle the methanol-rich sweep gas to alcohol synthesis reactor, since an injection of lower alcohols could enhance the higher alcohol production.

After cooling down of the butanol product to room temperature, the final product is obtained.

3.7 Process utilities

Most units in the thermochemical production process of biobutanol require additional heating, cooling or injection of oxygen or steam, meanwhile some units produce process wastes such as waste water or exhaust gas as well. The requirements on process utilities are met either through process integration or external source. Table 3.11 listed the process utilities required in the main process units. The process utilities supply is discussed in detail along with the energy integration section in next chapter.

Table 3-11: Required process utilities of corresponding units

Process units	Required process utilities
Biomass preparation	Heating load, power for grinding
Biomass gasification	Cooling load, oxygen, quench water, power
Gas cleanup and conditioning	Cooling load, CO_2 removal, waste water treatment, power, heating load
Alcohol synthesis	Cooling load (reaction heat removal)
Alcohol separation	Cooling load, heating load

4 Process optimization

To optimize an industrial process, there are usually two ways to be considered. One is the optimization for individual process units and their operation parameters. For example, a more suitable reactor type is employed or more beneficial reaction conditions such as temperature, pressure or flow rate etc. are set to achieve the optimization target. The relations between the individual parameters and the target are studied to find an optimal or enhanced operation point. The other is an optimization for the process design. For example, in a distillation process for a multicomponent product, the distillate sequences can have significant influence on the separation performance and the operating cost. An improved process design can be also realized by adding additional process unit or reducing unnecessary process steps. Besides, an energy analysis and subsequent heat integration contribute to improve the energy efficiency of the whole process and reduce the costs on process utilities.

In this thermochemical process for biobutanol production, a higher butanol yield is desired. The optimization target is through enhancing the butanol yield and the energy efficiency of process, to reduce the net product costs (NPC). To achieve the target, the latter optimization way, that is an optimization of the process design is discussed in this work. The influence of operation conditions on the final product yields is not the key point of this thesis and will not be further studied.

4.1 Recycle of unreacted syngas

The CO conversion in the alcohol synthesis reactor is conservatively assumed as 30%. Counting in the CO conversion to CO_2 through WGS reaction, still more than half of carbon monoxide is not taking part in any formation reactions in a single pass. The unreacted syngas can be combusted to produce process heat, steam or generate process power. However, a more meaningful and necessary usage is to recycle it to alcohol synthesis reactor to enhance butanol and the total alcohol yields.

The unreacted syngas mainly consists of hydrogen, carbon monoxide, carbon dioxide, methane and a small amount of other hydrocarbons. Among them the H_2:CO ratio is around 0.55, that is below the required H_2:CO ratio of 1 for the higher alcohol synthesis. Therefore, a gas conditioning to increase the H_2 content is needed as well for unreacted syngas if it is expected to be recycled for alcohol production.

The unreacted syngas is mixed with the cleaned product gas of gasification and sent together to the gas conditioning system. The gas conditioning process is already described in section 3.4. Note that methane and other hydrocarbons in the unreacted syngas are inert components that are produced in alcohol synthesis reactor but not further reacted or separated in any other units in the recycle. To prevent an infinite accumulation of these inert components, it is necessary to remove a portion of the recycle stream to keep the content of inert components within an acceptable level. 5% recycle stream is as purge stream and combusted for process heat or power generation (by Indirect 2011).

Through recycle of unreacted syngas, product yields are significantly enhanced. An 55 % increase of butanol yield is obtained according to the simulation results in Aspen Plus. The required volume of reactor and columns, capacity of separation units, compression work and heat duty are all increased as well. The portion of recycled unreacted syngas can be further studied in consideration of the yield enhancement and cost evaluation to find an optimal point, but it is not discussed in this work.

4.2 Reforming of produced hydrocarbons

As discussed in section 4.1, when syngas is recycled, methane and other hydrocarbons generated in the process will accumulate in the loop. With the assumed 5% purge stream, the content of total hydrocarbons in the recycle stream accounts to about 29.3 mol.%, among them ca. 82% is methane. A high content of inert components in the system results in unnecessary capital costs for larger process units and useless operation costs for process utilities. It reduces the partial pressure of syngas in the alcohol synthesis reactor as well. Therefore, a utilization or separation of those hydrocarbons in the recycle stream can be beneficial.

Since the majority of inert components is methane, a reforming of methane to produce additional hydrogen and carbon monoxide is meaningful and further discussed.

Methane reforming is an advanced and mature industrial process to produce hydrogen. Generally, there are three different reforming process: steam methane reforming (SMR), partial oxidation and autothermal reforming (ATR). In SMR, methane reacts with steam at high temperature (700 – 1100 °C) under high pressure in the presence of catalysts to produce hydrogen, carbon monoxide and a small amount of carbon dioxide. More hydrogen is recovered through WGS reaction by converting the produced carbon monoxide. Steam methane reforming is an endothermic reaction, thus additional heat supply is required. Partial oxidation occurs with a substoichiometric oxygen content. Partial oxidation is an exothermal process, which means a heat removal from reaction is needed. It produces less hydrogen per unit input of methane than steam reforming process. Different from SMR, autothermal reforming uses oxygen and steam or carbon dioxide to form syngas. The presence of oxygen results in a partially oxidation of methane, which is exothermic and provides the heat required of reforming reaction. Nickel-based catalysts are commonly employed in industry, Rh- and Pt-based catalysts are intensively studied as well. ATR is also a preferred technology for industrial GtL (gas to liquid) process. The chemical reaction of autothermal reforming with steam can be written as Equation 4.1. The value of x can vary depending on the reaction conditions (Matsumura, Nakamori 2004).

$$CH_4 + \frac{x}{2}O_2 + (1-x)H_2O \rightarrow CO + (3-x)H_2 \qquad 4.1)$$

An autothermal reforming of methane with steam is applied before unreacted syngas is recycled. As seen in the reaction equation, more hydrogen can be generated than carbon monoxide by autothermal reforming. Therefore, it is possible to adjust the final H_2:CO ratio in the inlet stream of alcohol synthesis reactor by changing the portion of catalytically reformed recycle stream instead of the WGS reaction.

A 5% of unreacted syngas is still as purge steam sent to be combusted for process heat and power generation. To be recycled stream is split into two streams. One stream is preheated to the reformer inlet temperature and sent to the reformer. The autothermal reformer is operated under the same pressure of 70 bar as the alcohol synthesis reactor, thus no pressure change is needed if the pressure loss in pipes and heat exchangers is ignored in the simulation. Pure oxygen and high temperature steam are injected to the reformer. In Aspen Plus, a Gibbs reactor is selected to simulate the autothermal reformer. The operating temperature is set to be 1100 °C. At such a high temperature and high pressure in presence of a proper catalyst, the thermodynamic equilibrium is supposed to be easily achieved and the conversion of methane and other hydrocarbons is nearly 100%. The required amount of oxygen is calculated by a Design-Spec module with the target that the net heat duty of the reformer is zero.

A possible problem at hydrocarbon reforming is the carbon deposition. The carbon formation and deposition can be sufficiently suppressed in a steam-rich condition. Hence, an excess of steam for the reforming process is needed. The required steam amount is calculated by the steam carbon ratio, which is defined as the mole ratio of water in the inlet stream and total carbon atoms in the reaction. A sufficient steam carbon ratio is usually 3.

The outlet stream from reformer is then mixed with the other split recycle stream and the cleaned product gas of gasification. By changing the split fraction of recycle stream, the H_2:CO ratio for the alcohol synthesis can be adjusted to desired value, in this case the H_2:CO ratio is 1. The WGS reactor is no more needed.

Still in the not reformed recycle stream, there is a certain amount of methane and other hydrocarbons. Another interesting possibility is to use carbon dioxide for the reforming of methane, which is also called dry reforming. The chemical reaction can be presented as Equation 4.2. Methane is partially oxidized for an autothermal operation.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad 4.2)$$

According to the reaction, the mole ratio of hydrogen and carbon monoxide in the product is 1, which is exactly required for this butanol synthesis. Carbon dioxide is produced in the process and separated as waste gas. If it can be utilized, not only the total product yield, but also the total efficiency of process can be enhanced. It is expected to discuss the dry reforming of methane more detailed in the future work.

The optimized process flow diagram is presented in Figure 4.1.

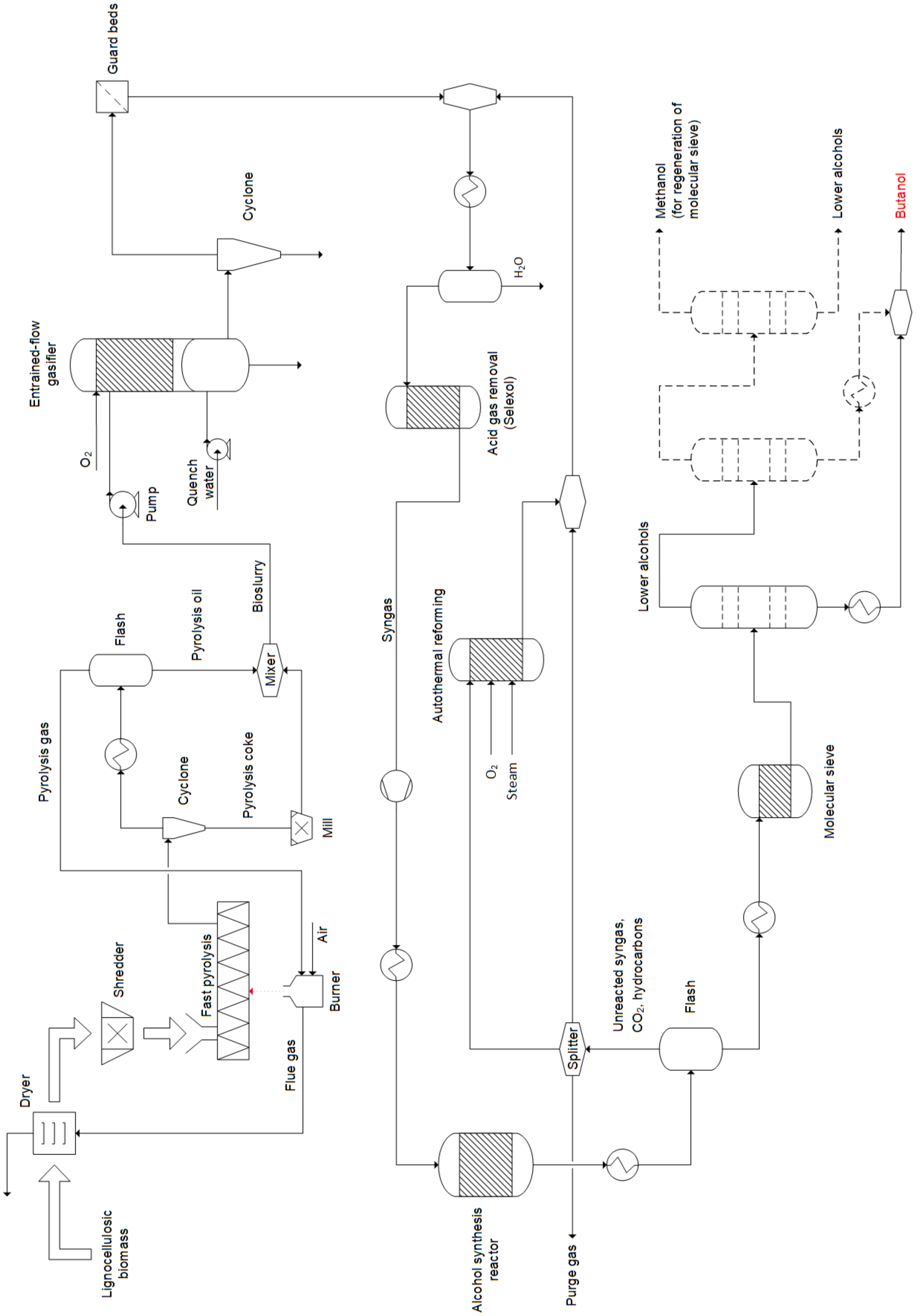


Figure 4-1: Process flow diagram after optimization of process design

4.3 Heat integration

As described in the process design, the most reactions or process units are operated at a certain temperature and pressure above atmosphere condition. Hence, heating or cooling of certain streams or reactors is requisite. Heat integration is a technique to minimize energy consumption and to maximize the heat recovery of a chemical process. More generally, it means the heat from a hot stream can be recovered to heat a cold stream in the process at a matched temperature level and vice versa. The energy efficiency of the process can be improved while the required external utilities reduced through heat integration.

A pinch analysis is conducted for the thermochemical process of biobutanol production. A heat exchanger network is designed based on the results of pinch analysis. Process utilities including heating, cooling and power is further discussed in detail.

4.3.1 Pinch analysis

Pinch analysis is the method to carry out heat integration. To find the pinch point is the key of pinch analysis. Process date including temperature and heat duty of all streams and reactors are extracted from Aspen Plus and plotted as a function of temperature against heat duty. Streams or reactors that should be cooled down are defined as hot streams while those should be heated up are defined as cold streams. All the hot streams and cold streams are combined to construct the hot and cold composite curves, respectively. The point, where the hot and cold composite curves have the closest approach is defined as pinch point. The temperature difference of hot and cold composite curve at this point is called ΔT_{min}, which is an important factor for heat exchanger network design. A smaller ΔT_{min} means more heat can be recovered from the process through heat integration while the required area of heat exchangers is larger, which results in higher capital costs. The choice of ΔT_{min} is usually a tradeoff between capital and utilities costs. For this chemical process, a ΔT_{min} of 10 °C is usually chosen. Figure 4.2 presented the composite curves of this butanol production process. The composite curves are constructed using the In-house software TEPET (Techno-Economic Process Evaluation Tool) by DLR.

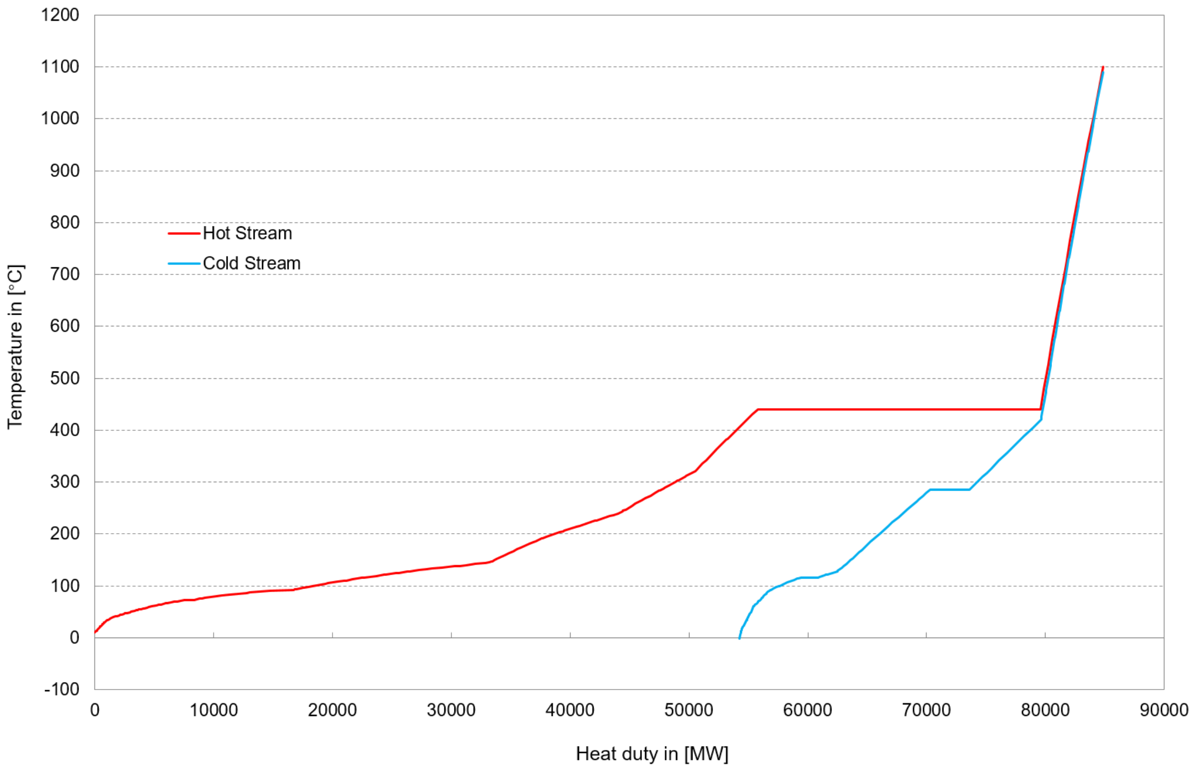


Figure 4-2: Composite curve from pinch analysis

According to the composite curves, the pinch is found at the rightmost point of cold composite curve. All the heating load can be covered through heat integration and a certain number of hot streams need external cooling utilities. The energy saving potentials for heating and cooling utilities are estimated to be 100% and about 39%, respectively.

Based on the results of pinch analysis, a heat exchanger network (HEN) design is conducted. For the HEN design, the following pinch rules should be followed to achieve the maximal heat recovery:

- No external heating below the Pinch;
- No external cooling above the Pinch;
- No heat transfer across the Pinch.

Any violation of the above rules results in higher energy demand than the theoretically minimal requirement. There are still possibilities further to reduce the total energy demand according to the so-called “plus-minus principle” (Chapter 10 Pinch point analysis 2008). It is conducted by changing the appropriate process parameters that can have a beneficial impact on energy consumption identified through pinch rules. It can be concisely summarized as following:

- Increase the proportion of the hot composite curve above the pinch, or
- Decrease the proportion of the cold composite curve above the pinch.

It would be infinite if all the energy saving methods are to be discussed. Hence, an energy optimization by process changing is not conducted in this thesis and is expected to be further studied in the future work.

Figure 4.3 presented the final process flow diagram with heat integration simulated in Aspen Plus. Heat streams of district heating and cooling water as well as work streams are not showed in the figure. 2-stream heat exchanger (HeatX) is selected to simulate the heat exchange process between hot and cold streams.

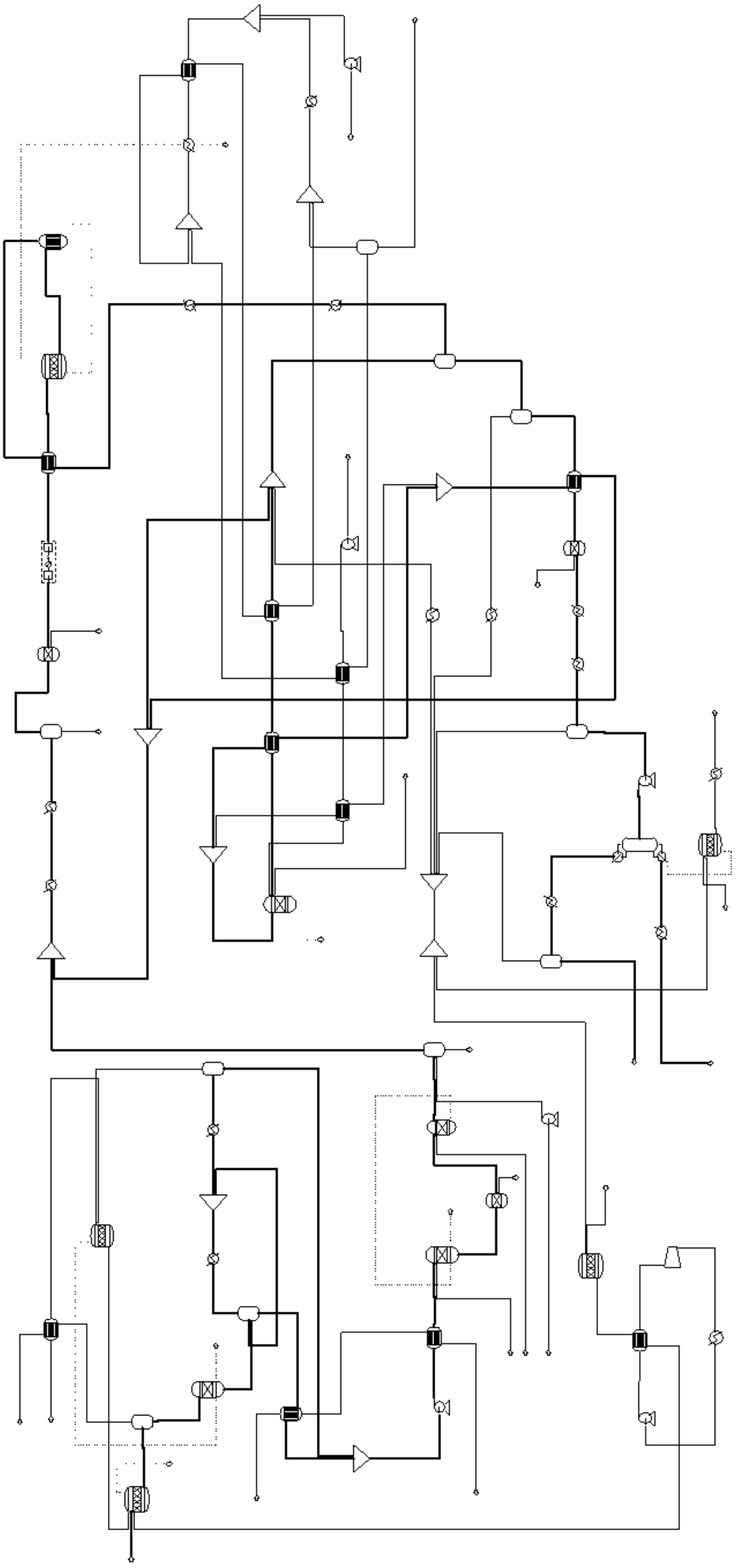


Figure 4-3: Biobutanol production process diagram with heat integration in Aspen Plus

As described in section 3.3, air for the combustion of pyrolysis gas should be preheated to ensure a completely heat supply of pyrolysis process through combustion of produced pyrolysis gas. The calculated preheating temperature of 46.8 °C is relatively low, exhaust gas from biomass dryer has a temperature of 105 °C and is used to preheat the combustion air. Biochar from biomass pyrolysis should be firstly cooled down from high pyrolysis temperature to 100 °C before mixed with biooil to form bioslurry. The heat can be recovered to preheat the bioslurry to 120 °C for gasification. Hot and cold streams are not directly coupled because they are solid or in pasty form. Forced-air heat exchangers are applied. Air is firstly warmed up by cooling down the biochar, the hot air is then sent to next heat exchanger to heat the bioslurry. The cleaned and conditioned syngas is initially supposed to be preheated to the reaction temperature of 440 °C. Yet the inlet temperature doesn’t have to be as high as the reaction temperature in a steady operation state since the alcohol synthesis reactions are strongly exothermic. It is expected that heat recovered from outlet stream of alcohol synthesis reactor is used to heat the syngas. Considering the temperature difference of heat transfer and to prevent a temperature crossover in heat exchanger, the preheating temperature of syngas is adjusted to 400 °C.

For alcohol synthesis reactor, heat removal for temperature control is a critical challenge. Water is usually used as cooling medium for fixed bed reactor due to its high enthalpy of vaporization. For the selected catalyst employed for butanol synthesis in this work, the reaction temperature is 440 °C, which is already beyond the critical temperature of water. However, the performance of supercritical fluid is not discussed in this work, it is assumed that the operation conditions of heat removal system is still below the critical point. Water at a high pressure of 85 bar is preheated to 280 °C and sent to the cooling system of synthesis reactor, where it is vaporized to remove the extra heat generated during the reactions. Outlet temperature of vapor is set to be 320 °C. A portion of outlet vapor is split to preheat the inlet water so that no external heat is needed. Indeed, more suitable heat removal solutions should be studied in the future work. On the other hand, low temperature modified methanol synthesis catalysts for higher alcohol synthesis have attracted more attention than the high temperature one in the recent years, advanced catalysts that works under lower temperature and still have sufficient activity and selectivity to desired alcohol products would be one of the targets of catalysts development. A lower reaction temperature is expected in the future.

For autothermal reforming of methane and other hydrocarbons from unreacted syngas, a steam injection is required. A preheating of inlet steams of gas and steam is beneficial for final alcohol product yields. Outlet stream of methane reformer has a high temperature of 1100 °C and is expected to be used to preheat the inlet streams. However, due to the constraint of ΔT_{min} and eventual temperature crossover in heat transfer, the total preheating load can't be met with only reformer outlet stream. A hot water stream of 280 °C and high-pressure steam are generated by heat removal from alcohol synthesis reactor, with the 2 heat sources the expected preheating is realized. Considering a separation of cooling system and primary production process, the high-pressure steam from cooling system is not directly injected into the reformer but to evaporate water which is then further superheated by reformer outlet stream to the desired inlet temperature.

After preheating, the outlet stream has still a relatively high temperature of around 300 °C, which is further sent to evaporate and superheat the molecular sieve inlet stream of mixed alcohols product. Finally, product stream of reformer is mixed with not reformed stream and recycled.

The remaining high-pressure steam is separated with condensed water phase and can be sell as additional product. Condensed water is then mixed with hot water and supplemented fresh water and recycled to cooling system.

4.3.2 Process utilities

After heat integration, there are still a number of hot streams that should be cooled using additional utilities. Depending on the different temperature level of hot steams, district heating production system and cooling water system are applied. The return temperature of district heating and supply temperature are supposed to be 60 °C and 120 °C, respectively. Inlet and outlet temperature of cooling water are supposed to be 15 °C and 30 °C, respectively.

Outlet stream from alcohol synthesis reactor should be active cooled down to 10 °C. Electricity is required for refrigeration. The power demand is simply estimated through cooling load and coefficient of performance (COP).

The purge gas and gas released from liquid alcohols by depressurizing from separation process are mixed and burned. A portion of the combustion heat is used to supply the heat demand of reboiler in separation column, while the rest to produce steam for power generation through Rankine cycle. Around 3.5 MW net electricity is generated with an electrical efficiency of 30.5 %. Still it is below the power demand of the whole production process. Additional power from grid is needed. Relevant technical parameters of power generation are listed in Table 4.1.

Table 4-1: Technical parameters of power generation

Parameters	Value
Fresh steam temperature	520 °C
Fresh steam pressure	120 bar
Condensation pressure	0.05 bar
Electricity generation	3617 kW
Electricity efficiency	30.5%

A distribution of power consumption in the process sections is shown in Figure 4.4. The gas cleanup and conditioning section makes the highest contribution to the power demand because of the compression of syngas to the required high reaction pressure. Electricity generated through the steam cycle can’t meet the total power demand, additional electricity of 910.5 kW from grid is necessary.

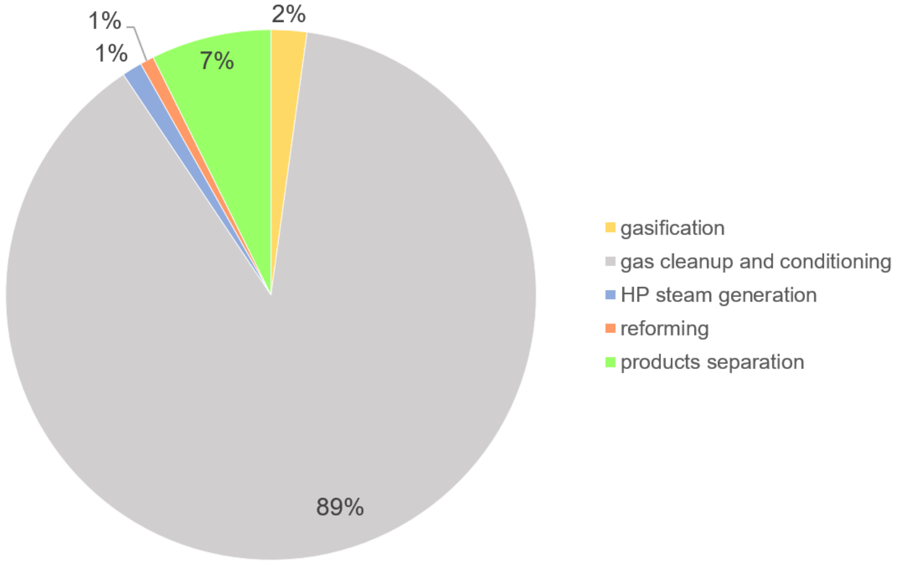


Figure 4-4: Distribution of power demand

A summary of all process utilities is given in Table 4.2.

Table 4-2: Summary of all process utilities

Process utilities	Value
Pure oxygen	487.7 kmol/h
Quench water	81.1 t/h
Clean water	16.4 t/h
Electricity from grid	910.5 kW
Cooling water	1,556.8 t/h (27.13 MW)
Waste water	114.9 m^3/h
District heating	431.8 t/h (30.3 MW)
HP steam	9,353 t/h (205 m^3/h)

4.4 Simulation results

Major process design parameters and simulation results are listed in Table 4.3. Biomass to liquid efficiency, overall plant efficiency and carbon conversion are defined as in Equation 4.3 to 4.5, respectively (Albrecht et al. 2017).

$$\eta_{BtL} = \frac{\dot{m}_{PR}.LHV_{PR}}{\dot{m}_{BIOMASS}.LHV_{Biomass} + P_{elec}} \tag{4.3)}$$

$$\eta_{Plant} = \frac{\dot{m}_{PR}.LHV_{PR} + P_{elec,out} + \sum \dot{Q}_{heat}}{\dot{m}_{BIOMASS}.LHV_{Biomass} + P_{elec}} \tag{4.4)}$$

$$\eta_{C} = \frac{\dot{n}_{C,PR}}{\dot{n}_{C,Biomass} + \dot{n}_{C,CO_2,feed}} \tag{4.5)}$$

Table 4-3: Summary of major design parameters and simulation results

Feed handling & preparation		Alcohol separation	
Wet biomass flow rate	42,874 kg/h	Capacity of molecular sieve	1,113.1 kg/h H_2O
Heat duty of dryer	6,966 kW	Flow rate of butanol fuel product	6232.5 kg/h (7787.0 L/h)
Gasification		Energy flows	
Pyrolysis temp.	500 °C	Wet biomass (25 wt.% moisture)	153.772 MW
Gasifier pressure	30 bar	Electricity from grid	0.911 MW
Gasifier temp.	1200°C	HP steam	6.931 MW
Outlet H_2:CO ratio	0.79	District heating	30.261 MW
Gas cleanup & conditioning		Fuel output	56.505 MW
Flow rate of removed CO_2	488.2 kmol/h	Efficiencies	
Outlet H_2:CO ratio	1	BtL efficiency	36.7%
Alcohol synthesis		Overall plant efficiency	60.9%
Productivity of butanol	75.1 kmol/h	Carbon conversion	26.5%
Productivity of total alcohols	122.9 kmol/h		

5 Techno-economic evaluation

Process simulation through Aspen Plus® and further optimization for process design and energy consumption evaluate the technical feasibility of the butanol production process. Whether the produced alternative fuel products can be successfully brought to the market is depending on the fuel net production costs (NPC), the expected cost reduction potentials and the policies on climate and environment. Therefore, an economic evaluation is necessary to analyze the economic feasibility for a comprehensive assessment of the designed production process.

5.1 Methodology

A standardized methodology developed by DLR for techno-economic evaluation of alternative fuels is applied in this thesis. Figure 5.1 presented an overview of the main steps of the methodology (Albrecht et al. 2017).

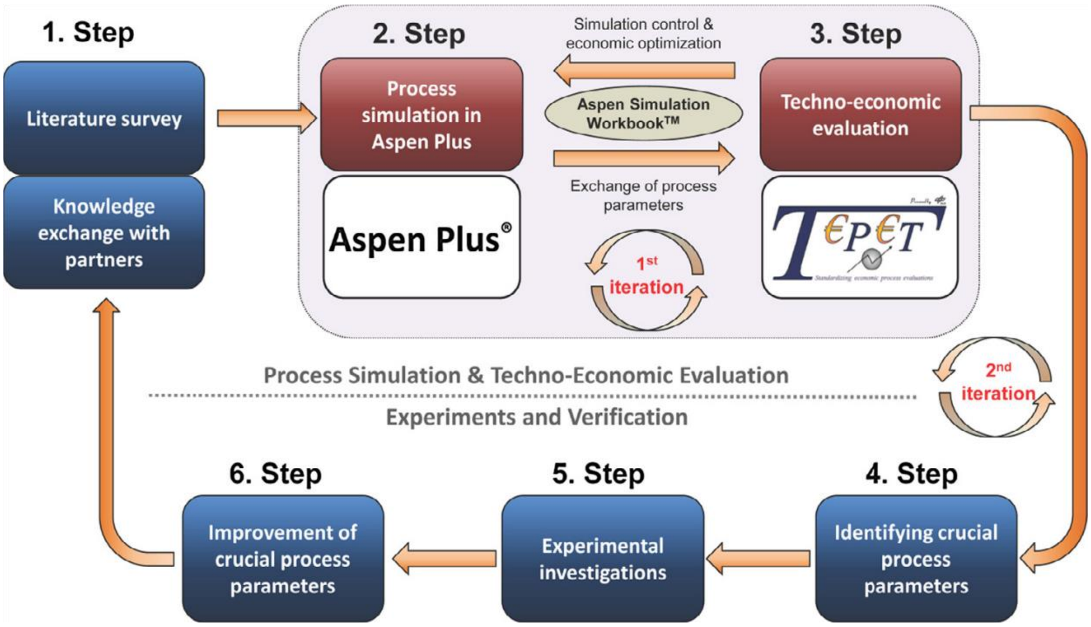


Figure 5-1: Methology of techno-economic evaluation developed by DLR

Firstly, an extensive literature survey on the production methods of desired fuel is carried out. The potential of possible feedstocks, available production routes and the current state of relevant technologies are investigated. Through a comparison of different production routes and technologies, a suitable process concept based on the fuel requirements is designed. Key process equipment and parameters are identified as well. The second step is a detailed simulation of the designed process using Aspen Plus. A heat integration through pinch analysis is conducted to minimize the energy consumption and utility costs by designing an optimized heat exchanger network. Operation conditions and cost-related simulation results are extracted from Aspen Plus and connected with TEPET by the Aspen Simulation Workbook®. In the third step the economic evaluation including costs estimation and sensitivity analysis is carried out by TEPET. Production costs composition and process factors that sensibly affect the production costs are identified. Results from economic evaluation can be used to modify the process design in simulation work with the purpose of reducing the net production costs, which is the first iteration loop in the procedure.

Step 4 to 6 is the experimental work, in which the technical feasibility of the selected process units and operation conditions is verified through small-scale experiments. Crucial process parameters and potentials of improvement are identified. Results from experiments can be used to modify the process design as well, which is seen as the second iteration loop. This work is focused on the first three steps, while the experimental works are expected to be conducted in the future.

A detailed process design and simulation as well as process optimization are already discussed in the preceding chapters. In this chapter, the economic evaluation will be introduced. The methodology applied for cost estimation in TEPET is presented in Figure 5.2 (Albrecht et al. 2017).

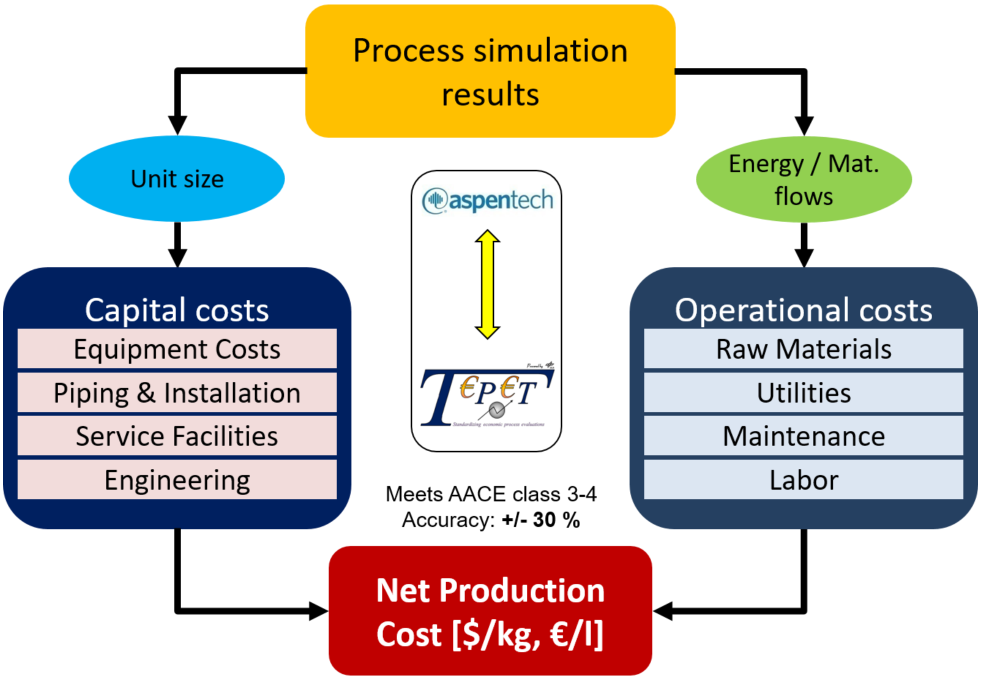


Figure 5-2: Methodology applied in TEPET for costs estimation

Production costs consist of capital investment costs (CAPEX) and operational expenditures (OPEX). The fixed capital investment (FCI) costs include equipment costs (EC) and other capital requirements in the construction phase of plant. Equipment costs are functions of characteristic capacity of operation units with modification factor taking into account high operation pressure, specific material requirements and if applicable the learning and experience curve effects. The costs functions for main chemical process equipment and relevant equipment for fuel synthesis from literatures are integrated in TEPET. Fixed capital costs are calculated by Equation 5.1. $F_{eco,i,j}$ is the ratio factor for estimating FCI of fluid processing chemical plants (Albrecht et al. 2017).

$$FCI = \sum_{i=1}^{m} EC_i * \left(1 + \sum_{j=1}^{10} F_{eco,i,j}\right) * \left(1 + \sum_{j=11}^{12} F_{eco,i,j}\right) \qquad 5.1)$$

Production costs consist of capital investment costs (CAPEX) and operational expenditures (OPEX). The fixed capital investment (FCI) costs include equipment costs (EC) and other capital requirements in the construction phase of plant. Equipment costs are functions of characteristic capacity of operation units with modification factor taking into account high operation pressure, specific material requirements and if applicable the learning and experience curve effects. The costs functions for main chemical process equipment and relevant equipment for fuel synthesis from literatures are integrated in TEPET. Fixed capital costs are calculated by Equation 5.1. Feco,i,j is the ratio factor for estimating FCI of fluid processing chemical plants.

The annual capital costs (ACC) is estimated by Equation 5.2 in consideration of the annuity method with the expected interest rate (IR) and lifetime of plant (Albrecht et al. 2017).

$$ACC = FCI * \left(\frac{IR * (1 + IR)^y}{(1 + IR)^y - 1} + \frac{IR * y}{9}\right) \qquad 5.2)$$

Operational expenditures can be divided into costs for raw materials and process utilities (direct OPEX) and other operational costs including maintenance, insurances, taxes etc. (indirect OPEX). Based on the results of material flows and energy flows from process simulation, direct OPEX are estimated by the Equation 5.3. Market prices in the base year for necessary materials and energy are required as well (Albrecht et al. 2017).

$$\sum OPEX_{dir}\left(\frac{€/\$}{year}\right) = \sum_{i=1}^{m} \dot{m}_{R\&B\_i} * c_{R\&B\_i} * \left(\frac{CPI_i}{CPI_{ref,i}}\right) + \sum_{j=1}^{n} E_{power_j} * c_{power_j} + \sum_{k=1}^{p} W_{heat_k} * c_{heat_k} \qquad 5.3)$$

After estimating the capital costs and operational costs, the net production costs are calculated according to Equation 5.4 (Albrecht et al. 2017).

$$NPC\left(\frac{€/\$}{l}\right) = \frac{ACC + \sum OPEX_{ind} + \sum OPEX_{dir} + h_{labor} * c_{labor}}{\dot{m}_{fuel} * \rho_{fuel}^{-1} * \frac{\omega_{fuel}}{\omega_{reference}}} \qquad 5.4)$$

The results of economic evaluation are expected to have an accuracy of ± 30% to meet class three and four of the classification system of AACE (Association for Advancement of Cost Engineering).

5.2 Evaluation results

The economic evaluation is carried out using the In-house software TEPET developed by DLR. According to the methodology of cost estimation, the basic economic assumptions are defined and listed in Table 5.1.

Table 5-1: Basic economic assumptions for evaluation

Economic parameters	
Cost year for analysis	2014
Interest rate	7%
Plant life	20 years
Full load hours	7884 h/a (90%)
Maintenance labor	0.02 of FCI
Maintenance materials	0.02 of FCI
Working capital	0.1 of TCI

The purchased costs of major equipment employed in this butanol synthesis process are summarized in Table 5.2. Because the butanol production through higher alcohol synthesis is not yet commercialized in chemical industry and no specific butanol reactor is available in the database of TEPET, the cost function of methanol synthesis reactor is selected for the cost estimation of butanol synthesis reactor. The results are sorted in the order of decreased costs and it is noted that the biomass gasification section consisted of pyrolysis reactor and entrained flow gasifier results in the most expenses on equipment purchase, followed by CO_2 removal unit, autothermal reformer and butanol synthesis reactor.

Table 5-2: Purchased equipment costs (EC)

Equipment	Costs in €
Entrained flow gasifier	59,216,819
Pyrolysis reactor (including burner)	14,367,893
Selexol CO_2 removal unit	10,540,074
Reformer	7,611,126
Heat exchanger network	5,183,949
Butanol synthesis reactor	4,505,194
Power generation system	3,060,956
Biomass dryer	2,832,489
Multi-compressor	2,417,438
Waste water treatment unit	2,158,907
Refrigeration and chilling system	882,068
Separation column (including burner)	386,033
Molecular sieve	335,062
Others	796,967

With the purchased equipment costs, the fixed capital investment costs can be calculated by the Equation 5.1. Figure 5.3 presented the FCI costs and its composition. The calculated total fixed capital cost is around 556 mio. €. It is observed that slightly more than half of the total capital investment falls on the entrain flow gasifier. Together with pyrolysis reactor, nearly two thirds fixed capital costs are from biomass gasification. Besides, the butanol synthesis reactor cost is estimated to be around 21.9 mio. €$_{2014}$, which equals to about 4% of total fixed capital investment.

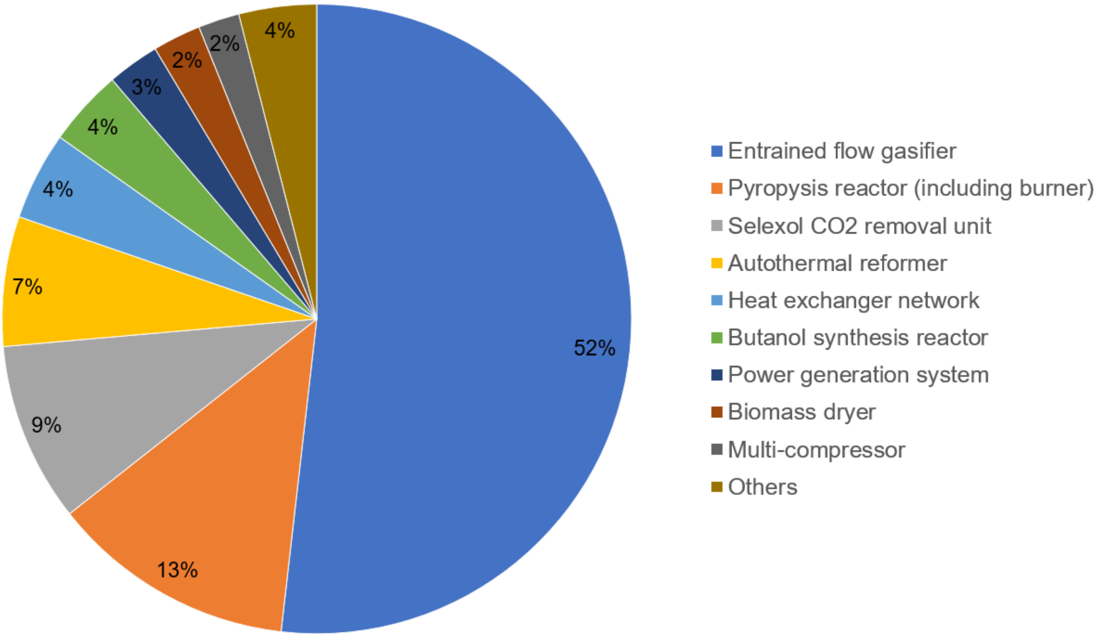


Figure 5-3: Distribution of fixed capital costs (FCI)

The applied market prices for raw materials, utilities and possible by-products are identified by TEPET and already updated to 2015. The related price data for this analysis are given in Table 5.3.

Table 5-3: Market prices (2015) applied in costs estimation

	Market price		Market price
Wet biomass (feedstock)	116.61 €/t	Cooling water	0.001 €/m^3
Oxygen	29.743 €/t	Waste water	0.478 €/m^3
Electricity from grid	125.725 €/MWh	District heating	0.048 €/kWh
Clean water	2.023 €/m^3	High pressure steam	34.724 €/t

In the production process, biomass, pure oxygen and clean water and electricity from grid are purchased as input materials or process utilities. Additional expenses are required for cooling water supply and waste water treatment. Through heat integration, high pressure steam and district heating are generated and can be sell as by-products. Figure 5.4 presented the expenses for acquisition of raw materials and utilities and the revenue from by-products.

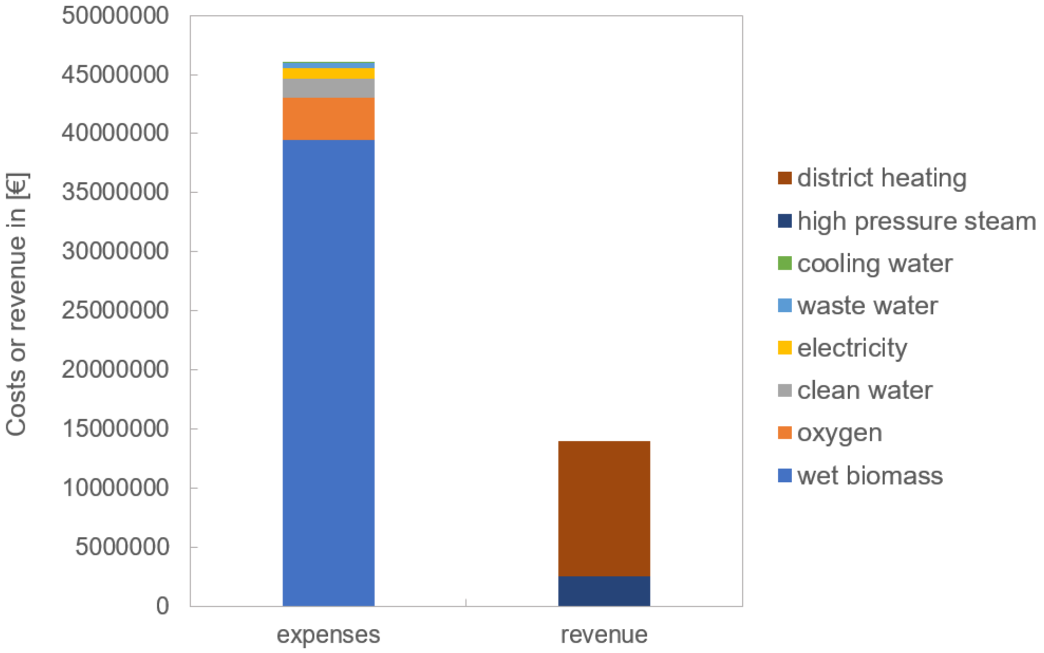


Figure 5-4: Process expenses and revenue

It can be seen from Figure 5.4 that biomass purchasing contributes to the largest expense as expected and accounts for about 85% of total expenses on raw materials and utilities. Thanks to the heat integration, the expense on cooling water is almost negligible. Around 30% expenses on raw materials and utilities can be compensated with revenue from selling by-products.

One of the main purpose of economic evaluation is to find out the net production costs of designed process. For this butanol fuel product, the specific net production cost is finally calculated to be 2.25 €/l, which is still much higher than the acceptable market price. Figure 5.5 presented the composition of the total production costs.

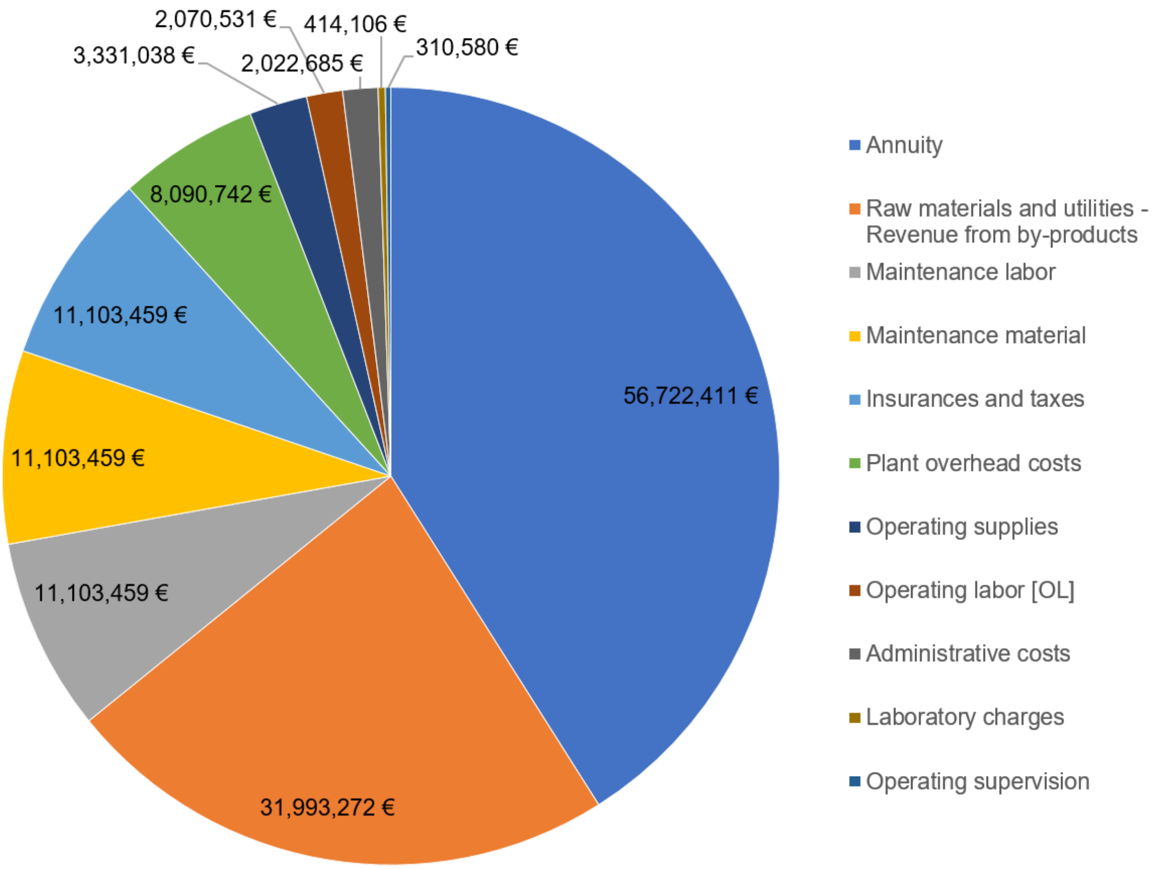


Figure 5-5: Total production costs of biobutanol

It is observed that the annuity derived from fixed capital costs accounts for the highest portion of about 41%, followed by the direct operational costs with a portion of 23%. Ca. one third is indirect operational costs including maintenance, labor, insurances and taxes, etc.

Table 5.4 summarized the relevant cost estimation results from economic evaluation by TEPET.

Table 5-4: Results from economic evaluation

CAPEX	
Total purchased equipment costs	114,127,444 €
Fixed capital investment	555,987,906 €
Total capital investment	617,764,340 €
Annuity	56,722,411 €

OPEX	
Direct operational costs	31,993,272 €
Indirect operational costs	49,550,058 €
NPC	
Specific net production costs	2.25 €/L
	2.81 €/kg

5.3 Sensitivity analysis

In the process design and economic evaluation, some key parameters are assumed based on the typical chemical plant design as well as the state of technologies. Considering the uncertainties of the relevant assumptions and possible developments of related technologies, it is important to carry out a sensitivity analysis to evaluate, what impacts from variation of those parameters will have on the specific net production costs, so that the cost reduction targets can be identified as well.

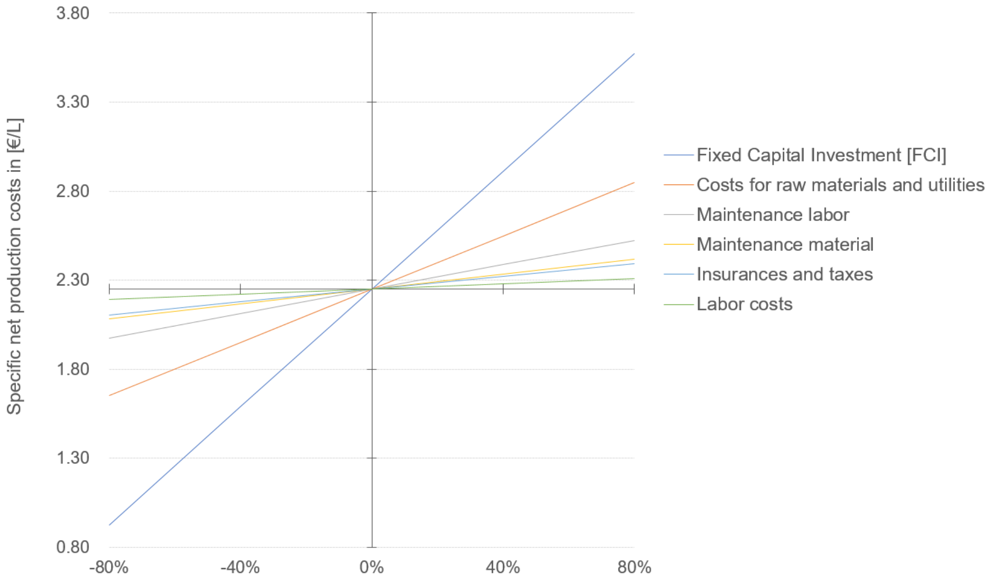


Figure 5-6: Sensitivity analysis – Total

Figure 5.6 presented the variation of specific net production cost when the fixed capital investment costs, direct operational costs and indirect operational costs vary from -80% to +80%, respectively. It is observed that the FCI is the most sensible parameter for net production costs and much more sensible than the others. A decrease of fixed capital investment of 68% can reduce the NPC by half, while 80% less expenses on raw materials and utilities results in only 23% reduction of NPC.

In Figure 5.7 the sensitivities of employed equipment or process units are presented. No surprise that the investment of entrained flow gasifier has the largest impact among all capital costs. By applying a more cost-efficient gasifier or gasification technology can significantly reduce the NPC. Yet the quality of raw gas from gasification must be taken into account alongside since the NPC is sensible to gas cleaning up costs as well. It is worth mentioning that the piping system is an important influence factor for NPC probably due to the complexity of the production process and the heat integration networks.

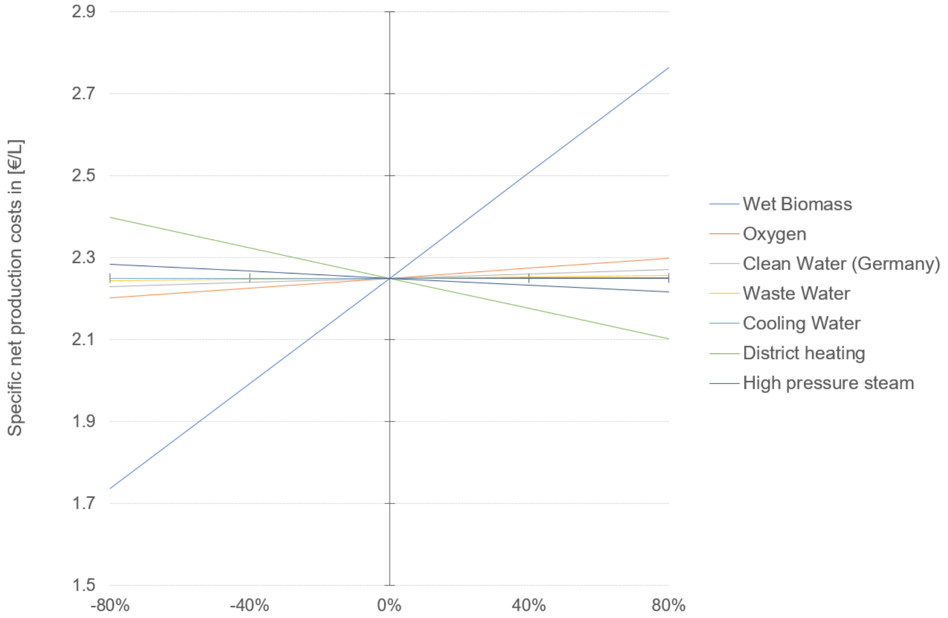


Figure 5-7: Sensitivity analysis – Direct operational costs

An advantage of second generation of biofuel is the much cheaper price of lignocellulosic biomass. In traditional biochemical routes for butanol production, the costs for biomass can contribute to 60% of the net production costs. The raw material prices play a significant role in the fuel production costs. According to Figure 5.8, biomass price is still the most sensible factor among all raw materials and utilities. It turns out that a cheaper biomass resource is desired either for biochemical production or thermochemical production. Also, higher revenues from byproducts helps to improve the economy of the plant and will benefit the NPC.

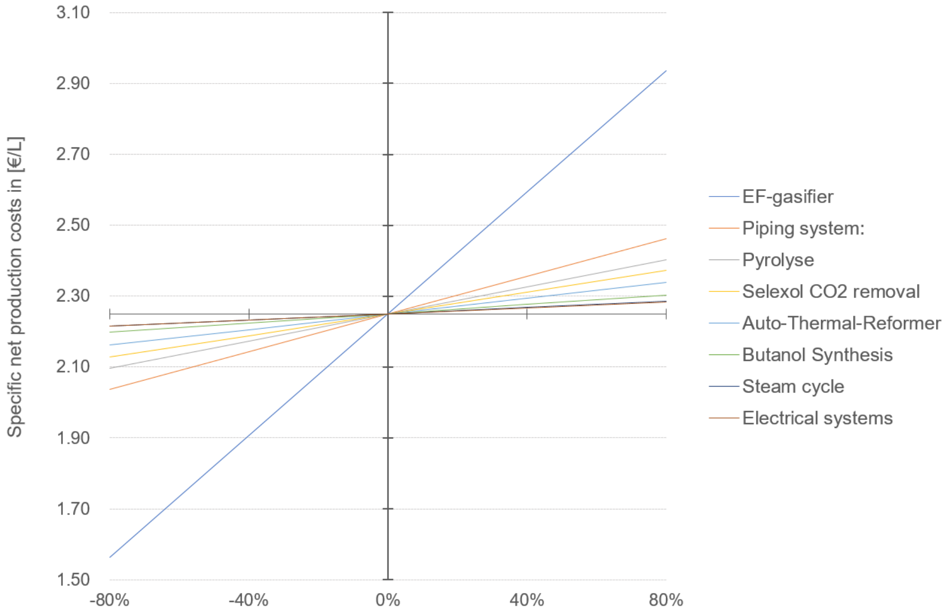


Figure 5-8: Sensitivity analysis – Fixed capital costs

Higher productivity of desired products apparently decrease the net production costs. Figure 5.9 presented the relation between product output and NPC.

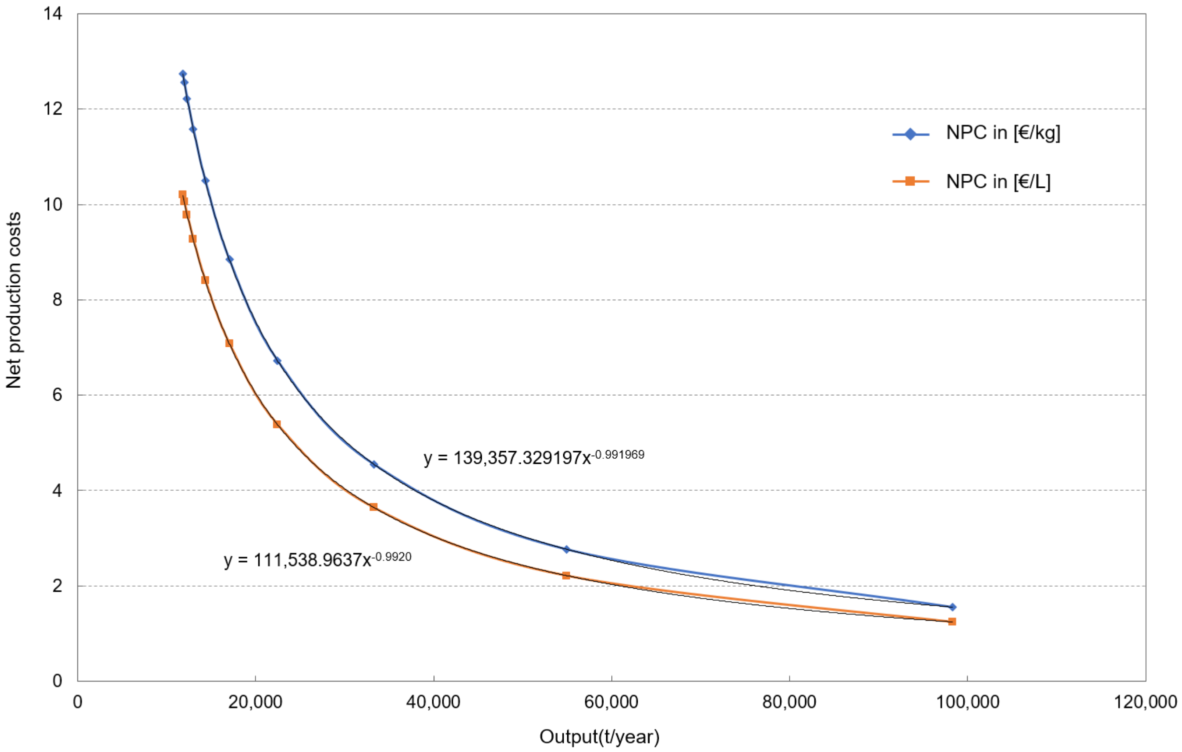


Figure 5-9: Correlation between NPC and Product Output

Process Productivity can be influenced by catalysts performance, process design as well as yearly operating hours. A sufficiently long yearly full load hours, improved catalysts provide high CO conversion and high Butanol and higher alcohol selectivity and an efficient process design contribute to a higher process productivity, which could bring down the net production costs to a competitive level.

6 Conclusion and outlook

6.1 Conclusion

Alternative liquid fuels have been developed for years and are considered to be the only competitive and feasible substitution for fossil fuel to meet the environmental protection targets in short to medium term in transport sector. Advanced biofuel such as biobutanol has attracted more attention in the recent years due to its better fuel properties and compatibility with conventional engines and pipelines. Using traditional cultivated energy crops as feedstocks resulted in a direct competition of bioenergy with food supply. The usage of lignocellulosic biomass as feedstock for biofuel production is a promising choice since they are mostly waste and residual materials from agriculture and forestry. Furthermore, it turns out to have much greater potentials, both technology-wise and in terms of reduction of greenhouse gas emission.

Two common production routes (i.e. biochemical route and thermochemical route) and the available technologies from each route are reviewed. Biochemical route is the conventional method in industry to produce alcohols. Yet further research and development on gene technology and metabolic engineering are needed to be carried out to overcome the limitations of specific bacteria for butanol fermentation. This thesis has focused on the thermochemical route which consists of a gasification of lignocellulosic biomass with subsequent gas cleanup and conditioning to produce syngas and the higher alcohol synthesis of syngas with subsequent alcohol product separation. Among the four possible catalysts groups for mixed alcohol synthesis, the modified methanol synthesis catalysts were chosen due to its relatively higher selectivity to butanol.

The designed production process including all relevant operation conditions was simulated in detail using Aspen Plus®. In the simulation work, several reasonable assumptions or simplifications are conducted. Gas cleanup section including cyclone, sulfur-, nitrogen and alkali components removal is not simulated in Aspen Plus but taken into account in the later economic evaluation.

To enhance the final butanol yield, unreacted syngas is recycled. Methane and other hydrocarbons generated in the synthesis reactor are reformed to produce additional syngas through autothermal reforming. After optimization of process design, the alcohol products yield was significantly enhanced from 55.5 kmol/h to 122.9 kmol/h, among which the butanol yield increased from 34 kmol/h to 75.1 kmol/h. After alcohol separation, a fuel product consists of 88 wt.% of isobutanol and 11 wt.% of propanol is obtained. A higher purity of butanol is probably not necessary since this fuel product already has quite similar fuel properties to pure butanol. More energy consumption for distillation can be saved. Biomass-to-liquid efficiency of 36.7% is obtained while the carbon efficiency is calculated to be 26.5%.

The process was further energetically optimized through heat integration. Based on the pinch analysis, an optimized heat transfer network was built to minimize the external energy utilities. All heating load and most power demand were covered by the heat recovered from process and power generation, respectively. The rest cooling load was met either by district heating supply or cooling water depending on the temperature level of the hot streams. An overall plant efficiency of 60.9% has been achieved.

Based on the simulation results from Aspen Plus, an economic evaluation was carried out by In-house software TEPET to estimate the specific net production costs, which is the key parameter to evaluate the economic feasibility of the designed process. With proper economic assumptions, the NPC of butanol fuel product was calculated to be 2.25 €/l, which is apparently much higher than the acceptable price in the fuel market. Sensitivity analysis was carried out then. It was found that the variation of expense on entrained flow gasifier has the largest impact on NPC, followed by the biomass cost and cost of maintenance labor. Higher output of butanol fuel product decrease the NPC significantly as well, a tendency to reach a comparable price with fossil fuel in the market can be expected when the product output increased by around 70 %. A sufficient cost reduction is strongly required for an eventual commercialized production of biobutanol fuel through thermochemical route in the future.

6.2 Outlook

Except lignocellulosic biomass, another promising feedstock for fuel production is algae, with the advantages such as higher specific yield of raw material and less land usage. Biofuel from algae, which is also called the third-generation biofuel, has appealed to researchers in the recent years. Several pilot plants have been demonstrated to investigate the feasibility of fuel production from algae.

For butanol fuel production through thermochemical route, catalysts research plays a key role in productivity enhancement. An ideal catalyst provides sufficient activity even at relatively low temperature as well as higher conversion and selectivity for butanol or higher alcohols. The operational window with further optimization of operation conditions should be identified by catalysts development. Another interesting possibility for butanol production is the condensation of short-chain alcohols through Guerbet reaction. Since the current mixed alcohol synthesis process produces primarily short-chain alcohols, an updating of those lower alcohols is becoming attractive either as a subsequent step to enhance the higher alcohol yields from mixed alcohol synthesis, or in combination with the mature industrial production process of methanol and ethanol.

Due to the lack of sufficient information in reaction kinetic model, a simplified products distribution of higher alcohol synthesis from relevant literature is assumed. It is expected that experiments based on an advanced catalyst can be carried out or literatures with more detailed kinetic information can be available, so that the simulation can be more precise, convincing and able to predict the products yield when changing the process parameters to find out the optimal point.

Further research on the requirements of alcohols as fuel in conventional engine is needed to identify the suitable composition or properties of produced higher alcohol fuel products, so that a more efficient alcohols separation based on the specific fuel requirements can be achieved.

It is suggested from economic evaluation that biomass gasification units contribute to the most portion of fixed capital investment costs. Taking account of the experience curve effect, the cost of n-th production unit is supposed to be decreased significantly. Higher productivity, well developed production units are desired to eventually bring the biobutanol into fuel market.

7 Index

7.1 List of Figures

7.2 List of Tables

7.3 Publication bibliography

Albrecht, Friedemann G.; König, Daniel H.; Baucks, Nadine; Dietrich, Ralph-Uwe (2017): A standardized methodology for the techno-economic evaluation of alternative fuels – A case study. In *Fuel* 194, pp. 511–526. DOI: 10.1016/j.fuel.2016.12.003.

Bain, Richard L.; Magrini-Bair, Kimberly A.; Hensley, Jesse E.; Jablonski, Whitney S.; Smith, Kristin M.; Gaston, Katherine R.; Yung, Matthew M. (2014): Pilot Scale Production of Mixed Alcohols from Wood. In *Ind. Eng. Chem. Res.* 53 (6), pp. 2204–2218. DOI: 10.1021/ie403631h.

Beretta, Alessandra; Sun, Qun; Herman, Richard G.; Klier, Kamil (1996): Production of Methanol and Isobutyl Alcohol Mixtures over Double-Bed Cesium-Promoted Cu/ZnO/Cr 2 O 3 and ZnO/Cr 2 O 3 Catalysts. In *Ind. Eng. Chem. Res.* 35 (5), pp. 1534–1542. DOI: 10.1021/ie9505219.

Brosowski, A.; Adler, P.; Erdmann, G.; Thrän, D.; Mantau, U.; Blanke, C. et al. (2016): Biomassepotenziale von Rest-und Abfallstoffen–Status quo in Deutschland (BIOPOT)(FKZ 22020114), FNR, Güstrow.

Bundestag, Deutscher (2009): Verordnung über Anforderungen an eine nachhaltige Herstellung von Biokraftstoffen (Biokraftstoff-Nachhaltigkeitsverordnung-Biokraft-NachV). In *Deutscher Bundestag, Berlin*.

Burcham, Maria M.; Herman, Richard G.; Klier, Kamil (1998): Higher Alcohol Synthesis over Double Bed Cs−Cu/ZnO/Cr 2 O 3 Catalysts. Optimizing the Yields of 2-Methyl-1-propanol (Isobutanol). In *Ind. Eng. Chem. Res.* 37 (12), pp. 4657–4668. DOI: 10.1021/ie9705620.

by Indirect, Thermochemical Pathway (2011): Process design and economics for conversion of lignocellulosic biomass to ethanol. In *Contract* 303, pp. 275–3000.

Chakraborty, Sumit; Piszel, Paige E.; Hayes, Cassandra E.; Baker, R. Tom; Jones, William D. (2015): Highly Selective Formation of n-Butanol from Ethanol through the Guerbet Process. A Tandem Catalytic Approach. In *Journal of the American Chemical Society* 137 (45), pp. 14264–14267.

Chapter 10 Pinch point analysis (2008). In Alexandre C. Dimian (Ed.): Integrated design and simulation of chemical processes, vol. 13. 1. ed., transferred to digital print. Amsterdam [u.a.]: Elsevier (Computer-aided chemical engineering, 13), pp. 393–434.

Dahmen, Nicolaus; Henrich, Edmund; Dinjus, Eckhard; Weirich, Friedhelm (2012): The bioliq® bioslurry gasification process for the production of biosynfuels, organic chemicals, and energy. In *Energ Sustain Soc* 2 (1), p. 3. DOI: 10.1186/2192-0567-2-3.

Dowson, George R. M.; Haddow, Mairi F.; Lee, Jason; Wingad, Richard L.; Wass, Duncan F. (2013): Catalytic conversion of ethanol into an advanced biofuel: unprecedented selectivity for n-butanol. In *Angewandte Chemie (International ed. in English)* 52 (34), pp. 9005–9008. DOI: 10.1002/anie.201303723.

Durre, Peter (2011): Fermentative production of butanol--the academic perspective. In *Current opinion in biotechnology* 22 (3), pp. 331–336. DOI: 10.1016/j.copbio.2011.04.010.

Dutta, Abhijit; Phillips, Steven (2009): Thermochemical ethanol via direct gasification and mixed alcohol synthesis of lignocellulosic biomass: National Renewable Energy Laboratory Golden, CO.

Ezeji, Thaddeus Chukwuemeka; Qureshi, Nasib; Blaschek, Hans Peter (2007): Bioproduction of butanol from biomass: from genes to bioreactors. In *Current opinion in biotechnology* 18 (3), pp. 220–227. DOI: 10.1016/j.copbio.2007.04.002.

Fachagentur Nachwachsende Rohstoffe e.V.: Basisdaten Bioenergie Deutschland 2016.

Gevo (2016).

Green, Edward M. (2011): Fermentative production of butanol--the industrial perspective. In *Current opinion in biotechnology* 22 (3), pp. 337–343. DOI: 10.1016/j.copbio.2011.02.004.

Greenwell, H. C.; Laurens, L. M. L.; Shields, R. J.; Lovitt, R. W.; Flynn, K. J. (2010): Placing microalgae on the biofuels priority list: a review of the technological challenges. In *Journal of the Royal Society, Interface* 7 (46), pp. 703–726. DOI: 10.1098/rsif.2009.0322.

Guo, Wenwen; Li, Guoneng; Zheng, Youqu; Wang, Shurong (2016): Simulation Study of Thermochemical Process from Biomass to Higher Alcohols. In *Energy Fuels* 30 (11), pp. 9440–9450. DOI: 10.1021/acs.energyfuels.6b01687.

Henstra, Anne M.; Sipma, Jan; Rinzema, Arjen; Stams, Alfons J. M. (2007): Microbiology of synthesis gas fermentation for biofuel production. In *Current opinion in biotechnology* 18 (3), pp. 200–206. DOI: 10.1016/j.copbio.2007.03.008.

Herman, R.G (2000): Advances in catalytic synthesis and utilization of higher alcohols. In *Catalysis Today* 55 (3), pp. 233–245. DOI: 10.1016/S0920-5861(99)00246-1.

Hoflund, Gar B.; Epling, William S.; Minahan, David M. (1999). In *Catalysis Letters* 62 (2/4), pp. 169–173. DOI: 10.1023/A:1019011408962.

Kaltschmitt, Martin; Hartmann, Hans; Hofbauer, Hermann (Eds.) (2016): Energie aus Biomasse. Grundlagen, Techniken und Verfahren. 3., aktualisierte Auflage. Berlin, Heidelberg: Springer Berlin Heidelberg (SpringerLink : Bücher).

Kreyenberg, Danny; Lischke, Andreas; Bergk, Fabian; Duennebeil, Frank; Heidt, Christoph; Knoerr, Wolfram et al. (2015): Erneuerbare Energien im Verkehr Potenziale und Entwicklungsperspektiven verschiedener erneuerbarer Energieträger und Energieverbrauch der Verkehrsträger.

Kujawska, Anna; Kujawski, Jan; Bryjak, Marek; Kujawski, Wojciech (2015): ABE fermentation products recovery methods—A review. In *Renewable and Sustainable Energy Reviews* 48, pp. 648–661. DOI: 10.1016/j.rser.2015.04.028.

Kumar, Ajay; Jones, David D.; Hanna, Milford A. (2009): Thermochemical Biomass Gasification. A Review of the Current Status of the Technology. In *Energies* 2 (3), pp. 556–581. DOI: 10.3390/en20300556.

Luk, Ho Ting; Mondelli, Cecilia; Ferre, Daniel Curulla; Stewart, Joseph A.; Perez-Ramirez, Javier (2017): Status and prospects in higher alcohols synthesis from syngas. In *Chemical Society reviews* 46 (5), pp. 1358–1426. DOI: 10.1039/c6cs00324a.

Matsumura, Yasuyuki; Nakamori, Toshie (2004): Steam reforming of methane over nickel catalysts at low reaction temperature. In *Applied Catalysis A: General* 258 (1), pp. 107–114.

Okoli, Chinedu; Adams, Thomas A. (2014): Design and Economic Analysis of a Thermochemical Lignocellulosic Biomass-to-Butanol Process. In *Ind. Eng. Chem. Res.* 53 (28), pp. 11427–11441. DOI: 10.1021/ie501204r.

Peters, Max Stone; Timmerhaus, Klaus D.; West, Ronald E. (2006): Plant design and economics for chemical engineers. 5. ed., internat. ed., [Nachdr.]. Boston [u.a.]: McGraw-Hill (McGraw-Hill chemical engineering series).

Qureshi, Nasib; Ezeji, Thaddeus C. (2008): Butanol, ‘a superior biofuel’ production from agricultural residues (renewable biomass). Recent progress in technology. In *Biofuels, Bioprod. Bioref* 2 (4), pp. 319–330. DOI: 10.1002/bbb.85.

Ryan, C.; Munz, D.; Bevers, G. (2011): Isobutanol-a renewable solution for the transportation fuels value chain. In *Pipeline Stress Corrosion Cracking (SCC) and Elastomeric Compatibility*.

2015: Specification for Butanol for Blending with Gasoline for Use as Automotive Spark-Ignition Engine Fuel.

Spivey, James J. (2014): Catalytic conversion of syngas to i-butanol–Synthesis routes and catalyst developments. A review. In *SPR Catalysis V26* 26, pp. 161–178.

the Linde Group. (2014).

Tremel, Alexander; Becherer, Dominik; Fendt, Sebastian; Gaderer, Matthias; Spliethoff, Hartmut (2013): Performance of entrained flow and fluidised bed biomass gasifiers on different scales. In *Energy Conversion and Management* 69, pp. 95–106. DOI: 10.1016/j.enconman.2013.02.001.

Tseng, Kuei-Nin T.; Lin, Steve; Kampf, Jeff W.; Szymczak, Nathaniel K. (2016): Upgrading ethanol to 1-butanol with a homogeneous air-stable ruthenium catalyst. In *Chemical communications (Cambridge, England)* 52 (14), pp. 2901–2904. DOI: 10.1039/c5cc09913g.

Umweltbundesamt (2015).

Verkerk, Kai A.N.; Jaeger, Bernd; Finkeldei, Caspar-Heinrich; Keim, Wilhelm (1999): Recent developments in isobutanol synthesis from synthesis gas. In *Applied Catalysis A: General* 186 (1-2), pp. 407–431. DOI: 10.1016/S0926-860X(99)00158-1.

Visioli, Luiz J.; Enzweiler, Heveline; Kuhn, Raquel C.; Schwaab, Marcio; Mazutti, Marcio A. (2014): Recent advances on biobutanol production. In *Sustain Chem Process* 2 (1), p. 15. DOI: 10.1186/2043-7129-2-15.