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A Review of Separation Technologies in Biomass-to-liquid Transportation Fuels Production Processes

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ABSTRACT: A critical review of separation methods and technologies for lignocellulosic biomass conversion through thermochemical processes to liquid fuels is presented. The multistep processing of biomass includes thermochemical conversion, product upgrading and final fuels separation. Chemicals and biofuels are produced from intermediate streams in each processing section. In the thermochemical conversion, product streams from gasification, liquefaction and pyrolysis require separation technologies for conditioning of main products and removal of impurities. In the upgrading the separation technologies play an important role in the definition of different process configurations for conversion of unstable hydrocarbon fractions into specific biofuel types and chemicals via upgrading reactions. In the final fuels' separation section, separation technologies must be implemented to separate desired biofuels from gases, chemicals, wastewater and solid products. Hence, for total BtL processes, separation technologies are important to improve the interface between the sections and to determine the substructures and subsequent processing methods and techniques. It is observed that separation is more demanding in such biorefinery processes for BtL productions. On the other hand, the widely used separation methods in refineries are also mostly employed in BtL processes including phase separation, scrubbing, filtration, extraction, absorption, distillation, fractionation.

Keywords: Separation technologies, lignocellulosic biomass, biofuels, thermochemical conversion, product upgrading and fuels recovery, mixture characterization.

1. Introduction

Separation technologies play an important role in the total production processes for chemical industries. In a thermochemical process route for the conversion of biomass to liquid transportation fuels, the processing streams are complex mixtures with many components. Therefore, separation and purification technologies are required in the recovery and purification of value-added materials, product streams, advanced biofuels, as well as in the purification of waste streams to prevent contaminants to be released to the environment.

Separation technologies generally account for a substantial part of both total capital and energy costs, since in most cases a chemical plant contains several separation steps. Depending on the chemical process, the investments in separations technologies can typically account for 30-70% of the total capital cost (Agrawal, 2001; de Haan, 2015). For instance, in biorefineries, the costs of separation and purification technologies account for 20–50% of the total costs (Huang and Ramaswamy, 2013).

Moreover, the separation technologies not only have an effect in the final production costs but also in the process configuration, product distribution and final product profiles. In recent studies, there has been limited research on the separation technologies involved in the thermochemical based biorefineries, also known as biomass-to-liquid (BtL) processes, as the majority of the work has focused on the reactor operation and design, as well as on the products upgrading obtained from the thermochemical conversion to advanced biofuels and chemicals.

The synthesis, design and modeling of BtL separation technologies depend on the characterization of the feedstocks and reactor effluent mixtures. BtL products are complex mixtures containing hundreds of distinct molecular species in inexact proportions, mainly composed of organic compounds (Chen, 2015). Describing the behavior of the mixtures is important to determine the real separation needs as well as to design and operate commercial

BtL processes. However, the identification of the thousands of molecular components and defining their reaction mechanisms has been a challenge.

Also, different refinery process configurations can be explored by employing different separation and upgrading technologies which can maximize the production of a specific fuel type to meet the fuel specifications.

1.1 Importance on Characterization of Product Streams: Analytical Methods and Selection of Model Compounds

In recent studies, the characterization of the main products from the thermochemical conversion of biomass, namely bio-oil, has been explored. Detailed understanding of the composition of bio-oil at the molecular level is important to optimize a processing and separation strategy in upgrading and valorization of biomass as fuels and other value added chemicals. Bio-oil is a complex mixture of hundreds of compounds with different functional groups and distinct physical and chemical properties, and therefore the identification of all the components with existent methods is a challenge. The most commonly used technique to identify and quantify bio-oil components is gas chromatography-mass spectroscopy (GC-MS), including techniques such as pyrolysis (py)-GC-MS and GC-quadrupole time-of-flight (Q-TOF)-MS, and GC-flame ionization detector (FID). However, GC-MS and other GC methods such as GC-FID has some limitations, as they are only able to analyze compounds with relatively low boiling points such as short-chain and/or nonpolar compounds (Khuenkaero and Tippayawong, 2020). For the analysis of larger polar compounds by GC methods, a derivatization step is usually required (Lu et al., 2017). For example, the analysis of bio-oils by high-resolution mass spectrometry (HRMS) techniques, which are able to detect small volatile compounds and polar compounds, revealed the presence of over 800 compounds in the bio-oils but only around 40 of these could be detected by GC-MS (Smith et al., 2012). This difference is due to higher resolution of the HRMS instruments but also due to the fact that bio-oils typically contains a large portion of polar lignin and carbohydrate derived components, which are nonvolatile and undetectable by GC-MS (Smith et al., 2012; Lu et al., 2017). Spectroscopic techniques such as Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectroscopy have been shown to be useful techniques for characterization and quantification of functional groups in bio-oils (Ben and Ragauskas, 2013; Fortin et al., 2015; Santos et al. 2015; Joseph et al., 2016; Lu et al., 2017). Mullen et al. (2009) explored the characterization of various fast pyrolysis bio-oils by NMR spectroscopy, including one dimensional (1D) ^{1}H NMR and ^{13}C NMR using distortionless enhancement by polarization transfer (DEPT) to determine the multiplicity of ^{13}C signals and found that these experiments can provide important information concerning the types of chemicals present in the bio-oil and their relative concentration. Likewise, this information could be useful for further refining of bio-oils into liquid transportation fuels. However, for a better characterization of bio-oil components, the signal resolution and sensitivity must be improved, and this could be done by using 2D NMR, which constitute another promising technique for detailed characterization of various types of compounds in bio-oils (Lu et al., 2017). Heteronuclear single-quantum correlation (HSQC) NMR has, for example successfully been used to characterize different types of C-H bonds and their presence in different moieties of compounds in bio-oils such as aliphatic, guaiacol, and ferulate structures (Ben and Ragauskas, 2013; Yu et al., 2016).

Elemental analysis is another method that has been employed in the characterization of bio-oil in combination with other spectrometric techniques. Sipilä et al. (1998) developed an analytical scheme for characterization of bio-oil by combination of solvent fractionation, elemental analysis (C,H,N) and GC-MS and py-GC-MS and found that these methods are more effective for determining the nature and behavior of pyrolysis oils and in drawing correlations between physical properties and chemical composition of the whole bio-oil. Venderbosch et al. (2010) reported the results of the characterization of pine derived bio-oil by a solvent fractionation method, GC-MS, py-GC-MS and elemental analysis (C,H,N) and concluded that the bio-oil can be divided in different compound types and functional groups, which are acids, alcohols, ketones, aldehydes, guaiacols, low and high molecular weight (MW) sugars. However, to complete understand the molecular complexity of bio-oils the application of analytical methods such as FTIR, NMR, GC-MS and elemental analysis are not sufficient. These analytical methods should be combined with HRMS techniques such as Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS), Orbitrap MS or quadrupole time-of-flight mass spectrometry (Q-TOF-MS) to obtain sufficient detailed information in order to make a proper characterization of the bio-oil. Analysis by HRMS techniques can be done by direct injection into the mass spectrometer via sample loop (Smith et al., 2012; Staš et al., 2015) but usually separation of the bio-oil components into nonpolar, polar and high MW compounds is performed by liquid chromatography such as high-performance liquid chromatography (HPLC) or ultra- performance liquid chromatography (UPLC) before HRMS analysis (Lu et al., 2017). The most used ionization techniques in HRMS are atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI) in positive and/or negative mode. APCI is less prone to matrix effects and is able to ionize a broad spectrum of molecules including nonpolar compounds, whereas electron spray ionization (ESI) typically require a heteroatom, e.g., oxygen or nitrogen, for ionization although ESI has been used to detect a relative wide range of compounds in bio-oils (Lu et al., 2017; Bjelić et al., 2018). However, a combination of APCI and ESI ionization methods is well suited for the characterization of different types of molecular species in bio-oils in order to obtain as complete a picture of the oil composition as possible. LC-HRMS has, for example been used to obtain detailed information on hydrothermal liquefaction (HTL) bio-crude produced from lignocellulosic biomass as well as the upgraded fuels obtained via catalytic hydrotreatment (Bjelić et al., 2018) and to characterize the molecular species of pine pellet and peanut hull pyrolysis bio-oils (Jarvis et al., 2012). More information on the analytical strategies for optimal separation of bio-oil components by the use of 2D chromatographic GC × GC and LC × LC methods as well as spectrometric and spectroscopic methods for the characterization of bio-oil components produced from lignocellulosic biomass can be found in the review of Lu et al. (2017).

At this stage, performing the characterization of the bio-oil allows the study of different product recovery pathways. For instance, recovery of the different compound fractions can be explored for production of value-added chemicals or for elimination of contaminants from the bio-oil, which can be further upgraded to liquid transportation fuels.

If the bio-oil is upgraded to transportation fuels, then the upgraded products composition is required for the definition of the separation process configuration. Several separation configuration networks can be explored depending on the feed composition and the desired product profile. Similarly, as in the bio-oil characterization, the analysis of the composition of hydrocarbon mixtures and aromatic fractions has been limited to the carbon and hydrocarbon content measurement by NMR and mass spectroscopy analysis of predominant compound types, and the boiling point distribution (Robinson and Cook, 1969). These mixtures are often characterized at best only in terms of average compositions of wide boiling fractions (Quann and Jaffe, 1992). In the same way as done for the bio-oil, the complex mixtures are grouped into compound classes or boiling range fractions (Quann and Jaffe, 1992).

For the modeling and simulation of BtL industrial processes, including reaction and separation technologies, the definition of a substitute mixture is required. Therefore, model compounds are used to represent the complex mixtures, namely pyrolysis oil, liquefaction bio-oil, FT hydrocarbon product, synthetic natural gas, bio-crude, upgraded fractions and final advanced transportation fuels. Most of the model compounds are available in the software databases, however, several are user defined compounds. Compound properties are based on experimental data or estimated if needed. For example, the National Renewable Energy Laboratory in collaboration with the Idaho National Laboratory and the Pacific Northwest National Laboratory developed the modeling in Aspen Plus of a thermochemical process for converting BtL transportation fuels via fast pyrolysis by using model compounds to represent the complex mixtures. Most of the model compounds were available in Aspen database and/or defined based in experimental data and data estimated by the UNIFAC contribution group method and ACD labs software (Jones et al., 2013).

2. Overview of the Biomass-to-liquid Process Technological Sections

The conversion of lignocellulosic biomass to liquid transportation fuels, also known as advanced biofuels, can be accomplished via biochemical or thermochemical routes. In this review, the separation needs, and technologies related to the conversion of lignocellulosic biomass via thermochemical-based technologies is explored, as presented in Figure 1.

[Figure 1 here]

Figure 1. Separation needs in the thermochemical-based biomass to liquid technologies

The first step in the thermochemical conversion of biomass, is the raw materials preparation and biomass pretreatment. Then, the biomass is converted to syngas via gasification or to bio-oil via pyrolysis or liquefaction. This step is best known as the thermochemical conversion section, as can be observed in Figure 1. The next step is the upgrading of the gasification syngas into Fischer-Tropsch (FT) hydrocarbon products or the upgrading of the pyrolysis or liquefaction bio-oil compounds into bio-crude containing gasoline, diesel and jet fuel range components via technologies such as catalytic cracking and hydroprocessing. Regarding the FT products, these can be further upgraded to transportation fuels via technologies such as olefin alkylation, oligomerization, naphtha hydrotreating and catalytic reforming, distillate hydrotreating, wax hydrocracking, and alcohols hydrogenation.

The final step is the advanced biofuels separation section, in which the recovery and/or fractionation of the bio-crude into gases, naphtha, distillate and wax range components is performed.

In all three sections, several separation technologies are required to accomplish the section's objectives. The separation needs in each section and the current separation technologies that have been studied are described in the following sections.

3. Separation Needs and Technologies in the Raw Materials Preparation and Biomass Pretreatment Section

The first step in the processing of biomass is the pretreatment, it allows the modification of undesirable properties of biomass and improves the conversion efficiency. For the thermochemical conversion processes, pretreatment is used to facilitate material handling, transportation, heat and mass transfer. Pretreatment techniques in the thermochemical conversion routes include mechanical (grinding), thermal (torrefaction, steam explosion/liquid hot water pre-treatment, and ultrasound/microwave irradiation), and chemical (treatment with acids, bases, and ionic liquids) (Liu, et al., 2017). However, for the lignocellulosic biomass conversion to liquid transportation fuels (biogasoline, green diesel and biojet fuel), the main properties considered in the pretreatment of lignocellulosic biomass are size distribution, particle shape, moisture content, bulk and particle densities, compressibility and compact ratio, which are performed without the need of separation technologies (Pandey et al., 2015).

Moreover, none of these pretreatment techniques require the separation of the lignocellulosic biomass components (lignin, hemicellulose and cellulose), as required for the biochemical conversion routes.

On the other hand, separation processes are essential for raw materials preparation. For instance, in the biomass gasification, Purified oxygen is preferred rather than air to prevent introducing large quantities of nitrogen into the syngas where it can act as an inert diluent. For this, a pressurized cryogenic air separation unit is necessary to provide purified oxygen for the gasifier (Zhu et al., 2011).

In the biomass pyrolysis, non-condensable gases (NCG) are used as fluidizing agents in the pyrolysis reactor. NCG are produced during the total process and could be recovered with the use of quench towers and demisters (Jones et al., 2013; Ibarra-Gonzalez and Rong, 2018).

With respect to biomass liquefaction, when using wet biomass as feedstock, a pumpable slurry with low solids content needs to be produced. For instance, Elliot et al. reported in their work that sorghum stalks should be chopped and processed through a wet ball mill and filtered through an 18 mesh screen to produce a slurry at 4–6% dry solids that can be pumpable at up to 21 MPa (Chen et al., 2011). Besides filtration, separation technologies are not used in the pretreatment section or in the preparation of raw materials.

4. Separation Needs and Technologies in the Thermochemical Conversion Section

In the thermochemical conversion section, several separation methods are employed for the recovery of the main products, for the removal of impurities and to isolate high-value chemicals. These actions facilitate the further upgrading of the main products into transportation fuels.

The main products from the lignocellulosic biomass conversion via thermochemical technologies (gasification, pyrolysis and liquefaction) are syngas or bio-oil, solid residues (biochar and ash), non-condensable gases, syngas contaminants, and an aqueous phase with soluble organic compounds as by-product from liquefaction. In addition, in the thermochemical section, sand is combusted and sent to the pyrolysis reactor and gasifier to provide the necessary heat and some of it is carried over with the products. Likewise, excess water is used during the process and therefore the aqueous fraction requires the application of separation technologies for its treatment and separation.

4.1 Removal of Solid Products

The fast pyrolysis reaction converts 50–75% of lignocellulosic biomass to pyrolysis gases, however, other products including biochar and non-condensable gases are produced (Papari and Hawboldt, 2018). From these, the gaseous streams exiting the pyrolysis reactor contain biochar particles of various sizes that should be removed before cooling down the product into pyrolysis oil. Likewise, from the gasification reaction, the main product is syngas, however by-products such as tar, ash and biochar are formed (Klinghoffer, 2013). The tars must be decomposed, as they can cause clogging in downstream equipment (Wright et al., 2010). On the other hand, the other by-products, biochar and ash must be removed. The amount and composition of by-products is important to determine the appropriate solid separation technologies and to improve the efficiency of the conversion of the main product into biofuels. Ash is the solid residue composed of inorganic elements that are inherently present in the lignocellulosic feedstock, whereas biochar is a solid residue that is composed primarily of carbon and ash. Moreover, the reaction conditions influence the distribution of these by-products at the reactor´s outlet stream. For instance, if the gasification is operated at higher temperatures or with more oxidant, it is more likely to form ash, whereas operating at lower temperatures or with less oxidant results in more residual carbon, namely biochar (Klinghoffer, 2013).

The reaction type and conditions also affect the particle size distribution. The solid particles from gasification present sizes of around 100 microns (NETL, 2009). On the other hand, the pyrolysis particles, compared to the solid particles generated from gasification, can be much smaller, with sizes less than 25 microns. The particle size is important because it affects the design and performance of the solid separators, such as cyclones and filters (Wright et al., 2010).

In a typical pyrolysis design, to improve the interface between the thermochemical conversion and the further upgrading into biofuels, gases from the pyrolysis reactor first pass through a solid separator to remove char and ash. As in gasification, solids removal designs differ depending on the overall process conditions and solid particles sizes. For example, one or two gas-solid cyclones can be used for the separation or can be also connected or not to a hot ceramic filter. Van de Velden et al. (2007) performed the fast pyrolysis of biomass under different configurations and proposed a final experimental design including a low-efficiency cyclone and a high efficiency cyclone. The first, is used for removing circulating bed material, namely sand with particle sizes of 100 microns, and the latter being used for char removal. Hwang et al. (2016) examined the conversion of an energy crop for production of bio-oil through fast pyrolysis, and found that a gas mixture with small amounts of char were discharged from the top outlet of the reactor. In addition, a high amount of heavy char particles and sand particles were discharged in the bottom outlet. The gas mixture with the small char particles were then sent to a single cyclone, where char particles were separated and collected (Hwang et al., 2016). Chen et al. (2011) evaluated the effect of hot vapor filtration (HVF) in the final bio-oil yield. The HVF was used to remove the biochar and other solid particles from the main product, and found that the total bio-oil yield decreased from 41.7%, when using only a cyclone, to 39.5% by weight when it was coupled with HVF. Moreover, when using HVF, the bio-oil presented higher water content, lower alkali metal content and higher pH.

Additionally, cyclones can be also coupled to baghouse filters in the pyrolysis conversion process, however, the conventional baghouse filters require modifications to be used in these applications, and after the modifications they could still reduce the bio-oil yield and require high-cost maintenance caused by vapor condensation and coking on the surface of the filter (Wright et al., 2010).

In the biomass gasification, as described before, the gas obtained is raw and not clean enough to use. A purification process is carried out to eliminate impurities like ash, char, tar, sulfur compounds, methane, water vapor and carbon dioxide. For the solid's removal, the same technologies employed for the pyrolysis process can be considered, as presented in Figure 2.

[Figure 2 here]

Figure 2. Solids removal using cyclones

The products from hydrothermal liquefaction are bio-oil, a gaseous stream containing carbon dioxide, biochar and an aqueous phase with small concentrations of soluble organic compounds. For example, the bio-crude produced from algae contains high concentrations of dry solids of up to 34 wt.% (Elliott et al., 2015), leading to low bio-oil yield. As observed, the yield of the bio-crude is a function of the concentration of dry solids in the wet feedstock. As the product from liquefaction is already in liquid phase then filtration is a viable technique for separation of solids. Posmanik et al. (2017) and Karagöz et al. (2005) performed the separation of solids from the aqueous, and oil phases by vacuum filtration.

4.2 Pyrolysis Bio-oil Condensation and Purification

After the pyrolysis gases are generated and the solid particles have been removed, it is critical to thermally quenched the gaseous products. This is done to avoid secondary reactions and to preserve the compounds that form the bio-oil, as well as for the removal of undesirable compounds. If failing to do so, most of these compounds can crack to gases impossible to be further liquified or can polymerize to biochar (Ringer et al., 2006).

For the bio-oil recovery, there are three different techniques: electrostatic precipitation, indirect condensation, or combined scrubbing-condensation. Among these techniques, combined scrubbing and condensation is recommended because electrostatic precipitation presents high costs and indirect condensation can lead to fouling of the surface of the heat exchangers due to preferential deposition of lignin fraction (Van de Velden et al., 2007).

Therefore, a general pyrolysis process consists of two main sections, the reactor followed by the solid separators and a condensing system. In the reactor the biomass is converted to volatile vapors, non-condensable gases and biochar, and from the condensing system the condensable gases are recovered as a liquid product. Moreover, in the condensing system or volatile vapor recovery unit, the condensable gases are separated from non-condensable gases.

Condensing systems include single condenser, multi-condenser and fractional systems. Single condenser and multi-condenser systems are employed for bulk separation of non-condensable gases and water to produce one liquid. On the other hand, fractional systems generate more than one liquid product. For the pyrolysis bio-oil separation, fractional methods include liquid chromatography, centrifugation, molecular distillation, extraction, fractional condensation and precipitation by adding water. However, from these, liquid chromatography, centrifugation, extraction and molecular distillation are not cost-effective for large-scale application. In addition, molecular distillation, to overcome the thermal instability of compounds in bio-oil, presents high energy consumption and it is time consuming (Papari and Hawboldt, 2018).

The use of condensers to separate the bio-oil is a promising alternative, because its application is less energy intensive, and higher quality liquids and product streams are produced, which can be further refined to high value chemicals and fuels (Cai and Liu, 2016).

Common condensers used in biomass pyrolysis systems include spray towers or scrubbers and shell and tube heat exchangers. In large-scale applications, scrubbers recirculate bio-oil or an immiscible hydrocarbon solvent or water to quench pyrolysis gases. Spray towers are commonly connected to a heat exchanger to cool the spray and bio-oil. Cai and Liu (2016) developed a commercial-scale biomass fast pyrolysis plant and for the recovery of the bio-oil a spray tower system was considered. The pyrolysis gases were quenched in the spray tower by recirculating liquid bio-oil that was previously cooled with water at atmospheric conditions in a tubular heat exchanger. Even though spray towers provide excellent heat transfer and are efficient technologies for the collection of aerosols, the direct contact of the pyrolysis gases at high temperatures and the spray can result in cracking reactions in the spray, which lowers the bio-oil yield (Papari and Hawboldt, 2018).

Westerhof et al. evaluated the effects of the condensation conditions on the bio-oil composition and yield. A system for the condensation of the pyrolysis vapors considering two counter-current spray condensers connected in series was evaluated. From the results, it was concluded that fractional condensation is a promising cheap method to control the quality of pyrolysis oils by concentrating compounds classes, making it more suitable for further applications, such as upgrading reactions (Westerhof et al., 2011). Tumbalam Gooty et al. (2014) performed the fractional condensation of bio-oil from birch bark pyrolysis using a series of three condensers working at different temperatures. The results proved that fractional condensation can successfully recover bio-oil with a water content of less than 1 wt.%.

On the other hand, in lab and pilot-scale applications, shell and tube heat exchangers are commonly used. In the pyrolysis process to quench the pyrolysis gases circulating in the tubes or shell, a coolant, such as ethylene glycol or water, is used in the shell or tubes, and no posterior cooling of the liquid bio-oil is necessary (Papari and Hawboldt, 2018).

4.3 Recovery of Non-condensable Gases

The non-condensable gases from biomass pyrolysis, including vapors, gases and aerosols, are composed mainly of carbon monoxide, carbon dioxide, hydrogen, methane, ethylene, ethane, propylene, and propane (Pattiya, 2018). In a pyrolysis process, these gases can be used as a fluidization gas for a fluid bed reactor or can be combusted to supply the heat for heating biomass and/or to deliver the reaction heat (Van De Velden et al., 2007). Due to its applications, non-condensable gases should be recovered and collected during the process.

As described in the previous section, on the condensing system, bio-oil is separated from non-condensable gases. For instance, in a system including spray towers placed in series, the non-condensable gases are gradually recovered at the top of the columns. In a study performed by Jones et al. (2013) two spray towers in series were considered in the pyrolysis plant design. In the first spray tower, the non-condensable gases were recovered together with some remaining bio-oil components and therefore a second column was required to separate completely the non-condensable gases from the bio-oil. In addition, in some process configurations, the spray towers are coupled with a demister, as presented in Figure 3. Aerosols as part of the non-condensable fraction still contain liquid droplets (Rengel, 2007), which should be removed. The demister assists in the separation of the liquid droplets from the permanent gases. Commonly, an electrostatic precipitator is used as a demister. The electrostatic precipitator allows the removal of liquid droplets from permanent gases by means of an electrostatic field of force produced by a discharge electrode and a collecting electrode (Mussatto, 2016).

[Figure 3 here]

Figure 3. Removal of non-condensable gases with spray towers coupled to a demister

4.4 Syngas Cleaning and Conditioning

Due to the large variety of biomass feedstocks that can be processed via gasification, different raw syngas products with fluctuating compositions can be produced. Generally, the raw syngas contains CO, CO_2, H_2 and CH_4 as well as minor quantities of undesirable impurities, which are significant depending on the end use of the syngas. These impurities also known as syngas contaminants include particulates, tar, nitrogenous compounds (hydrogen cyanide and ammonia), sulfur compounds (carbonyl sulfide and carbon disulfide, hydrogen sulfide), hydrogen halides and halogens (chlorine and hydrogen chloride), and trace metals (Abdoulmoumine et al., 2015). The presence of these impurities in the syngas can highly affect the operation of the total BtL process and can interfere with downstream applications (Chiche et al., 2013; Woolcock and Brown, 2013). Therefore, the application of technologies for its removal is of high importance.

The technologies for removing contaminants from raw syngas are classified as cold, warm and hot, according to the outlet temperature of the syngas coming from the cleaning device. Cold gas cleanup technologies operate near ambient conditions, warm gas cleanup technologies operate at temperatures higher than the water boiling point and finally hot gas cleanup technologies are applied at temperature ranges from 400-1300 °C or higher (Woolcock and Brown, 2013).

Moreover, depending on the condensation temperatures of the undesired compounds, these technologies can be defined. For instance, cold gas cleanup technologies, such as water wash cleaning, allow contaminants to be absorbed into the water droplets or to serve as nucleation sites for water condensation. Some type of impurities that can be condensed at the gasifier outlet are KCl, NaCl, ZnS, HgS. These impurities contained in the raw syngas in the form of aerosols are usually removed by water wash cleaning technologies, namely scrubbers or spray towers, or removed by filtration. Moreover, elements like F, Cl and Br, which present high solubility in water, are also expected to be removed completely with water spray towers or scrubbers (Chiche et al., 2013).

Warm gas cleanup occurring at temperatures up to 300 °C allow for ammonium chloride condensation and hot gas cleanup occurring at higher temperatures results in condensation of several alkali compounds (Hirohata et al., 2008). The separation technologies can be further described depending on the type of impurity.

As mentioned before, one of the main impurities in syngas is tar. Tar is defined as "*all organic compounds with molecular weights greater than that of benzene*" (Maniatis and Beenackers, 2000; Devi et al., 2003). Tars include a wide range of compounds like oxygenates, phenolic compounds and olefins, aromatic and polyaromatic hydrocarbons (Milne et al., 1998). Biomass gasification processes produce a large number of different tar species depending on the process operation conditions (temperature, pressure, type and amount of oxidant, and residence time) and feedstock composition (Kinoshita et al., 1994). The removal of the tar contained in the syngas should be highly considered because it causes fouling and blocking in downstream processing equipment (Tarnpradab et al., 2017). Generally, removal of tar from syngas is carried out in scrubbers with the use of a liquid absorbent. The most common liquid absorbent for scrubbing tars is water because it is cheaper (Unyaphan et al., 2017). Water scrubbing can remove light and oxygenated tar compounds due to their natural polarity, however, a low removal efficiency has been reported for heterocyclic and non-polar heavy tar compounds. The main disadvantages of the use of water scrubbing for tars removal are low removal efficiency and the need of wastewater treatment, which adds extra cost to the process (Abdoulmoumine et al., 2015). Thus, the selection of the solvent is critical to maximize the removal efficiency. Recent advancements have focused on oil-based absorbents that afford high efficiency for tar removal (Phuphuakrat et al., 2011). Phuphuakrat et al. (2011) studied the absorption efficiency of different hydrophobic absorbents and compared them with water. The results showed that by water-based scrubbing only 31.8% of gravimetric tar could be removed, whereas vegetable oil-based scrubbing could achieve a 60.4% removal efficiency of gravimetric tar. Moreover, in the biomass gasifier plant installed at Güssing Austria, the cleaning of the raw gas is performed in two stages. First, the raw gas passes a fabric filter to separate the particles and then in the second stage the tar is removed with the help of a scrubber. The scrubber uses rape oil methyl ester as solvent and reaches high tar removal efficiencies (Hermann et al., 2002).

Regarding the nitrogenous compounds, ammonia and N_2 are the major compounds produced during biomass gasification, whereas hydrogen cyanide and nitric oxide are produced at lower concentrations (Zhou et al., 2000). These compounds are undesirable in the downstream applications of the syngas. For instance, for liquid fuel production, ammonia poisons the catalysts employed in the FT synthesis (Boerrigter et al., 2004). Raw syngas cleanup of nitrogen compounds is conventionally achieved through wet scrubbing, as depicted in Figure 4, although spray and wash towers are also suitable for this application. Water scrubbing is known as the conventional technique for removal of nitrogenous compounds because ammonia and hydrogen cyanide present high solubility in water (Abdoulmoumine et al., 2015). Boerrigter et al. evaluated gas cleaning technologies for application in an integrated biomass gasification and FT system. During the gas cleaning, the syngas without tar was sent to a quenching column to cool down the gas and then scrubbed with water for removal of inorganic impurities, such as ammonia and hydrogen cyanide. The results from the tests showed that the FT catalyst presented no loss of selectivity or activity (Boerrigter et al., 2004).

[Figure 4 here]

Figure 4. Scrubbing system for raw gas cleanup

Other type of impurities from raw syngas are sulfur containing contaminants. As well as for the other contaminants, syngas sulfur content varies from hundreds to thousands parts per million as function of the biomass, as reported by Chiche et al. (2013). Woody biomasses have generally lower sulfur contents than agricultural co-products and energy crops. In woody biomass feedstocks, the sulfur content is around 800 ppm, whereas for agricultural biomass the sulfur content is generally around 1500 ppm (Vassilev et al., 2009). Sulfur removal in the order of parts per billion is most of the time required to avoid detrimental effects, such as, metal surfaces corrosion, produce sulfur dioxide if syngas is burned, and catalyst poisoning in the upgrading stages (Woolcock and Brown, 2013).

In a typical design, a series of process steps are used to recover sulfur as a useful by-product from gasification processes. First, the cooled syngas is treated in an absorber unit, where, a chemical solvent is employed for the removal of almost all the hydrogen sulfide and part of the carbon dioxide (NETL, 2012). The remains are removed in a filter. In a study performed by Boerrigter et al. (2004), sulfur impurities like hydrogen sulfide were removed with ZnO filters and active carbon filters were used for final polishing and efficient cleaning of the gas.

Similarly, as with the nitrogenous compounds, chlorine species, hydrogen halides and trace metal contaminants may cause serious problems if liquid fuel production from syngas is desired. For instance, syngas impurities can cause FT catalyst poisoning (Tijmensen, 2002), downstream corrosion, and fouling in syngas cooler tubes (Wang et al., 2016). Chlorine species in syngas are mainly represented as HCl, NH_4Cl and alkali chlorides (Chan et al., 2019). From these species, HCl, can be removed by reaction with particulates in a bag filter, absorbed using dolomite in a tar cracker, or wet scrubbed using NaOH (Tijmensen, 2002). HCl and other hydrogen halides are commonly removed by wet scrubbing usually through a caustic solution or with simply water (Bailon Allegue and Hinge, 2012). The use of a caustic solution, NaOH dissolved in water, allows the HCl to react with NaOH to produce NaCl, which can be precipitated out of solution. Thus, for this application, caustic scrubbing is a good alternative compared to water scrubbing. Water scrubbing requires an additional ionic exchanger to strip chlorine from the solution, which increases the costs of this alternative (Van Paasen et al., 2006).

Therefore, if syngas is used as an intermediate product to be upgraded to liquid fuels, then severe syngas specifications regarding its purity are required.

4.5 Separation and Purification of Bio-oil from Hydrothermal Liquefaction

Several hydrothermal liquefaction (HTL) studies have been carried out to produce bio-crude, and chemical characterization of the products has been performed. The studies reported that the bio-crude produced from HTL presents properties that are not comparable with fossil-based diesel and biodiesel (Ramirez et al., 2015). Post-treatment of the obtained bio-crude oil (bio-oil phase and aqueous phase) by separation of the phases and by removal of unwanted compounds can improve its physical and chemical properties. This can be accomplished using strategies such as separation via solvent division/extraction, and/or upgrading via hydrodeoxygenation and catalytic cracking (Quitain et al., 2015; Ramirez et al., 2015).

As described in section 4.1, the bio-crude produced from HTL contains bio-oil and an aqueous phase. To achieve the separation and extraction of the two-phase product, addition of a solvent is the most common approach. The resulting liquid product can be decanted to separate aqueous and oil fractions, as depicted in Figure 5. However, due to the complexity of bio-crude as a mixture, many researchers have investigated various chemicals to determine the most appropriate solvent (Garcia-Perez et al., 2007; Valdez et al., 2011). The selection of solvent is initially based on its immiscibility with water, and its efficiency to extract the organic components from the bio-oil to increase the bio-oil yield. The most efficient solvent is to some extent dependent on the composition of the bio-crude and the lignocellulosic feedstock (Ramirez et al., 2015).

[Figure 5 here]

Figure 5. Bio-oil separation via solvent addition and decantation

For instance, Karagöz et al. (2005) performed the recovery of bio-oil produced via hydrothermal liquefaction of sawdust (from pine wood) and rice husk using various solvents (diethyl ether and ethyl acetate). First, the bio-oil portion was extracted from the liquid product with diethyl ether, and then, the water phase was further extracted with ethyl acetate to recover the water-soluble hydrocarbons, as presented in Figure 6 (Karagöz et al., 2005). Minowa et al. (2002) recovered phenolic compounds from wood tar by extraction using methanol as solvent. These experiments show the possibility of the selective extraction of compounds based on the solvent selection.

[Figure 6 here]

Figure 6. Separation and extraction of bio-oil

5. Separation Technologies Application in the Upgrading Section

Bio-oils obtained from hydrothermal liquefaction and pyrolysis are complex mixtures composed of a varied range of compounds from different functional groups. Xiu and Shahbazi (2012) and Stankovikj et al. (2016) reported that bio-oils consist of of organic compounds including acids, alkanes, alcohols, aliphatics, aromatics, aldehydes, esters, ketones, phenols, furfurals, and lignin derived oligomers, from which, some of these products are undesirable. These compounds affect properties such as viscosity, density, heating value, oxygen, nitrogen and sulphur content. Therefore, chemical composition should be modified via upgrading techniques to meet fuel standards. However, due to its complex composition, bio-oil cannot be upgraded directly to high-quality transportation fuels and thus, separation technologies for recovery of bio-oil fractions with similar physical and chemical properties are required. This means that the components in the same family should be recovered and collected as fractions for upgrading in their corresponding reaction units. Lindfors et al. (2014) presented as alternative the separation of bio-oil into fractions before their upgrading and consider that it is a more efficient route to produce liquid biofuels compared to the total bio-oil stream upgrading.

Regarding gasification, synthetic liquid fuels may be produced from syngas through the Fischer-Tropsch (FT) process. The resulting liquid hydrocarbons mixture, called syncrude, presents different compositions depending on the FT process temperature schemes, namely low-temperature Fischer–Tropsch (LTFT) and high-temperature Fischer–Tropsch (HTFT). Likewise, the syncrude from FT synthesis, is not present as a single-phase product but as a product with multiple phases. The compounds distribution of each phase varies as well depending on the FT scheme. There are mainly four product phases; gases, organic liquid, organic solid and aqueous liquid (Rodríguez Vallejo and de Klerk, 2013).

To use the FT syncrude as transportation fuel, conventional crude oil refining infrastructure can be used. However, this often requires the separation of the phases and the recovery and upgrading of FT fractions, as well as the removal of compound classes that are not compatible with the current infrastructure like gas stations, storage tanks and engines. In addition, some product fractions can be recovered and refined to chemicals.

Therefore, no matter what thermochemical conversion technology is explored (pyrolysis, hydrothermal liquefaction and gasification), separation technologies are needed to recover the product fractions for further upgrading. Likewise, separation technologies are required for the recovery of auxiliary reactants, such as catalysts, fluidization agents, solvents and so on.

In the thermochemical-based upgrading processes, the process routes are defined based on the desired final products and are dependent to the different configuration arrangements of the separation technologies.

In the following sections, application of separation technologies for recovery of bio-oil/syncrude fractions, removal of solvents, recovery of by-products, as well as recovery of auxiliary reactants will be described.

5.1 Recovery of Bio-oil/Syncrude Fractions

Bio-oil is a mixture of different compound groups that react under different conditions and with different catalysts. Although, upgrading of bio-oil has usually been carried out by treating the whole oil in a reactor, fractionation of bio-oil before upgrading might be more efficient to produce biofuels and chemicals. Primary fractionation separates bio-oil into less complex fractions or mixtures. Several separation technologies have been evaluated including chromatography, solvent extraction, atmospheric distillation, molecular distillation, fractional distillation and phase separation by water addition followed by decantation. Most of these technologies are particularly employed for the separation of specific high-quality chemicals.

In column chromatography, the substances are separated based on their different adsorption capabilities on a stationary phase. Regularly, as the stationary phase, silica gel is employed, and depending on the polarity of the components in the mixture, an eluent is selected (Wang, 2013). Li et al. (2005) performed the separation of bio-oil from fast pyrolysis via liquid chromatography. For its separation, a silica gel column was employed, in which the bio-oil was washed down using different solvents like cyclohexane, benzene and methanol. The fractions obtained from the separation were analyzed by GC-MS. The results showed that aromatics with up to four rings predominated in the first fraction, one ring aromatics in the second fraction and polar compounds were found in the third fraction. Moreover, it was found that chemicals like phenol and naphthalene and methyl-naphthalene are produced from lignin and cellulose, respectively. (Li et al., 2005).

Recovery of bio-oil fractions through solvent extraction is a method that combines light oil separation and production of chemicals. This method is more economical for refining pyrolysis bio-oil and producing alternative fuels for fossil fuels. Yang et al. (2010) evaluated a two-step fractionation process to separate light oil and chemicals from pyrolysis bio-oil. In the two-step fractionation process, first, bio-oil was mixed with water and emulsified. Then the emulsion was separated by precipitation into two phases. From the two phases, a light oil phase composed mainly of alkenes and low molecular lignin was separated from heavy oil (water insolubles). The light oil phase was further extracted with a solvent mixture containing pentane and furans. This solvent mixture was found to be the most effective in the separation of chemicals and light oil from the pyrolysis bio-oil. From the extraction, a residual aqueous phase was also collected. To determine the composition of the fractions from bio-oil, the fractions were further characterized by GC-MS analysis. The results showed that light oil is mostly composed by biphenyl, phenols, aliphatic hydrocarbons, furan derivatives, esters, benzene, acids, etc. Heavy oil is composed of phenols with high molecular weight and the water fraction is composed of mainly anhydrosugars (Yang et al., 2010).

Atmospheric distillation is a mature and commonly used separation technology in petroleum refineries. In biorefineries, it is the most economical, scalable and feasible technology used for the recovery of chemical fractions from the bio-oil. Zhang et al. (2013) evaluated the separation of bio-oil through atmospheric distillation without adding any solvent, and several fractions were distilled and collected at different temperatures. Then, the compounds concentrations in the distillate fractions were quantified by GC-FID and identified by GC/MS. It was found that the distillate consisted mainly of oxygenated compounds with boiling points ranging between 353- 521 K. From the GC/MS analysis, phenols, guaiacols, furan derivatives, acetic acid, propanoic acid, and acetol were identified as major compounds. Further separation of the fractions into pure chemicals can be achieved based in their boiling points difference.

The main drawbacks in the application of atmospheric distillation of bio-oil fractions, is the thermal sensitivity of bio-oil, which makes it difficult to efficiently separate bio-oil at high temperatures (Wang, 2013). Moreover, atmospheric distillation produces residues that are difficult to handle, as well as unpredictable chemicals produced from chemical reactions between bio-oil components (Zhang et al., 2013).

Several authors have shown molecular distillation as a potential approach for the separation of bio-oil (Wang, et al., 2009; Guo et al., 2010; Wang, 2013). Molecular distillation operates at short heating time, low temperature, and presents high separation efficiency (Wang, 2013).

The molecular distillation of pyrolysis bio-oil is carried out at high vacuum conditions, and thus, a vacuum system prior to the column is required. In the molecular distillation system, the light molecules escape from the warm liquid, which are then cool down in the condenser. On the other hand, the heavy molecules return to the liquid phase when they collide with other molecules (Lindfors et al., 2014), as presented in Figure 7. Guo et al. (2010) used molecular distillation to separate bio-oil into three fractions: light fraction, middle fraction and heavy fraction. The light fraction was rapidly cooled down and collected. Then, the middle fraction was cooled using liquid nitrogen in a cold trap, and finally, the heavy fraction was collected in a flask. The chemical composition of each fraction was obtained by GC–MS and the results showed that the light fraction contained mainly water, hydrocarbons, alcohols and acids in different concentrations depending on the temperature range used. The middle fraction contained mostly phenols derived from the pyrolysis of lignin and the heavy fraction contained phenols and saccharides, which leads to high amounts of char (Guo et al., 2010).

[Figure 7 here]

Figure 7. Principle of a molecular distillation system

Fractional distillation has also been presented as an effective alternative in bio-oil separation even when its operation is energy intensive. Capunitan and Capareda (2013) evaluated the fractional distillation of corn stover-derived bio-oi at atmospheric and vacuum pressure. During the experiment, several fractions at different boiling points were collected and further chemically analyzed. The distillation of bio-oil yielded three fractions; the first fraction consisted of aromatics and oxygenates, whereas the second fraction also consisted of aromatics, oxygenates and some phenolic compounds, and the third fraction was composed of phenolic compounds. The authors found that the distillate recovery was higher under atmospheric conditions compared to vacuum pressure, and that the use of vacuum conditions produced a higher loss of compounds due to the escape of vapors, which also resulted in lower yield of the organic fractions (Xiu and Shahbazi, 2012). Likewise, Huang et al. (2018) performed the fractional distillation of pyrolysis bio-oil and demonstrated that this technology is efficient for recovery of the bio-oil fractions. The experiments by Huang et al. were carried out in a four stage fractional distillation column, in which the bio-oil was separated into two fractions; a light fraction containing C_4–C_7 hydrocarbons as well as high content of acetic acid, and a heavy fraction consisting of C_7–C_{10} hydrocarbons and high concentrations of phenolic compounds (Huang et al., 2018).

Phase separation by water addition is usually applied to bio-oils available as single-phase liquids. For instance, bio-oil produced from a dry raw material, such as forest and agricultural residues, is usually composed of 15 to 30 wt. % water and 20 to 30 wt. % water-insoluble compounds. These types of bio-oils due to the presence of hydroxyl compounds and polar carboxyl compounds tend to be single-phase liquids. Moreover, water contents of more than 30 wt. % produce phase separation. From the phase separation, the fraction with water-insoluble material settles at the bottom and the water-soluble fraction goes to the top (Lindfors et al., 2014). The amount of added water to obtain phase separation in the oil depends on how the bio-oil is condensed, the process conditions and on the nature of the feedstock (Oasmaa and Czernik, 1999). Furthermore, the separation of bio-oil from water can be performed by gravity or by centrifugation (Lindfors et al., 2014).

Concerning the gasification- FT routes, the selection of the separation technologies required in the upgrading section depends on the type of FT syncrude. For HTFT syncrude, a typical industrial operation design considers a stepwise cooling system. First, the FT product gas is cooled down in a heat exchanger to around 150 °C (Rodríguez Vallejo and de Klerk, 2013). At this temperature, a heavy oil fraction condenses and settles producing two phases: decanted oil (typically composed of $C_{11}-C_{50}$ olefins (de Klerk, 2011a), and a small fraction containing heavy oil and solids. Likewise, from the first cooling step, a gaseous product is also recovered. The gaseous product is then cooled down to separate the tail gas and to condense the light oil fraction and the aqueous product. The aqueous product contains mainly C_1-C_4 polar oxygenates. On the other hand, the recovered tail gas still contains organic compounds in the C_1-C_7 range, and thus, it requires to be cooled down and separated to recover the remaining light hydrocarbons. Comparing this design with the oil refinery design, they mainly differ in that in an oil refinery the light oil and heavy oil are separated using a conventional atmospheric distillation unit (Rodríguez Vallejo and de Klerk, 2013).

Contrary to the HTFT reaction, the LTFT synthesis produces a liquid mixture under reaction conditions. The product is separated in phases at the reactor´s outlet in a wax liquid phase and a gaseous light phase. For LTFT syncrude, a typical industrial cooling system considers a single cooling and condensation step carried out in a 3-phase separator, as depicted in Figure 8. In the 3-phase separator, the separation of the light oil from the aqueous product and uncondensed gases is carried out.

[Figure 8 here]

Figure 8. Stepwise cooling and separation of LTFT syncrude

Rodríguez Vallejo and de Klerk (2013) have suggested to replace these designs with feeding the HTFT and LTFT product directly into a pressure distillation unit without reboiler or preheater, as presented in Figure 9. Moreover, for the LTFT, because the reactor outlet is already separated in two fractions, their design suggests that the wax stream should be fed to the column above the gaseous product feed, so that the remaining lighter compounds in the wax can be stripped and the separation improves. A different design considered by these authors suggests that the pressure distillation unit can be designed with side-draws to directly recover naphtha and kerosene fractions (Rodríguez Vallejo and de Klerk, 2013).

[Figure 9 here]

Figure 9. Cooling and separation of FT product by distillation and three-phase separation

In the FT biorefinery design, the separation technologies play an important role in the efficient manipulation of the carbon number distribution of the syncrude fractions. After cooling and separation of the gaseous, oil, wax and aqueous fractions, different refinery designs can be explored depending on the desired product profiles and fuel specifications. The separation and upgrading technologies (olefin oligomerization, hydrogenation, hydrocracking, catalytic reforming, aromatic alkylation, etc.) can be arranged in several ways to maximize the production of a specific fuel type, namely gasoline, jet fuel and diesel.

In a previous work by Ibarra-Gonzalez and Rong (2019), some of the possible separation configurations for the recovery of the FT fractions were presented. For instance, the gaseous product (C_1-C_4) can be further separated in a cryogenic distillation column into a C_1-C_2 fraction and C_3-C_4 fraction, which can be further upgraded to synthetic natural gas and gasoline, respectively. The light oil (C_5-C_{10}) can be upgraded in the same reaction unit or separated in two or more different ways using a pressure distillation unit: C_5-C_6 fraction and C_7-C_{10} fraction or C_5 fraction and C_6-C_{10} fraction. The selection of the following upgrading technologies will depend on the desired fuel type. Likewise, the heavy oil (C_{11}-C_{22+}) can be fractionated in several cuts depending in the desired fuel type. For example, for jet fuel production, a fraction containing C_{11}-C_{14} components could be recovered by atmospheric distillation and be upgraded via hydroisomerization. Or a C_{11}-C_{22} fraction and a C_{23}+ fraction could be separated by atmospheric distillation for diesel and gasoline production via hydrogenation and hydrocracking, respectively (Ibarra-Gonzalez and Rong, 2019).

5.2 Separation of Solvents, Purification of Aqueous Products and Recovery of Chemicals

Depending on the separation technology used for the recovery of the bio-oil and syncrude fractions, as well as, on the upgrading technology selected, solvent recovery and purification technologies can be applied. For instance, if bio-oil is upgraded via hydroprocessing or catalytic cracking there is no need of solvent recovery techniques, because during this process no solvent is added. On the other hand, if bio-oil is fractionated using solvent extraction or liquid chromatography or phase separation by water addition and/or if it is upgraded in supercritical monoalcohols, then solvent separation technologies are required in the process. Moreover, if phase separation of the FT syncrude is carried out, then an aqueous phase is produced, which can be purified for later use in the process. Likewise, from the aqueous phase some chemicals can be recovered.

After solvent extraction, the chemicals extracted by the organic solvent are recovered through an evaporator, which evaporates the solvent from the mixture as depicted in Figure 10. In liquid chromatography, the bio-oil fractions are eluted by solvent using a packing material like silica gel, then the solvent is distilled away from the bio-oil fractions (Wang et al., 2011).

[Figure 10 here]

Figure 10. Solvent recovery via evaporation

Concerning the recovery of solvents and chemicals after the upgrading of bio-oil in supercritical alcohols, Zhang et al. (2012) performed the upgrading of bio-oil from Pinus sylvestris L. with the use of methanol and ethanol at supercritical conditions, and achieved the total conversion of aldehydes and acids, and thus, their complete removal. Likewise, a reduction on the production of phenols, ketones, polycyclic aromatic hydrocarbons and sugars was achieved, which increased the stability of the pyrolysis bio-oil. After the processing, an effective solvent recovery system consisting of distillation and condensation is required as proposed by Cheremisinoff (1995).

As mentioned, separating chemicals from the bio-oil is important to improve the bio-oil stability and for further biorefinery applications as feedstocks. Ren et al. (2017) performed the separation of chemical groups from the aqueous fraction by liquid-liquid extraction using different organic solvents, like hexane, ethyl acetate and others. The extraction experiments were performed to isolate chemicals (acids, phenols, ketones, furans, etc) that can be upgraded and used in other applications, such as organic acids for use as fuel additives.

In the gasification-based routes, a scrubbing system is applied, and excess water is used to remove the nitrogenous compounds, carbon monoxide, sulfur compounds and so on from the syngas product. At the bottom of the scrubber, the wastewater stream containing the impurities is collected (Ibarra-Gonzalez and Rong, 2018) and purified in a stripper before releasing the water and chemical impurities as emissions or using them as feedstock for other processing units. In the stripper, an air stream entering at the bottom of the tower removes the impurities, such as ammonia, from the water (Yuan et al., 2016), as presented in Figure 11. On the other hand, if the water is going to be reused in the facility, then the wastewater streams are biologically treated (de Klerk, 2011b).

[Figure 11 here]

Figure 11. Air stripping for wastewater treatment

The aqueous phase separated from the FT syncrude via stepwise cooling contains alcohols, carbonyls and carboxylic acids (de Klerk, 2011a) and some remaining gases. This stream can be purified, first, by removal of the remaining gases in a flash column and then in a train of distillation columns to remove the organic compounds.

Alcohols are not only present in the aqueous phase but in the light oil hydrocarbon stream (C_4 -C_6) as well. From the hydrocarbon stream, excess alcohol can be removed first through a single stage water wash, where most of the alcohol is removed, and then to remove the remaining alcohol, multistage water wash is employed (Jones, 1994).

5.3 Recovery of Catalysts

During bio-oil catalytic upgrading several and complex reactions take place, such as catalytic cracking, decarboxylation, decarbonylation, hydrodeoxygenation, hydrocracking, hydrogenation, and polymerization. However, the selection of the catalyst type depends on the bio-oil composition and the reaction that can upgrade the bio-oil fractions to desired fuel components. For biofuel production, catalytic cracking and hydrodeoxygenation are two of the most promising bio-oil upgrading processes. Heterogeneous catalysts are essential for upgrading bio-oil into hydrocarbon biofuel and separation technologies are also indispensable in the recovery of catalysts. Elkasabi et al. (2014) performed the hydrodeoxygenation of bio-oil using carbon-supported catalysts (Ru, Pt or Pd on carbon supports). After the reaction, the catalyst was removed from the reactor through a polytetrafluoroethylene (PTFE) membrane filter with acetone washings, and then by rotary evaporation, the acetone was removed. Grilc et al. (2014) conducted experiments for the hydrotreatment of liquefied biomass using bifunctional catalysts like nickel–molybdenum catalysts s supported on Al_2O_3. The catalyst particles together with the tar residues were separated from the reactor's outlet liquid stream by filtration.

On the other hand, when considering FT syncrude fractions, several catalysts have been identified as suitable for FT upgrading. For instance, catalysts like H-ZSM-5, alumina, solid phosphoric acid (SPA), unsulfided Pt/SiO_2-Al_2O_3 and nonacidic Pt/L-zeolite have been tested successfully for alkene oligomerization, alkene isomerization, aromatic alkylation, hydrocracking and catalytic reforming, respectively (de Klerk and Furimsky, 2010). After several experiments, the activity of the catalysts declines and thus catalysts must be periodically removed and replaced. Some separation methods applied for the recovery of heterogeneous catalysts are centrifugation, filtration and solvent addition followed by gravity.

6. Separation of Advanced Biofuels and Value-added Products from the Upgraded Bio-oil/Syncrude Streams

The successfully scale up and commercialization of advanced biofuels processes depends on the compatibility of the processing technologies with existing fuel infrastructure (refining facilities, distribution systems, fueling stations, storage tanks and engines) and their capability to meet fuel specifications. To meet fuel specifications, advanced biofuels require the efficient distribution of intermediates and desired product components. For this, separation systems must be designed to achieve the final product profiles and desired fuel components' distributions.

6.1 Advanced Biofuels Separation from Upgraded Bio-oil and Syncrude

For the separation of advanced biofuels from the upgraded bio-oil, separation technologies such as fractionation columns and distillation columns have been studied. Mccall and Brandvold (2009) proposed a process for the conversion of pyrolysis oil to liquid fuel blending components. The process considered a two-steps deoxygenation of the biomass-based pyrolysis oil and the following separation of the diesel range, aviation range, and naphtha range fuel blending products. The separation of the final biofuels was performed through a fractionation zone, which separates the hydrocarbon compounds in different boiling point range groups including (1) naphtha range products into a gasoline blending stream, (2) kerosene range into an aviation fuel blending stream and (3) diesel range compounds into a diesel blending stream.

On the other hand, Jones et al. (2013) and Ibarra-Gonzalez and Rong (2018) proposed that the upgraded oil from hydrotreating and hydrocracking of pyrolysis oils can be fractionated in gasoline and diesel range products in a train of distillation columns. First, a small fraction of C_3-C_4 components, which were produced during hydroprocessing and that remained together with liquid products in the light hydrocarbons stream, are removed in a flash unit (debutanizer), where the gases are separated from the hydrotreated oil. Then, the hydrotreated oil is fractionated in a train of distillation columns. In the first distillation column, the upgraded oil is separated in a light oil stream containing naphtha range components and a heavy oil stream containing both diesel range components and wax. The heavy oil is further separated in a distillation column into a diesel stream and a wax stream. The wax stream is collected and cracked to additional gasoline and diesel range components. Finally, the product stream from hydrocracking is sent to a product separation column to distill products in the gasoline and diesel range (Zhu et al., 2011).

Furthermore, in a total FT process design, as described in section 5.1, the syncrude composition and the application of separation technologies for the recovery of fractions with different carbon distributions determine the possible upgrading paths to produce refined fuel products. In the same way, the composition of the upgraded syncrude's fractions defines the downstream refining designs. For instance, in a HTFT refinery design that considers the maximization of gasoline production, the product from the oligomerization of C_3-C_4 hydrocarbons (blending stream containing LPG range components, gasoline range components and jet fuel range components) (de Klerk, 2011a) can be separated into a synthetic gas stream, a gasoline stream and a jet fuel stream using flash units and distillation columns. Likewise, the product from the hydrocracking of the heavy hydrocarbon fraction (wax) is a mixture of components in the LPG and gasoline range, as well as some in diesel range. Therefore, after the hydrocracking unit, the gas can be vent out or separated in a flash unit, and the remaining gasoline and diesel can be separated into two main fuel streams in a distillation column (Betchel, 1998). The same separation methods can be applied for the separation of the products from other upgrading units, since most of the final upgraded mixtures contain components in different fuel ranges.

Other approach explored by Ibarra-Gonzalez and Rong (2018) proposes the blending of all the upgraded streams and the further recovery of the fuel streams (synthetic gas, gasoline, diesel and unconverted wax) by means of a fractionation column.

7. Case Study: Gasification-LTFT- Fractional Upgrading- Final Products Separation

In this section, a case study to illustrate the importance of the separation technologies in the total BtL production processes is presented. In an earlier work (Ibarra-Gonzalez and Rong, 2018), we have compared several thermochemical process routes for BtL production from lignocellulosic biomass, where process synthesis, simulation and evaluation were implemented for the studied process routes. Figure 12 presents the gasification following Fischer-Tropsch process route, where the separation units required in the thermochemical conversion, FT fractional upgrading and final products separation are are highlighted with the unit blocks in bluecolour. As shown in Figure 12, the introduced separation operations include cyclones to remove solid fractions, water-based scrubber to remove inorganic impurities, distillation columns to separate the different LTFT product fractions and a fractionation column to recover the gasoline and diesel range products, as well as the aqueous and gaseous by-products. Furthermore, the capital costs of the separation units in the sections of thermochemical conversion, upgrading, and final products is depicted in Figure 13.

[Figure 12 here]

Figure 12. Separation needs in the Gasification-LTFT- Fractional Upgrading-Final Products Separation case study

[Figure 13 here]

Figure 13. Capital costs of separation units in the process sections of the case study

From Figure 13, it is observed that the separation units account for 28%, 46%, 87% of the capital costs in the sections of the thermochemical conversion, upgrading and separation, respectively.

8. Future Perspective

Biomass thermochemical conversion technologies produce gaseous and liquid fuels with complex compositions and thus, application of chemical characterization techniques is critical. Chemical and physical analysis should be performed to provide sufficient information for the synthesis of new plant designs based on the component's distribution. Better bio-oil, syncrude and downstream products characterizations will allow to explore and develop novel separation and upgrading process configurations.

Moreover, while many researchers have focused on the evaluation of reaction routes and catalysts, most of the separation needs and technologies have not been tested in laboratory or pilot scale. The study of the separation of complex mixtures in laboratory scale is almost impossible and therefore model compounds are selected to represent the mixtures, which in some cases do not approach the real industrial separation process needs. On the other hand, the use of simulation software packages, such as Aspen Plus, has shown its capability to investigate and simulate better the real process configurations and find the optimal separation operation conditions. During process simulation, set up of BtL processes considering detailed mixtures to represent the real mixtures' compositions allow the analysis of real separation needs and the evaluation of the performance of different separation methods in different stages of the process. Moreover, from experimental and simulation studies, the possible application of existent fossil-based infrastructure in BtL refineries, where fossil is replaced with biomass as feedstock, could be explored. However, at some extent modifications to current technologies are required, which represents high costs in terms of capital investment and energy consumption. Therefore, to increase the feasibility of BtL biorefineries by reducing capital and energy costs, synthesis of novel separation processes based on intensified equipment and process integration should be explored.

9. Conclusions

Thermochemical technological routes are promising processes to produce advanced biofuels from lignocellulosic biomass. Biomass conversions, subsequent upgrading and final products recovery and purification are the typical process sections to formulate the whole production processes. In this review, separation needs, and separation methods are discussed along the different process sections within the whole production process context. It is indicated that separations are pivotal in such thermochemical biomass-to-liquid (BtL) production process for advanced biofuels and that separations play a critical role in all the different process sections. The optimal selection, design and operation of separation processes can improve the process efficiency and maximize the biofuels or chemicals productivity. Separation is not only necessary for final products recovery and purification, but also crucial to determine the downstream upgrading techniques and process configurations. Separation designs in determining downstream upgrading and final products recovery processes also give significant information for upstream conversion and reaction process optimization in terms of product profiles. Separation has a great impact in the synthesis and integration of the different process sections to design total production process, which is crucial to determine the optimal total process configurations.

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Notes

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10. References

Abdoulmoumine, N., Adhikari, S., Kulkarni, A., and Chattanathan, A. (2015). A review on biomass gasification syngas cleanup, *Appl. Energy*, **155**, 294–307.

Agrawal, R. (2001). Separations: Perspective of a process developer/designer, Am. Inst. *Chem. Eng. J.*, **47**, 967–71.

Bailon Allegue, L., and Hinge, J. (2012). Biogas and bio-syngas upgrading, Danish Technical Institute Report.

Ben, H., and Ragauskas, A.J. (2013). Comparison for the compositions of fast and slow pyrolysis oils by NMR characterization, *Bioresource Technol.,* **147**, 577–584.

Betchel. (1998). Aspen Process Flowsheet Simulation Model of a Battelle Biomass-Based Gasification, Fischer−Tropsch Liquefaction and Combined-Cycle Power Plant, Topical Report, U.S. Department of Energy, DE-AC22-93PC91029.

Bjelić, S., Yu, J., Iversen, B.B., Glasius, M, and Biller, P. (2018). Detailed investigation into the asphaltene fraction of hydrothermal liquefaction derived bio-crude and hydrotreated bio-crudes, *Energy& Fuels*, **32**, 3579−3587.

Boerrigter, H., Calis, H.P., Slort, D.J., and Bodenstaff, H. (2004). Gas cleaning for integrated biomass gasification (BG) and Fischer-Tropsch (FT) systems: experimental demonstration of two BG-FT systems, 2nd World Conf. Technol. Exhib. Biomass Energy, Ind. Clim. Prot., Rome, Italy, ECN, 1–8.

Cai, W., and Liu, R. (2016). Performance of a commercial-scale biomass fast pyrolysis plant for bio-oil production, *Fuel*, **182**, 677–686.

Capunitan, J.A., and Capareda, S.C. (2013). Characterization and separation of corn stover bio-oil by fractional distillation, *Fuel*, **112**, 60–73.

Chan, W.P., Veksha, A., Lei, J., Oh, W.-D., Dou, X., Giannis, A., Lisak, G., and Lim, T.-T. (2019). A hot syngas purification system integrated with downdraft gasification of municipal solid waste, *Appl. Energy*, **237**, 227–240.

Chen, H. (2015). Lignocellulose biorefinery product engineering. In *Lignocellul. Biorefinery Eng.*, ed. Chen, H., 125-165, Woodhead Publishing.

Chen, T., Wu, C., Liu, R., Fei, W., and Liu, S. (2011). Effect of hot vapor filtration on the characterization of bio-oil from rice husks with fast pyrolysis in a fluidized-bed reactor, *Bioresource Technol.*, **102**, 6178–6185.

Cheremisinoff, P.N. (1995). Waste Reduction, In *Waste Minimization Cost Reduction for the Process Industries*, ed Cheremisinoff, P.N., 1-51, Elsevier.

Chiche, D., Diverchy, C., Lucquin, A., Porcheron, F., and Defoort, F. (2013). Synthesis gas purification, *Oil Gas Sci. Technol.*, **68**, 707–723.

de Haan, A.B. (2015). Process Technology: An Introduction, 1st ed., De Gruyter.

de Klerk, A. (2011a). Fischer–Tropsch fuels refinery design, *Energy & Environ. Sci.*, **4**, 1177-1205.

de Klerk, A. (2011b). Fischer-Tropsch refining, Wiley-VCH.

de Klerk, A., and Furimsky, E. (2010). Catalysis in the Refining of Fischer-Tropsch Syncrude, Cambridge, Royal Society of Chemistry.

Devi, L., Ptasinski, K.J., and Janssen, F.J.J. (2003). A review of the primary measures for tar elimination in biomass gasification processes, *Biomass & Bioenergy*, **24**, 125–140.

Elkasabi, Y., Mullen, C.A., Pighinelli, A.L.M.T., and Boateng, A.A. (2014). Hydrodeoxygenation of fast-pyrolysis bio-oils from various feedstocks using carbon-supported catalysts, *Fuel Process Technol.*, **123**, 11–18.

Elliott, D.C., Biller, P., Ross, A.B., Schmidt, A.J., and Jones, S.B. (2015). Hydrothermal liquefaction of biomass: Developments from batch to continuous process, *Bioresource Technol.*, **178**, 147–156.

Fortin, M., Beromi, M.M., Lai, A., Tarves, P.C., Mullen, C.A. Boateng, A.A., and West N.M. (2015). Structural analysis of pyrolytic lignins isolated from switchgrass fast-pyrolysis oil, *Energy&Fuels*, **29**, 8017−8026.

Garcia-Perez, M., Chaala, A., Pakdel, H., Kretschmer, D., and Roy, C. (2007). Characterization of bio-oils in chemical families, *Biomass & Bioenergy*, **31**, 222–242.

Grilc, M., Likozar, B., and Levec, J. (2014). Hydrodeoxygenation and hydrocracking of solvolysed lignocellulosic biomass by oxide, reduced and sulphide form of NiMo, Ni, Mo and Pd catalysts, *Appl. Catal. B Environ.*, **150-151**, 275–287.

Guo, X., Wang, S., Guo, Z., Liu, Q., Luo, Z., and Cen, K. (2010). Pyrolysis characteristics of bio-oil fractions separated by molecular distillation, *Appl. Energy*, **87**, 2892–2898.

Hermann, H., Reinhard, R., Klaus, B., Reinhard. K., and Christian, A. (2002). Biomass CHP plant Güssing-A success story, In *Expert meeting on pyrolysis and gasification of biomass and waste*, Strasbourg, France.

Hirohata, O., Wakabayashi, T., Tasaka, K., Fushimi, C., Furusawa, T., Kuchonthara, P., and Tsutsumi, A. (2008). Release behavior of tar and alkali and alkaline earth metals during biomass steam gasification, *Energy&Fuels*, **22**, 4235–4239.

Huang, A.-N., Hsu, C.-P., Hou, B.-R., and Kuo, H.-P. (2018). Production and separation of rice husk pyrolysis bio-oils from a fractional distillation column connected fluidized bed reactor, *Powder Technol.*, **323**, 588–593.

Huang, H.J., and Ramaswamy, S. (2013). Overview of biomass conversion processes and separation and purification technologies in biorefineries. In *Sep. Purif. Technol. Biorefineries* eds. Ramaswamy, S. and Huang, H.J., and B.V. Ramarao, B.V., 1-36, John Wiley & Sons, Ltd.

Hwang, J.G., Park, H.C., Choi, J.W., Oh, S.Y., Moon, Y.H., and Choi, H.S. (2016). Fast pyrolysis of the energy crop "Geodae-Uksae 1" in a bubbling fluidized bed reactor, *Energy*, **95**, 1–11.

Ibarra-Gonzalez, P., Rong, B.-G. (2018). Systematic synthesis and evaluation of thermochemical conversion processes for lignocellulosic biofuels production: total process evaluation and integration, Ind. Eng. Chem. Res., **57**, 9925–9942.

Ibarra-Gonzalez, P., and Rong, B.-G. (2019). A review of the current state of biofuels production from lignocellulosic biomass using thermochemical conversion routes, *Chinese J. Chem. Eng.*, **27**, 1523-1535.

Jarvis, J.M., McKenna, A.M., Hilten, R.N., Das, K.C., Rodgers, R.P., and Marshall, A.G. (2012). Characterization of pine pellet and peanut hull pyrolysis bio-oils by negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry, *Energy&Fuels*, **26**, 3810–3815.

Jones, E.M. (1994). Recovery of alcohol from hydrocarbon streams, US5430197A.

Jones, S., Meyer, P., Snowden-Swan, L., Padmaperuma, A., Tan, E., Dutta, A., Jacobson, J., and Cafferty, K. (2013). Process design and economics for the conversion of lignocellulosic biomass to hydrocarbon fuels: fast pyrolysis and hydrotreating bio-oil pathway, PNNL-23053, NREL/TP-5100-61178.

Joseph, J., Rasmussen, M.J., Fecteau, J.P., Kim, S., Lee, H., Tracy, K.A. , Jensen, B.L., Frederick, B.G., and Stemmler, E.A. (2016). Compositional changes to low water content bio-oils during aging: An NMR, GC/MS, and LC/MS study, *Energy&Fuels*, **30**, 4825–4840.

Karagöz, S., Bhaskar, T., Muto, A., and Sakata, Y. (2005). Comparative studies of oil compositions produced from sawdust, rice husk, lignin and cellulose by hydrothermal treatment, *Fuel*, **84**, 875–884.

Khuenkaeo, N., and & Nakorn Tippayawong, N. (2020). Production and characterization of bio-oil and biochar from ablative pyrolysis of lignocellulosic biomass residues, *Chemical Engineering Communications*, **207**, 153-160.

Kinoshita, C.M., Wang, Y., and Zhou, J. (1994). Tar formation under different biomass gasification conditions, *J. Anal. Appl. Pyrolysis*, **29**, 169–181.

Klinghoffer, N. (2013). Utilization of char from biomass gasification in catalytic applications, PhD Thesis, Columbia University.

Li, S., Xu, S., Lu, Q., and Lau, S. (2005). Column chromatographic separation of bio-oil from fast pyrolysis of biomass, *Acta Energiae Solaris Sinica*, **26**, 546–552.

Lindfors, C., Kuoppala, E., Oasmaa, A., Solantausta, Y., and Arpiainen, V. (2014). Fractionation of bio-oil, *Energy& Fuels*, **28**, 5785–5791.

Liu, Q., Chmely, S.C., and Abdoulmoumine, N. (2017). Biomass treatment strategies for thermochemical conversion, *Energy&Fuels*, **31**, 3525–3536.

Lu, Y., Li, G.-S., Lu, Y.-C., Fan, X., and Wei, X.-Y. (2017). Analytical strategies involved in the detailed componential characterization of biooil produced from lignocellulosic biomass. *Int. J. Anal. Chem.,* paper ID 9298523.

Maniatis, K., and Beenackers, A.A.C. (2000). Tar protocols, IEA bioenergy gasification task, *Biomass & Bioenergy*, **18**, 1–4.

Mccall, M.J., and Brandvold, T.A. (2009). Fuel and fuel blending components from biomass derived pyrolysis oil, PCT/US2009/039291.

Milne, T.A., Evans, R.J., and Abatzoglou, N. (1998). Biomass Gasifier “Tars”: Their Nature, Formation, and Conversion, NREL/TP-570-25357.

Minowa, T., Sato, S., Matsumura, A., Inoue, S., Hanaoka, T., and Saito, I. (2002). Methanol mediated extraction of phenolic compounds from wood tar, *Chem. Lett.*, **31**, 546–547.

Mullen, C.A., Strahan, G.D., and Boateng, A.A. (2009). Characterization of various fast-pyrolysis bio-oils by NMR spectroscopy, *Energy&Fuels*, **23**, 2707–2718.

Mussatto, S.I. (2016). Biomass Fractionation Technologies for a Lignocellulosic Feedstock Based Biorefinery, Elsevier.

NETL: National Energy Technology Laboratory, (2012). Sulfur Recovery and Tail Gas Treating, https://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/ sulfur-recovery, (accessed 1 July, 2019).

NETL: National Energy Technology Laboratory, 2009. Gasifier By-Product Handling Experience. https://www.netl.doe.gov/research/Coal/energy-systems/gasification/ gasifipedia/byproduct-handling, (accessed June 26, 2019).

Oasmaa, A., and Czernik, S. (1999). Fuel oil quality of biomass pyrolysis oils-state of the art for the end users, *Energy&Fuels*, **13**, 914–921.

Pandey, A., Bhaskar, T., Stöcker, M., and Sukumaran, R.K. (2015). Recent advances in thermochemical conversion of biomass, Elsevier.

Papari, S., and Hawboldt, K. (2018). A review on condensing system for biomass pyrolysis process, *Fuel Process Technol.*, **180**, 1–13.

Pattiya, A. (2018). Fast pyrolysis. In *Direct Thermochem. Liq. Energy Appl.*, ed Rosendahl L., Woodhead Publishing, 3–28.

Phuphuakrat, T., Namioka, T., and Yoshikawa, K. (2011). Absorptive removal of biomass tar using water and oily materials, *Bioresource Technol.*, **102**, 543–549.

Posmanik, R., Cantero, D.A., Malkani, A., Sills, D.L., and Tester, J.W. (2017). Biomass conversion to bio-oil using sub-critical water: Study of model compounds for food processing waste, *J. Supercrit. Fluids*, **119**, 26–35.

Quann, R.J., and Jaffe, S.B. (1992). Structure-oriented lumping: describing the chemistry of complex hydrocarbon mixtures, *Ind. Eng. Chem. Res.*, **31**, 2483–2497.

Quitain, A.T., Herng, C.Y., Yusup, S., Sasaki, M., and Uemura, Y. (2015). Conversion of biomass to bio-oil in sub- and supercritical water, In *Biofuels - Status Perspect*, ed Biernat, K., 459–476.

Ramirez, J.A., Brown, R.J., and Rainey, T.J. (2015). A review of hydrothermal liquefaction bio-crude properties and prospects for upgrading to transportation fuels, *Energies*, **8**, 6765–6794.

Ren, S., Ye, X.P., and Borole, A.P. (2017). Separation of chemical groups from bio-oil water-extract via sequential organic solvent extraction, *J. Anal. Appl. Pyrolysis*, **123**, 30–39.

Rengel, A. (2007). Study of Lignocellulosic Biomass Pyrolysis: State of the Art and Modeling, Master of Science Thesis, Royal Institute of Technology.

Ringer, M., Putsche, V., and Scahill, J. (2006). Large-scale pyrolysis oil production: a technology assessment and economic analysis, NREL/TP-510-37779.

Robinson, C.J., and Cook, G.L. (1969). Low-resolution mass spectrometric determination of aromatic fractions from petroleum, *Anal. Chem.*, **41**, 1548–1554.

Rodríguez Vallejo, D.F., and de Klerk, A. (2013). Improving the interface between Fischer–Tropsch synthesis and refining, *Energy& Fuels*, **27**, 3137–3147.

Santos, R.M., Santos, A.O., Sussuchi, E.M., Nascimento, J.S., Lima, A.S., and Freitas, L.S. (2015). Pyrolysis of mangaba seed: Production and characterization of bio-oil, *Bioresource Technol*., **196**, 43–48.

Sipilä, K., Kuoppala, E., Fagernäs, L., and Oasmaa, A. (1998). Characterization of biomass-based flash pyrolysis oils, *Biomass & Bioenergy,* **14**, 103–113.

Smith, E.A., Park, S., Klein, A.T., and Lee, Y.J. (2012). Bio-oil analysis using negative electrospray ionization: comparative study of high-resolution mass spectrometers and phenolic versus sugaric components, *Energy&Fuels*, **26**, 3796–3802.

Stankovikj, F., McDonald, A.G., Helms, G.L., and Garcia-Perez, M. (2016). Quantification of bio-oil functional groups and evidences of the presence of pyrolytic humins, *Energy&Fuels*, **30**, 6505–6524.

Staš, M., Chudoba, J., Kubička, D., and Pospšíl, M. (2015). Chemical characterization of pyrolysis bio-oil: application of Orbitrap mass spectrometry, *Energy&Fuels*, **29**, 3233−3240.

Tarnpradab, T., Unyaphan, S., Takahashi, F., and Yoshikawa, K. (2017). Improvement of the biomass tar removal capacity of scrubbing oil regenerated by mechanical solid–liquid separation, *Energy&Fuels*, **31**, 1564–1573.

Tijmensen, M. (2002). Exploration of the possibilities for production of Fischer-Tropsch liquids and power via biomass gasification, *Biomass & Bioenergy*, **23**, 129–152.

Tumbalam Gooty, A., Li , D., Briens, C., and Berruti, F. (2014). Fractional condensation of bio-oil vapors produced from birch bark pyrolysis, *Sep. Purif. Technol.*, **124**, 81–88.

Unyaphan, S., Tarnpradab, T., Takahashi, F., and Yoshikawa, K. (2017). An investigation of low cost and effective tar removal techniques by Venturi scrubber producing syngas microbubbles and absorbent regeneration for biomass gasification, *Energy Procedia*, **105**, 406–412.

Valdez, P.J., Dickinson, J.D., and Savage, P.E. (2011). Characterization of product fractions from hydrothermal liquefaction of *Nannochloropsis* sp. and the influence of solvents, *Energy& Fuels*, **25**, 3235–3243.

Van De Velden, M., Fan, X., Ingram, A., and Baeyens, J. (2007). Fast pyrolysis of biomass in a circulating fluidised bed. 12th Int. Conf. Fluid. - New Horizons Fluid. Eng., ECI Digital Archives, 897–904.

Van Paasen, S.V.B., Cieplik, M.K., and Phokawat, N.P. (2006). Gasification of Non-woody Biomass: Economic and Technical Perspectives of Chlorine and Sulphur Removal from Product Gas, Corpus ID: 32944678, ECN-C-06-032.

Vassilev, S.V., Baxter, D., Andersen, L.K., and Vassileva, C.G. (2009). An overview of the chemical composition of biomass, *Fuel*, **89**, 913–933.

Venderbosch, R.H., Ardiyanti, A.R., Wildschut, J., Oasmaa, A., and Heeres, H.J. (2010). Stabilization of biomass-derived pyrolysis oils, *J Chem. Technol. Biotechnol.*, **85**, 674–686.

Wang, B., Kurian, V., Mahapatra, N., Martens, F., and Gupta, R. (2016). Investigation of corrosion and fouling in syngas cooler tubes, *Fuel Process Technol.*, **141**, (202–209.

Wang, S. (2013). High-efficiency separation of bio-oil, In *Biomass Now: Sustainable Growth and Use,* ed Matovic, M.D., 401–418, IntechOpen.

Wang, S., Gu, Y., Liu, Q., Yao, Y., Guo, Z., Luo, Z., and Cen. K. (2009). Separation of bio-oil by molecular distillation, *Fuel Process Technol.*, **90**, 738–745.

Wang, Z., Lin, W., Song, W., Du, L., Li, Z., and Yao, J. (2011). Component fractionation of wood-tar by column chromatography with the packing material of silica gel, *Chinese Sci. Bull.*, **56**, 1434–1441.

Westerhof, R.J.M., Brilman, D.W.F., Garcia-Perez, M., Wang, Z., Oudenhoven, S.R.G., van Swaaij, W.P.M., and Kersten, S.R.A. (2011). Fractional condensation of biomass pyrolysis vapors, *Energy&Fuels*, **25**, 1817–1829.

Woolcock, P.J., and Brown, R.C. (2013). A review of cleaning technologies for biomass-derived syngas, *Biomass & Bioenergy*, **52**, 54–84.

Wright, M.M., Daugaard, D.E., Satrio, J.A., and Brown, R.C. (2010). Techno-economic analysis of biomass fast pyrolysis to transportation fuels, *Fuel*, **89**, 2–10.

Xiu, S., and Shahbazi, A. (2012). Bio-oil production and upgrading research: a review, *Renew. Sustain. Energy Rev.*, **16**, 4406–4414.

Yang, C., Zhang, B., Moen, J., Hennessy, K., Liu, Y., Lin, X., Wan, Y., Lei, H., Chen, P., and Ruan, R. (2010). Fractionation and characterization of bio-oil from microwave-assisted pyrolysis of corn stover, *Int. J. Agric. Biol. Eng.*, **3**, 54–61.

Yu, Y., Chua, Y.W., and Wu, H. (2016). Characterization of pyrolytic sugars in bio-oil produced from biomass fast pyrolysis, *Energy&Fuels*, **30**, 4145–4149.

Yuan, M.-H., Chen, Y.-H., Tsai, J.-Y., and Chang, C.-Y. (2016). Removal of ammonia from wastewater by air stripping process in laboratory and pilot scales using a rotating packed bed at ambient temperature, *J. Taiwan Inst. Chem. Eng.*, **60**, 488–495.

Zhang, J., Luo, Z., Dang, Q., Wang, J., and Chen, W. (2012). Upgrading of bio-oil over bifunctional catalysts in supercritical monoalcohols, *Energy&Fuels*, **26**, 2990–2995.

Zhang, X.-S., Yang, G.-X., Jiang, H., Liu, W.-J., and Ding, H.-S. (2013). Mass production of chemicals from biomass-derived oil by directly atmospheric distillation coupled with co-pyrolysis, *Sci. Rep.*, **3**, 1–7.

Zhou, J., Masutani, S.M., Ishimura, D.M., Turn, S.Q., and Kinoshita, C.M. (2000). Release of fuel-bound nitrogen during biomass gasification, *Ind. Eng. Chem. Res.*, **39**, 626–634.

Zhu, Y., Tjokro Rahardjo, S.A., Valkenburg, C., Snowden-Swan, L.J., Jones, S.B., and Machinal, M.A. (2011). Techno-economic analysis for the thermochemical conversion of biomass to liquid fuels, Pacific Northwest National Laboratory, PNNL-19009.

Figures

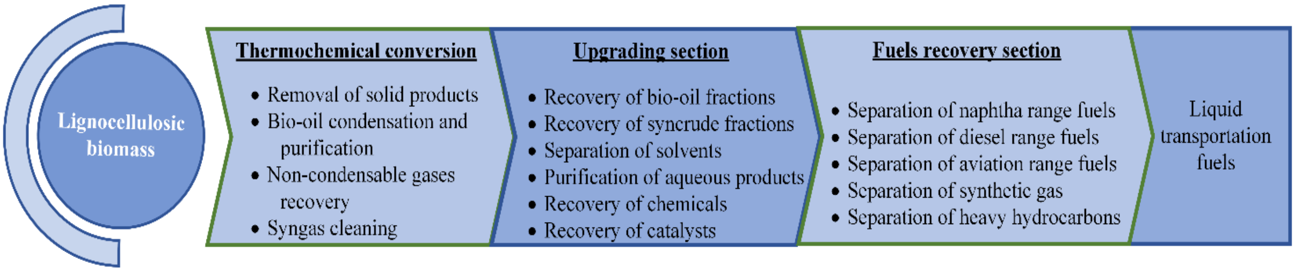

Figure 1. Separation needs in the thermochemical-based biomass to liquid technologies

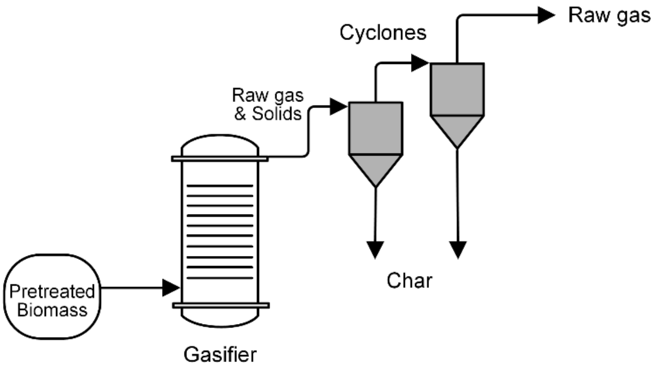

Figure 2. Solids removal using cyclones

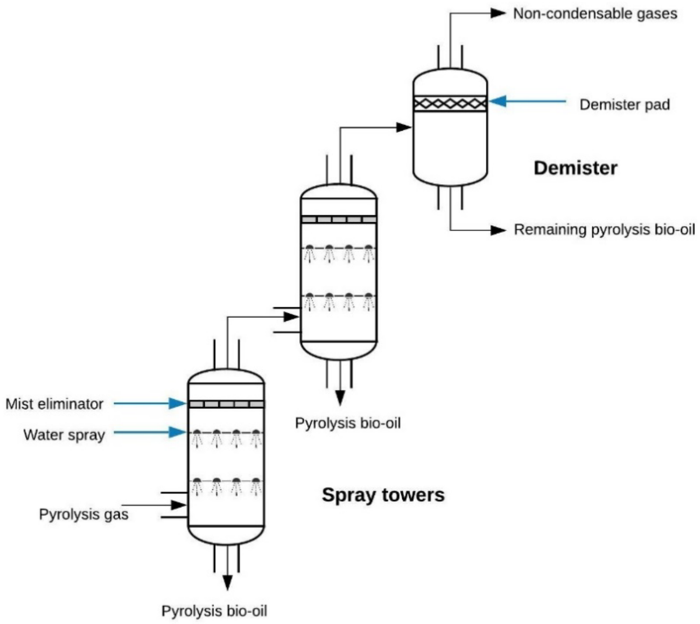

Figure 3. Removal of non-condensable gases with spray towers coupled to a demister

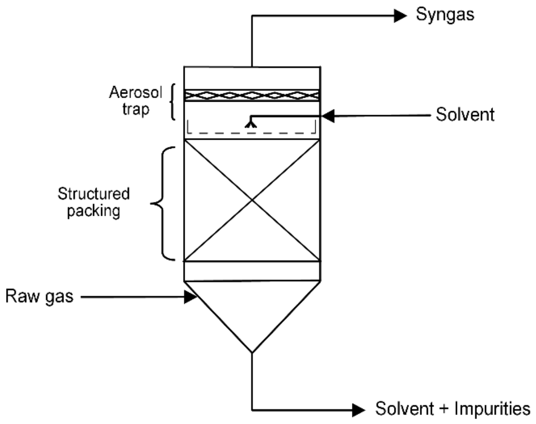

Figure 4. Scrubbing system for raw gas cleanup

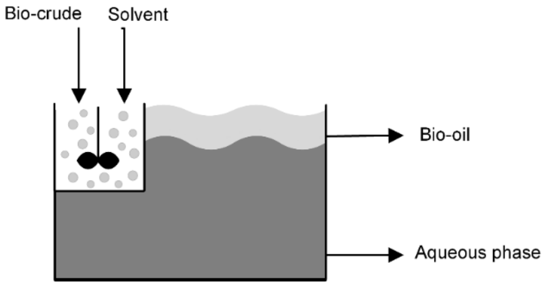

Figure 5. Bio-oil separation via solvent addition and decantation

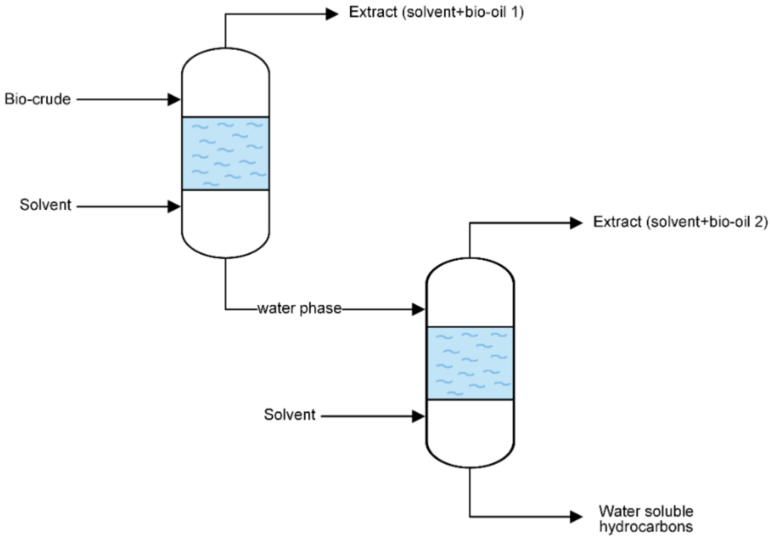

Figure 6. Separation and extraction of bio-oil

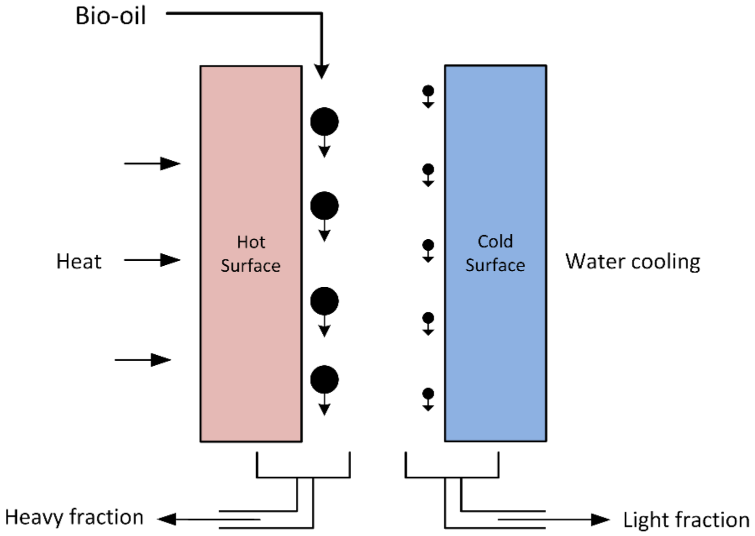

Figure 7. Principle of a molecular distillation system

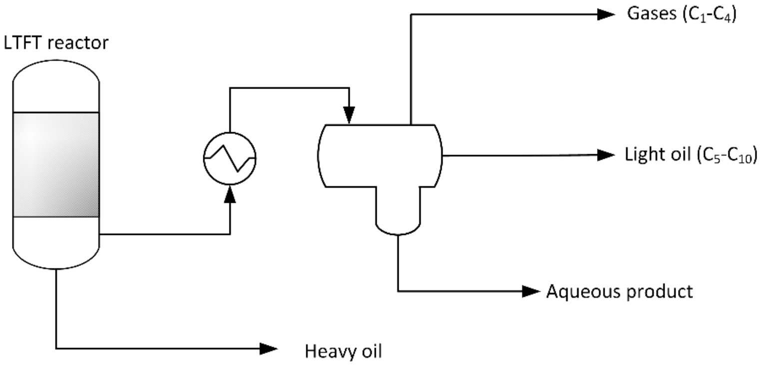

Figure 8. Stepwise cooling and separation of LTFT syncrude

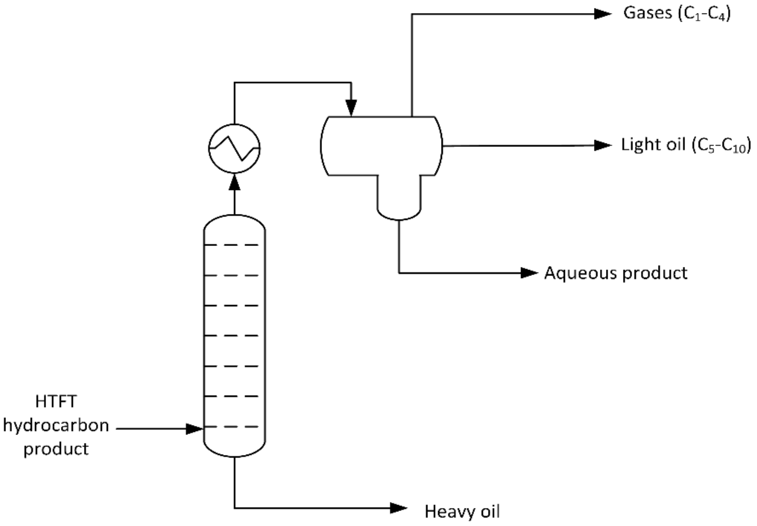

Figure 9. Cooling and separation of FT product by distillation and three-phase separation

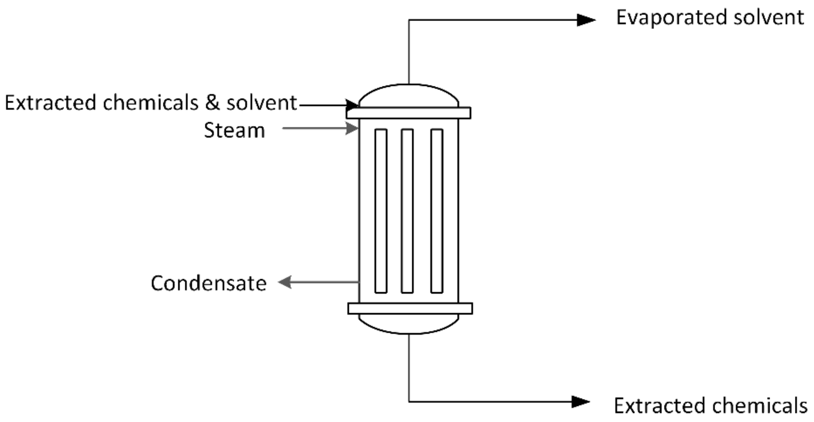

Figure 10. Solvent recovery via evaporation

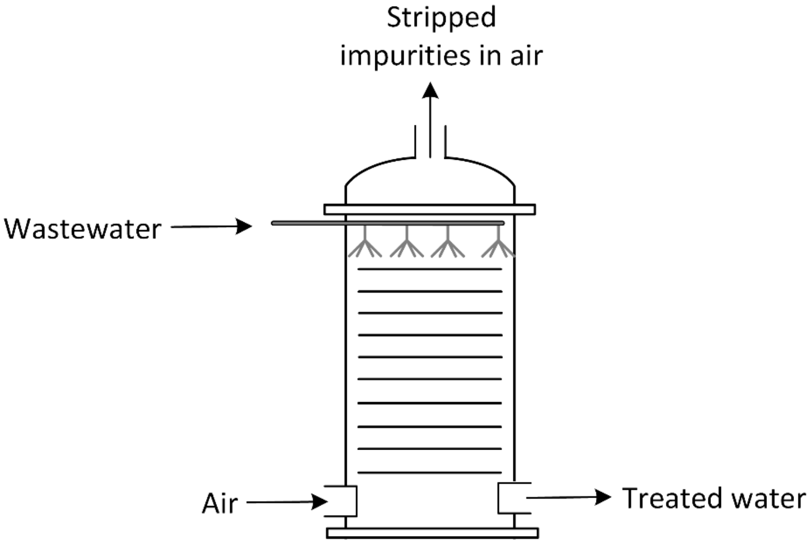

Figure 11. Air stripping for wastewater treatment

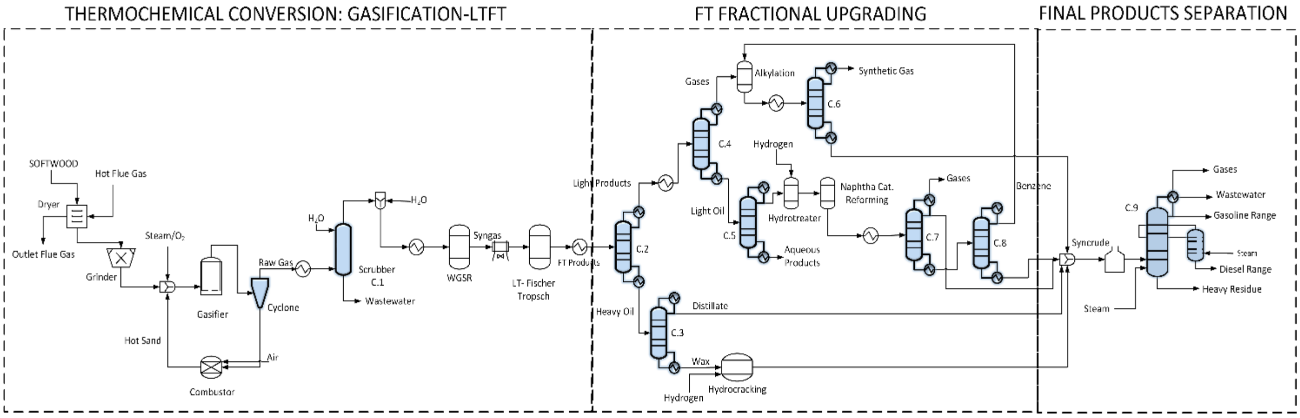

Figure 12. Separation needs in the Gasification-LTFT- Fractional Upgrading-Final Products

Separation case study

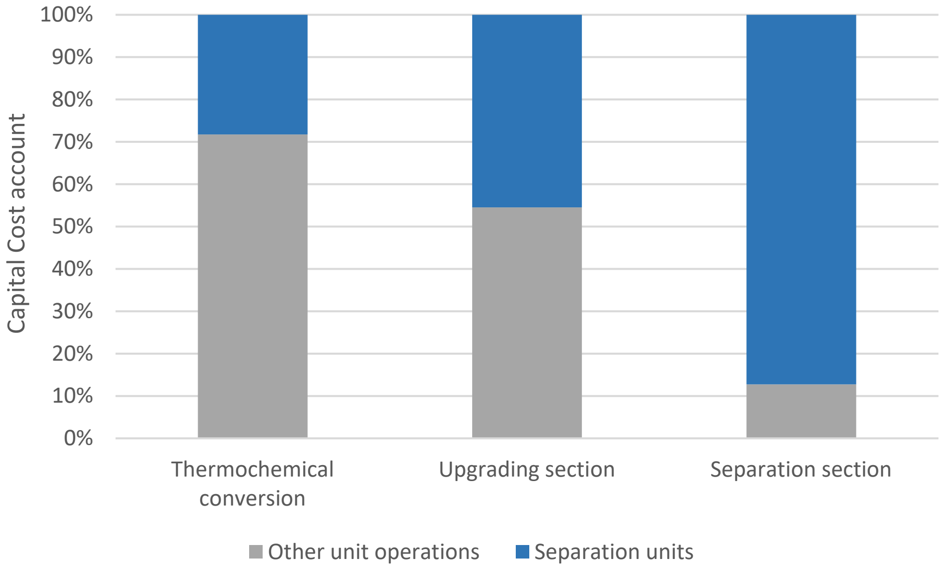

Figure 13. Capital costs of separation units in the process sections of the case study