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1. simulation-based superstructure synthesis and development

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ABSTRACT:

Thermochemical process routes are promising technological routes to convert lignocellulosic biomass into biofuels with similar properties as fossil fuels. In a previous work (*Ind. Eng. Chem. Res.* 57, 9925-9942, 2018), we have studied five base case processes for biofuels production with fixed process structures. This work presents an integrated methodology to consider new process structures for optimal synthesis of lignocellulosic biomass-to-liquid fuels production processes. Given that the five base cases showed not only significant difference of production costs among the process sections, but also distinct biofuel product profiles in terms of gasoline and diesel productivity, the current methodology is developed in two parts: Part 1 presents the superstructure synthesis through the step-by-step definition of unit operations' possible interconnections to include all possible new process alternatives than base cases. The superstructure is developed based on the data collected from unit operations' rigorous simulation of the base cases. Part 2 presents the superstructure algorithm set-up and optimization for optimal synthesis of BtL process flowsheets with specified product profiles of gasoline and diesel productivity. Rigorous simulation results for process units and process sections are used in the superstructure formulation and its algorithm development. Three case studies have showed that the integrated methodology can generate new production process with specified product profiles while having lower total manufacturing costs than base cases.

Keywords: biofuels, lignocellulosic biomass, thermochemical route, process synthesis, integrated methodology.

1. INTRODUCTION

The European Expert Group in their report on "Future Transport Fuels" has stated that advanced renewable fuels are the ultimate solution to decarbonize transport by gradually substituting fossil energy sources.[1] Renewable hydrocarbon biofuels represent an opportunity to move away from fossil fuels towards a set of lower greenhouse gas (GHG) transportation fuels, and a chance for a still-developing technology sector to grow.[2]

Renewable hydrocarbon biofuels are fuels produced from biomass sources through a variety of biological and thermochemical processes. They can be used in vehicles due to their similarities in chemical makeup to petroleum gasoline, diesel, or jet fuel. These fuels are also considered as infrastructure-compatible fuels because they can utilize existing petroleum distribution systems.[3]

Currently, cornstarch ethanol is the predominant renewable fuel in use, however, it has been envisioned that the majority of growth over time will come from advanced biofuels.[2] Advanced renewable biofuels are those produced from lignocellulosic biomass, including wood wastes, agricultural residues and wastes, grasses, municipal wastes and energy crops.[4] They can be determined by their advantages over conventional biofuels and fossil fuels. For instance, advanced renewable biofuels, including BtL fuels, give lower GHG emissions than conventional biofuels[1]. Additionally, these can often be grown on lands that are unusable for food crops and thus, are considered to have minimal negative impacts on food production.[5] Although the first-generation biofuels are based on well-established technologies, the development of advanced biofuels' processes utilizing wood biomass is still in the early stages of research. Moreover, fuel demand and GHG challenges will require the use of a mix of fuels produced from a large variety of these primary energy sources.[1] Clearly, production of advanced biofuels represents a challenge in finding a feasible path that involves proven technologies.

Modern lignocellulosic biorefineries attempt to parallel the workings of a crude-oil refinery, where, an abundant raw material, consisting mainly of renewable lignin, cellulose, and hemicellulose, enters the biorefinery and is converted through a number of different processes into a mixture of products, including biofuels, valuable chemicals, heat, and electricity.[6]

Thermochemical-based processes including pyrolysis, gasification, supercritical fluid extraction and direct liquefaction can convert lignocellulosic biomass into syngas or bio-oil.[7] The bio-oil obtained is composed of more than 300 compounds, which belong to different functional groups and have distinct physical and chemical properties and therefore, a single upgrading technique is not suitable to produce high quality biofuels.[8] Multi-step processing of bio-oil to transportation fuels, including upgrading and separation methods, is not economic, although technically feasible. Therefore, the biofuels success not only depends on the conversion costs, but in the upgrading and separation technologies costs as well, which account for almost 50% of the total production costs.[9] The high investments in manufacturing and production, the high biomass feedstock costs and the possible different product profiles in the thermochemical-based BtL systems are strong motivating factors for investigating various process routes which can transform lignocellulosic biomass into promising biofuels and simultaneously can refine the biofuels at lower costs. Process systems engineering methods and tools including synthesis, modeling, simulation, integration and optimization can be used to formulate an integrated methodology to investigate different BtL process routes that can increase the feasibility of transportation fuels production. In particular, process synthesis has been established as an important subject which has developed various process synthesis methods and which has contributed to novel process designs and configurations in many refinery areas.[10,11] It is expected that process synthesis is also significant to biorefinery, which through developing systematic synthesis methods can contribute to the early process design stage for novel biorefinery processes and products.

Several research institutions have investigated the potential of the production of transportation fuels from lignocellulosic biomass applying modeling and optimization tools. For instance, previous

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reports from the National Renewable Energy Laboratory (NREL) proposed and evaluated the thermochemical conversion of biomass into liquid transportation fuels via fast pyrolysis followed by hydroprocessing of pyrolysis oil using Aspen Plus as a simulation tool.[12,13] In addition, a study made by Betchel to support the NREL in the thermochemical conversion of BtL was developed with Aspen Plus for a biomass-based gasification and Fischer-Tropsch (FT) plant.[14] Martin and Grossman[15] proposed a superstructure for the production of diesel from switchgrass via gasification followed by different FT reaction schemes. Baliban et al.[16,17] proposed a process superstructure for the production of gasoline, diesel, and jet fuel via gasification of hardwood biomass and FT hydrocarbons synthesis. The earlier superstructure-based works have used either simple linear models or estimates from several literature sources to calculate the capital and energy costs, which does not guarantee the same consistency as rigorous simulation-based in the process synthesis, evaluation and technologies comparison. Moreover, it is well known that simulation, synthesis, superstructure and optimization are all the metaphysical elements in PSE, however, to this topic of BtL production a superstructure with several thermochemical-based process alternatives has not been addressed in the earlier works.

In this work, an integrated methodology for combined process synthesis, design, modeling, simulation and optimization is presented for the development and implementation of a BtL superstructure. The main scope of the superstructure approach is to synthesize more feasible process structures that can reduce the manufacturing costs of BtL fuels and increase their productivity compared to the base cases. This methodology considers the production of gasoline, diesel, and by-products from softwood biomass through various confirmed thermochemical conversion technologies and feasible upgrading and separation technologies. In Part 1, the main contribution is the development of a step-by-step methodology for synthesis of a BtL superstructure including the thermochemical conversion of softwood via pyrolysis or gasification followed by product upgrading technologies such as catalytic cracking, hydroprocessing, syngas Fischer−Tropsch (FT) reaction, FT fractional upgrading and required separation units. To support the superstructure development and evaluate the technical and economic potential of the unit operations required in these conversion

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steps, process modeling and simulation in Aspen Plus with consistent data and information is performed. From the simulation results and experimental data collected from the literature, the possibility of combining unit operations into processing blocks performing major tasks, and their subsequent interconnection into a BtL superstructure is performed. The resulting superstructure presented here in Part 1 is the starting point for the conceptual analysis of the different processing networks that can be considered for the conversion of lignocellulosic biomass into biofuels, whereas Part 2 of this work covers the superstructure mathematical programming for optimization and synthesis of new thermochemical-based processes considering different product profile scenarios and the minimization of the manufacturing costs of BtL fuels and maximization of biofuels productivity.

2. Problem statement and the integrated methodology

The problem stated in this work is to develop an integrated methodology with a superstructure which contains all possible process alternatives by different interconnection and integration between the process sections in the base cases. The operation units and blocks in the superstructure have the same data and information as the base cases including their capital and operating costs. This will ensure the equal comparison between the new process routes and the base cases. The development and formulation of the integrated methodology is presented in Figure 1, which simultaneously considers the processing of data and information of the individual units in the base cases and the structural formulation of the superstructure. The procedure in the superstructure development consists of the following main steps:

1) Formulate the base cases which are the basic thermochemical routes to transform the given biomass to biofuel products.

2) Rigorous simulation to obtain the technical data and economic costs information for the units and process sections in the base cases.

3) Establish the processing block flowsheets from the base cases through combining the composition-not-change units into the composition-change units as reaction and separation

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blocks, recalculating the data and economic information for the combined reaction and separation blocks.

4) Establish the detail superstructure through interconnecting of the blocks and process sections among the processing block flowsheets, registering the structural and numerical information for the blocks in the detail superstructure.

5) Establish the simplified superstructure through formulating the lumped blocks in the detail superstructure which will simplify the modelling and optimization algorithm development, registering the structural and numerical information for the lumped blocks in the simplified superstructure.

For the superstructure formulation, first, synthesis and design of individual base case processes is performed by sequencing the softwood biomass and desired biofuel products with selected thermochemical, upgrading and separation technologies required for the conversion. From the sequencing of technologies, five base case processes are proposed, and process flowsheets are designed including all the unit operations required to accomplish the tasks. For its further evaluation and simulation, specific information needs to be collected from the literature, such as:

- Unit operating conditions

- Catalyst and auxiliary streams ratios

- Reaction yields

- Stoichiometric reactions

- Model compounds to represent product mixtures

- Biomass proximate and ultimate analyses

- Diesel and gasoline fuel properties

- Market prices for raw materials, utilities, and intermediate chemicals

- Catalysts loadings and lifetimes

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Then, the set-up and rigorous simulation of the required unit operations are performed in the process simulator Aspen Plus® V8.8 considering the information previously collected. The rigorous simulation of each unit operation and its auxiliary units (pump, heater, etc.) is performed in separate flowsheets. This is done to prepare information for each unit operation, which will be necessary for the superstructure formulation. The information collected from the rigorous simulations includes:

– Mass and energy balances

– Calculation of conversion factors for the reactors

– Calculation of separation factors for the separators

– Solid, liquid and gas emission streams

– Capital costs of operation units

– Energy costs of operation units

– Product properties

– Product profiles of different base processes

After performing the rigorous simulations and collecting the data, it is possible to proceed with the superstructure formulation by analyzing the possible interconnection between the unit operations belonging to the base case process routes. The modelling of the interconnections of all the individual operations units by their process streams within the entire superstructure is possible but is too complex because of a large number of unit operations included. For example, all the streams information including components and costs need to be stored for all the unit operations included in the base cases. Moreover, the transporting of all the streams between unit operations needs to be logically registered. To simplify the task, for the unit operations in the process routes (e.g. pumps and compressors), where the mass compositions do not change, are grouped into processing blocks, namely reaction blocks and separation blocks. The definition of processing blocks allows passing from the base case process flowsheets including all unit operations to lumped flowsheets consisting of processing blocks.

The processing block flowsheets facilitate the modelling of the interconnections between the blocks while significantly reducing the complexity of the optimization programming work. The interconnections are defined by sequencing the blocks that allow the conversion of biomass into the final biofuels. Different interconnections can be proposed, since different paths from feedstock to products can be taken. The result is a detailed network superstructure formed by several processing blocks.

Initially, it is important to keep the superstructure disaggregated to detect all the possible interconnections. Afterwards, the detailed (disaggregated) superstructure can be further simplified by detecting standalone sequential blocks which can be grouped into a major lumped block. For instance, in some cases, processing blocks not shared between paths can be grouped into a larger lumped-process block. In other cases, if some blocks are appeared in different paths, then they can be combined into a lumped block if and only if they perform the same tasks and present similar capital and energy costs. This treatment leads to a final lumped superstructure with corresponding structural and techno-economic information. The resulting superstructure considers the conversion of different softwood feedstocks into gasoline, diesel and by-products via several thermochemical, upgrading and separation technologies.

In part 2, modelling of the superstructure as a mathematical optimization problem will be implemented, which will synthesize new processes with objective to minimize the manufacturing costs and to maximize the productivity for different products profiles.

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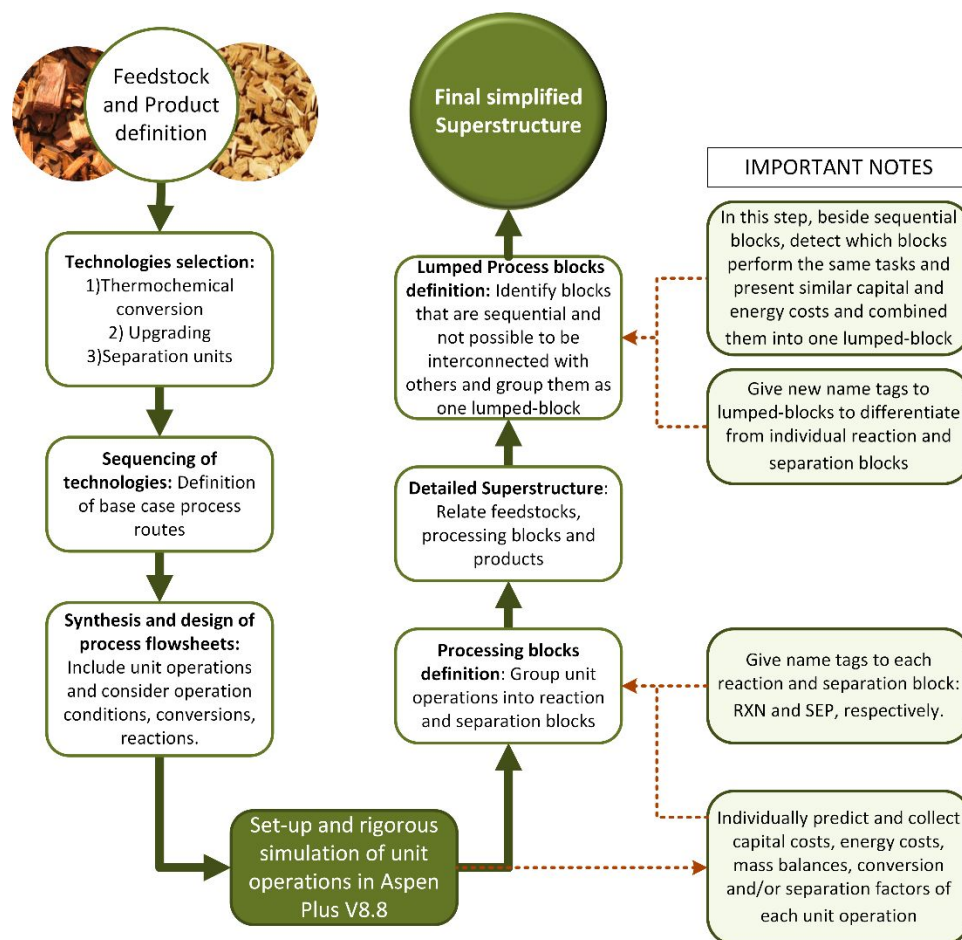
Figure 1. Integrated methodology for development and formulation of the superstructure for softwood BtL conversion

In the following sections, the steps mentioned above starting from the superstructure concept framework to the synthesis of the final lumped superstructure will be described in detail.

3. Superstructure concept framework

To determine the optimal process route, it is required to postulate a superstructure including the process units and sections that can be potentially selected in the final flowsheet, as well as their interconnection.[18] A biomass network superstructure refers to the interconnection of dependent biomass conversion processes that utilize one or more biomass resources to produce single or multiple bio-products.[19]

In this work, the feedstocks, thermochemical conversion routes, upgrading technologies and separation units selected are presented in Figure 2. These process routes will provide the process units

and sections, which are the structural elements for the superstructure development. By applying the superstructure concept, these technologies are interconnected to create the generic superstructure depicted in Figure 3. The generic superstructure diagram is the starting point for the subsequent formulation of a detailed superstructure including all the required unit operations' performance and costs data.

It is important to prepare the rigorous data and information including capital and operation costs for all the process units and sections to be included in the superstructure. To do so, the feedstock, technologies and products were initially combined for the synthesis of base case process routes, which provide the unit operations' information necessary for their subsequent interconnection into a superstructure. By rigorous simulations, these base cases will provide the rigorous data and information for all the process units and sections in the superstructure. On the other hand, new process routes other than the base cases can be included in the superstructure. The superstructure will then be modelled as an optimization problem for synthesis of new process flowsheets, which will be presented in Part 2. The process units and sections together with their rigorous data and information prepared from rigorous simulation will guarantee that the obtained new process flowsheets in the optimization are evaluated on the same basis as the base cases in the integrated methodology.

For the synthesis of the base case process routes, the sequencing of three technological sections (thermochemical conversion, upgrading and separation technologies) is considered. For instance, for the thermochemical conversion, pyrolysis or gasification followed by low temperature and/or high temperature Fischer−Tropsch (FT) were considered. Then, the upgrading technologies consisted of bio-oil hydroprocessing or catalytic cracking, FT syncrude fractional upgrading (olefin alkylation, oligomerization, naphtha hydrotreating and catalytic reforming, distillate hydrotreating, wax hydrocracking, and hydrogenation), and high temperature Fischer−Tropsch (HTFT) syncrude hydroprocessing. Finally, for the separation processes, distillation columns, solid separators, flash units, scrubbers, and fractionation columns were included.

In the following section, brief descriptions of the thermochemical, upgrading and separation steps are presented. Further detail on the modeling and simulation of the unit operations required by these processing steps, and their transformation into a superstructure will be discussed in Sections 5 and 6.
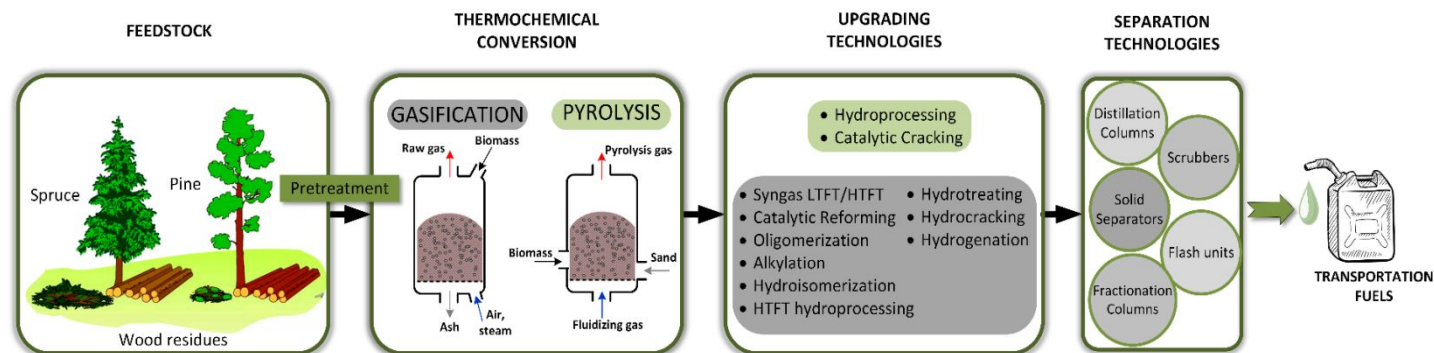
Figure 2. Feedstocks and technologies considered in the process routes and superstructure synthesis
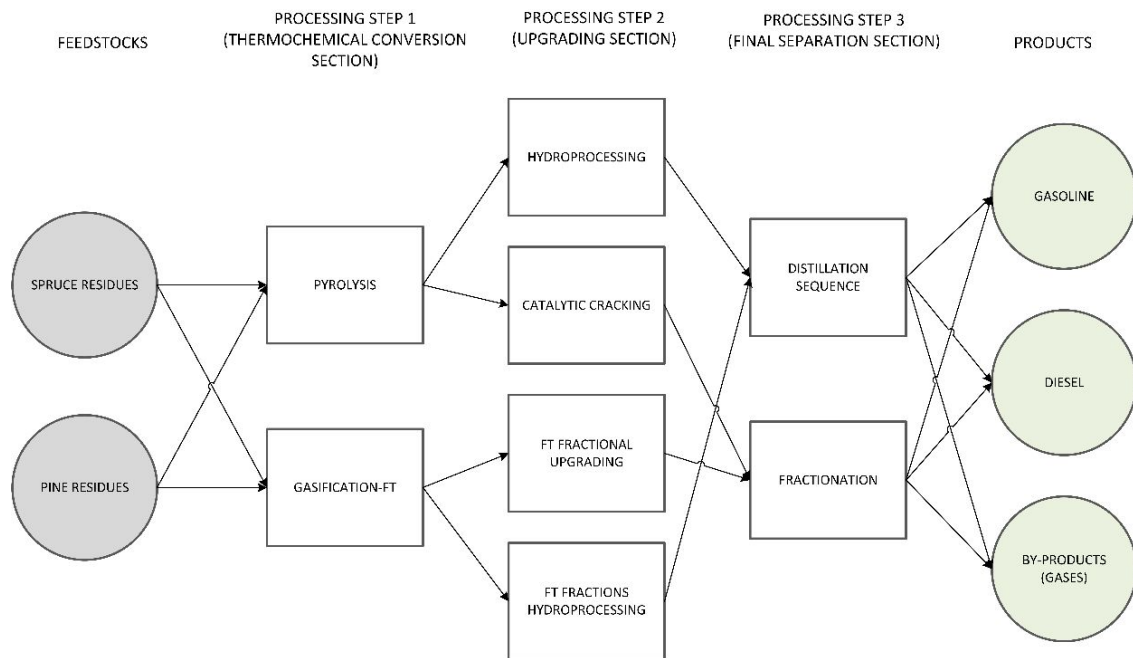

Figure 3. Thermochemical-based softwood conversion to liquid transportation fuels: Generic superstructure

4.   Softwood BtL process superstructure: Conceptual Design

This section outlines the conceptual design of the thermochemical, upgrading and separation technologies considered in the synthesis of the process routes and in the formulation of the softwood BtL superstructure.

4.1 Feedstock selection, handling and pretreatment

The BtL conversion methods are selected depending on the feedstocks, processing technologies and desired products. From the technological point of view a wide variety of lignocellulosic biomass materials including agricultural wastes, forestry residues, grasses, energy crops and woody materials are available as potential sources for conversion into high value chemicals and fuels[4]. However, if biomass is to be considered in a larger extent to contribute to the world's energy supply, then the availability of the biomass in the region is an important factor.

The European continent has nearly 215 million ha of forest land and other wooded land, which accounts for almost 30% of the continent´s land area and around 5% of the world´s forests.[20] One of the major resources in Northern Europe is softwood. A mixture of Scots pine and Norway Spruce is the most common softwood stand in the Nordic Countries.[21] Therefore, due to the availability of resources, a strategy to promote the better utilization of softwood biomass must be established.

The production of transportation fuels from biomass can be performed through biochemical or thermochemical methods. Thermochemical methods of conversion have certain advantages over biochemical methods in terms of processing time of biomass and pretreatment requirements. For instance, there is no need of separation of all the components of lignocellulosic biomass and hence, no chemical pretreatment is required. The pretreatment techniques are very much physical in the case of solid biomass for any thermochemical method. These techniques consider different properties, such as, softwood biomass size distribution, moisture content, and bulk and particle densities. Size reduction is carried out using hammer mills, ball mills, crushers and so on. Moreover, to reduce the

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moisture content of biomass, drying is the most important step. Likewise, the chemical composition

in terms of elemental analysis is also very important to anticipate the decomposition behavior and

product portfolio.[20]

In this work, spruce and pine residues were selected as raw material and were defined based on

their chemical composition as depicted in Table 1[22,23]. The moisture content of the softwood biomass

was reduced from 30 wt. % to 7-10 wt. % and the particle size was reduced from 25 mm to 2−6 mm

through preliminary drying and grinding steps.

Table 1. Spruce and Pine Residues Proximate and Ultimate Analyses

	Proximate analysis (wt. %, db)	Ultimate analysis (wt. %, db)					Calorific values MJ/kg	
	Ash content	C	H	N	S	O	LHV	HHV
Pine[22]	1.33	51.30	6.10	0.40	0.02	40.85	19.34	20.67
Spruce[23]	2.50	50.10	6.30	0.32	0.02	40.70	18.65	19.89

db- Dry base

After the feedstock selection and pretreatment, the synthesis and design of base case process

routes are carried out by selecting and combining three distinct process technological sections for

each process route: thermochemical conversion technologies, upgrading technologies, and separation

technologies. Each section contains several unit operations that allow the conversion of the biomass

into biofuels. These unit operations include reactors, distillation columns, fractionation columns,

mixers, splitters, pumps, solid separators and heat exchangers. In the following sections, the

importance of these technologies in each step and the main products produced are described.

4.2 Thermochemical conversion

4.2.1 *Pyrolysis*

Pyrolysis is the thermal decomposition of biomass in the absence of oxygen, it is carried out at 500 °C in less than two seconds at atmospheric pressure.[12] The products from the pyrolysis reaction are solid char, non-condensable gases and pyrolysis gas. After the reaction, these products are sent to a cyclone to remove the solid product from the gaseous products. Then, the gases are sent to a train of quench columns where the products are rapidly cooled down and the pyrolysis oil is separated from the non-condensable gases (NCGs). The pyrolysis oil or bio-oil is finally sent to a liquid filtration unit to remove the fine char that could not be removed in the cyclone.[24]

The pyrolysis oil product is a candidate to reduce the dependence of fossil fuels. However, it is a complex mixture of water, solid particles and hundreds of organic compounds and thus, it is considered as thermally and chemically instable, highly oxygenated, acidic and corrosive.[25] Therefore, if pyrolysis oil is to be considered as replacement for fossil fuels further upgrading is required.

4.2.2 *Gasification*

Biomass gasification is a mature technology pathway that uses heat, steam, and oxygen to convert biomass without combustion into a gaseous mixture known as raw gas. The reaction is carried out at temperatures around 800 °C to 1000 °C , residence times of three to four seconds and atmospheric pressures.[26,27]

Similar as in pyrolysis, the solid residues must be removed and thus a cyclone is employed. Then, to completely remove other impurities (such as, nitrogen compounds and solids) from the raw gas, the gas is sent to a scrubber. In the scrubber, the raw gas is put in contact with a high amount of water, which simultaneously cools down the product and reduces the concentration of ammonia and other impurities. After the cleaning, the H_2/CO ratio of the gas is adjusted by water-gas-shift reaction (WGSR) and the resulting product is called syngas. The syngas can be used for pure power production

or can be upgraded to transportation fuels by adding processing steps, such as, Fischer-Tropsch (FT) synthesis and product upgrading operations.

4.3 Upgrading technologies

As mentioned before the products from the thermochemical conversion are not suitable for direct use as liquid transportation fuels. Therefore, after the production of the pyrolysis oil and syngas, these products are sent to their corresponding upgrading units for hydrocarbon production. Several upgrading technologies can accomplish the conversion. In this work, the upgrading technologies considered for the superstructure formulation are described below.

4.3.1 *Pyrolysis oil hydroprocessing and hydrocracking*

Upgrading operations are needed to remove the oxygen (as high as 45 wt. % wet basis) from the pyrolysis oil and to breakdown the high molecular weight fragments present in the mixture [28]. Hydroprocessing is a technology that can improve the quality of the product by rejecting oxygen as water by catalytic reaction at elevated temperatures in the presence of high-pressure hydrogen and sulfided catalysts. Multi-stage processing, where mild hydrotreating is followed by more severe hydrotreating, has been found as the solution for efficient and continuous operation.[28,29] First, the pyrolysis oil pretreatment is carried out in a stabilization bed under relatively mild process conditions followed by processing under more severe hydrotreating conditions in two hydrotreating reactors in series.[30] Through these steps, the pyrolysis oil is deoxygenated and upgraded bio-oil is obtained. The final products are gas (light hydrocarbons), hydrotreated bio-oil, and an aqueous fraction containing water and carbon dioxide. The hydrotreated bio-oil is mainly formed by hydrocarbons in the naphtha and diesel range, as well as a heavy fraction (wax range). The wax fraction can be hydrocracked to additional gasoline and diesel products and some by-product gas.[12]

4.3.2 *Pyrolysis oil Catalytic Cracking*

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Catalytic cracking is another promising technique for the upgrading of the highly oxygenated pyrolysis oil. Through catalytic cracking the oxygen in the pyrolysis oil is rejected as carbon dioxide. This conversion technology produces mainly aromatic hydrocarbons and a high amount of solid residue (coke), which can deposit on the catalyst and reduce the efficiency of the process. For instance, 18 wt. % of the final product corresponds to solid products, 29 wt. % to upgraded bio-oil, and 46 wt. % to by- products such as gases and aqueous products.[31–33] The main advantages of this technology and the use of zeolites is that the aromatics are produced at atmospheric pressures without H_2 requirements.

4.3.3   *Fischer-Tropsch hydrocarbons production*

The syngas produced in the gasification section needs to go through a series of chemical reactions to produce liquid fuels. In this work, first, to produce hydrocarbons, the syngas is sent to a Fischer-Tropsch (FT) reactor. The FT reaction is carried out at two different temperature ranges. One is the syngas *high temperature FT* (HTFT) reaction conducted over iron-based catalyst and temperatures between 320 °C and 375 °C, which gives mainly components in the gasoline range and gases that can be further upgraded to produce more gasoline products. The other one is the *low temperature FT* (LTFT) reaction, which gives components in the distillate and wax range. The LTFT reaction is conducted under working temperatures between 200 °C and 250 °C, and employing cobalt-based catalyst.[34]

From the FT synthesis, a product mixture called syncrude with similarities to crude oil is produced. The syncrude consists of a mixture of linear hydrocarbons (paraffins and olefins), aromatics and oxygenates, and therefore, needs to be upgraded in a different way than the crude oil.

4.3.4   *Fischer-Tropsch products upgrading*

The FT syncrude is present as a mixture containing three to four different phases[34] and thus, different upgrading technologies are required to obtain a single phase product mixture. The FT phases are gases, light oil, aqueous fraction, and heavy oil. The gas phase is mainly composed of tail gas (C_1-C_2), and liquefied petroleum gas (LPG) containing C_3-C_4 hydrocarbons. The light oil contains naphtha range components with C_5-C_{10} alkanes, alkenes, aromatics and oxygenates. The heavy oil is composed of distillate and wax range components (C_{11}-C_{22+}) and the aqueous fraction contains mainly alcohols, carbonyls and carboxylic acids.[34] For its upgrading, these phases are recovered using distillation columns, and each fraction is converted to transportation fuels by the following reactions.

FT tail gas. Synthetic natural gas consisting of methane, ethylene and ethane gases is usually not upgraded to transportation fuels and is instead used to produce energy in the form of heat and/or electricity.[35]

Light hydrocarbons alkylation. The best refining pathway for the olefinic gases fraction is defined depending on the technology selected for the upgrading of the naphtha range products. In this work, the naphtha fraction is reformed and the benzene produced is further alkylated with the olefinic gases to produce more gasoline range products and variable amounts of LPG as subproducts.[36] From the benzene alkylation with the olefinic gases, alkyl aromatics are produced. The alkyl aromatics such as ethylbenzene and propylbenzene are high-octane gasoline and jet fuel components that can also mixed with the diesel fuel to increase its density.[35,37]

Olefin oligomerization. The olefin oligomerization converts short chain hydrocarbons into longer chain liquid products. Olefin oligomerization by a motor-gasoline selective technology, such as solid phosphoric acid (SPA) based oligomerization, is a natural choice.[35] In the *oligomerization* reactor, the light olefins catalytically react over SPA to produce gasoline and diesel fuel. Likewise, zeolite catalysts such as HZSM-5 can be employed in the reaction.[38,39]

As described above, the C$_3$-C$_4$ olefins can be upgraded via alkylation or oligomerization or used as a combination depending on the desired product properties and product profile. The latter indirectly facilitates the separation of propylene and propane.[40] In this work, all alternatives have been considered.

FT naphtha catalytic reforming. To increase the octane number of the naphtha products, the paraffins and cycloparaffins are converted into aromatics via catalytic reforming, which can be conducted in fixed bed or moving reactors under operation conditions of 500 °C and atmospheric pressure. In the reformer, the low octane naphtha reacts with hydrogen and multifunctional metal catalysts to produce high-octane gasoline.[41,42]

FT wax catalytic cracking. The conversion of FT biowaxes to biofuels is achieved by a catalytic cracking process under the presence of hydrogen and bifunctional catalysts (acid and hydrogenation function). The main products from the hydrocracking of waxes are diesel and gasoline range components [43].

Distillate hydroprocessing. The most common technology for the upgrading of the distillate fraction is hydrogenation, from which diesel fuel components are produced. The distillate stream can be upgraded to diesel range components under working temperatures of 340 °C, 34 bar over CoMo catalyst and high pressure hydrogen [44].

Aqueous Fraction refining. From the Fischer-Tropsch synthesis, short-chain alcohols, carbonyl compounds, and carboxylic acids are produced. These products form an aqueous phase when dissolved in the water produced in the Fischer-Tropsch process. The recovery of the aqueous fraction involves complex separations. For this, the separation can be simplified by catalytic dehydration of alcohols to olefins.[45] Alternatively, the oxygenate-rich product can be partially hydrogenated to convert the aldehydes and ketones into their corresponding alcohols and facilitate their separation into carbonyl-rich and alcohol-rich products.[34] However, due to the high costs that implies its

treatment and its low concentration compared to the other fractions, in this study, the aqueous product was not upgraded and instead was considered as emission.

4.3.5 *HTFT product hydroprocessing*

When hydroprocessing is selected for the upgrading of the syncrude, the FT product is only divided in three main fractions: naphtha product, distillate product and wax product. The FT distillate and naphtha products are upgraded in their corresponding hydrotreating units and the wax is sent to a hydrocracking unit.[14] The distillate hydrotreating unit yields high-quality diesel components and the naphtha hydrotreating yields saturated naphtha, which is further sent to a reformer to produce high-octane gasoline components.[44,14] The wax hydrocracking yields naphtha and diesel products as well as some by-product gas. Finally, the naphtha produced in the hydrocracking is sent to an *isomerization* reactor to yield high-octane gasoline components and increase its stability.[46]

4.4 Separation Technologies

In the production of biofuels from lignocellulosic biomass, the separation technologies are not only essential in the recovery of the final products, but also are indispensable in the synthesis and design of different upgrading configurations, as well as in the purification of the syngas and bio-oil produced from the thermochemical conversion.

Furthermore, through all the BtL processes, different physical separation technologies are required to recover the main products either in liquid or gas phase, to isolate by-products, and to remove impurities and excess reactants. In the gasification-based routes, the separation technologies play an important role in the upgrading of the FT product into biofuel components, because depending on the FT fractions recovered, the posterior reactions needed are selected. Therefore, different process configurations can be defined by implementing different separation methods to change the materials conditions and destinations. Likewise, different product profiles can be defined depending on the

separation and upgrading technologies configurations. The separation technologies considered in this work are described as follows.

4.4.1 Solid separators. The products in gas phase from the pyrolysis and gasification reactor, as well as from the catalytic cracking unit contain char and other solid particles, which are removed with cyclones. However, some of the solids are inevitably carried over with the gas phase. Then, when the gas phase is cooled down and liquid products are obtained, the remaining solid components are removed by solid-liquid filtration.

4.4.2 Quench columns and scrubbers. The pyrolysis gas and the raw gas produced from the gasification-based routes are usually quenched and scrubbed with water in a tray column to remove impurities such as ammonia, and solid particles that were not completely removed in the cyclone.

4.4.3 Three phase separator. The separation of the gas (NCGs), hydrotreated bio-oil and aqueous fraction produced from the pyrolysis hydroprocessing route is performed in a three-phase separator. Likewise, remaining hydrotreated bio-oil products in the NCGs stream and excess water are separated in three-phase separators. Concerning the gasification-FT routes, the FT product is composed of light products and heavy oil, and the light products stream is further separated in a three-phase separator into gas, light oil and aqueous fractions.

4.4.4 Distillation columns. If pyrolysis followed by hydroprocessing is considered, then a series of distillation columns are required to fractionate the hydrotreated bio-oil into final fuels. In the first distillation column, the naphtha range products, which represent the gasoline, are recovered from the heavy oil containing wax and diesel components. Then, the heavy oil is separated into diesel range products and wax products in a second distillation column. On the other hand, distillation columns are also employed in the separation of FT products, where the light products are separated from the heavy oil and when the recovery of the different syncrude fractions is required.

4.4.5 Fractionation column. The final biocrude and syncrude produced from catalytic cracking and FT hydrocarbon upgrading units respectively, are sent to a fractionation column to recover the different substances boiling at different temperatures. In the case of the BtL processes, the biocrude/syncrude is divided into gases, aqueous products, gasoline, diesel and heavy residues.

4.5   Base case lignocellulosic BtL process flowsheets

The synthesis and design of the base case process routes are performed following two main steps. First, the thermochemical conversion, upgrading and separation technologies are selected among the process sections described in the sections 4.2, 4.3 and 4.4, which enable the conversion of the softwood into the desired fuel products. Then, the sequencing of the technologies for the softwood biomass to the desired final fuel products is performed and base case process route is then obtained. In this work, five base case process routes were defined as starting point for superstructure formulation, which are named as: Pyrolysis-Hydroprocessing-Separation (BC-PHS), Pyrolysis-Catalytic Cracking- Fractionation (BC-PCCF), Gasification-HTFT-Fractional Upgrading-Fractionation (BC-GHTUF), Gasification-LTFT-Fractional Upgrading- Fractionation (BC-GLTUF) and Gasification-HTFT-Hydroprocessing (BC-GHTH).

After the definition of the base case process routes, the synthesis of the process flowsheets is performed by determining all the unit operations required to accomplish the tasks in each section. To exemplify the synthesis of the base case process flowsheets, the BC-PHS and BC-GLTUF process flowsheets are illustrated in Figure 4.

The five base cases represent the initial conceptual designs of the thermochemical process routes for BtL biofuels from lignocellulosic biomass, which have been compared in terms of economy and product profiles in our previous work[47]. The objective here is to construct a superstructure which not only includes the initial base cases but also includes new process routes through interconnecting of the process sections and unit operations in the base cases. The motivation is that there are many other

22

options for the process integrations and interconnecting of the unit operations in the process sections,

which can generate new process flowsheets other than the base case processes. This will be developed

as an integrated optimization-based methodology for optimal synthesis of thermochemical processes

for BtL biofuels production. To do so, the performance and economic data need to be prepared and

registered for all the unit operations in the base cases. In the following section, the rigorous simulation

and economic analysis will be described.

THERMOCHEMICAL CONVERSION: PYROLYSIS

UPGRADING TECHNOLOGY: HYDROPROCESSING

SEPARATION TECHNOLOGY

THERMOCHEMICAL CONVERSION: GASIFICATION

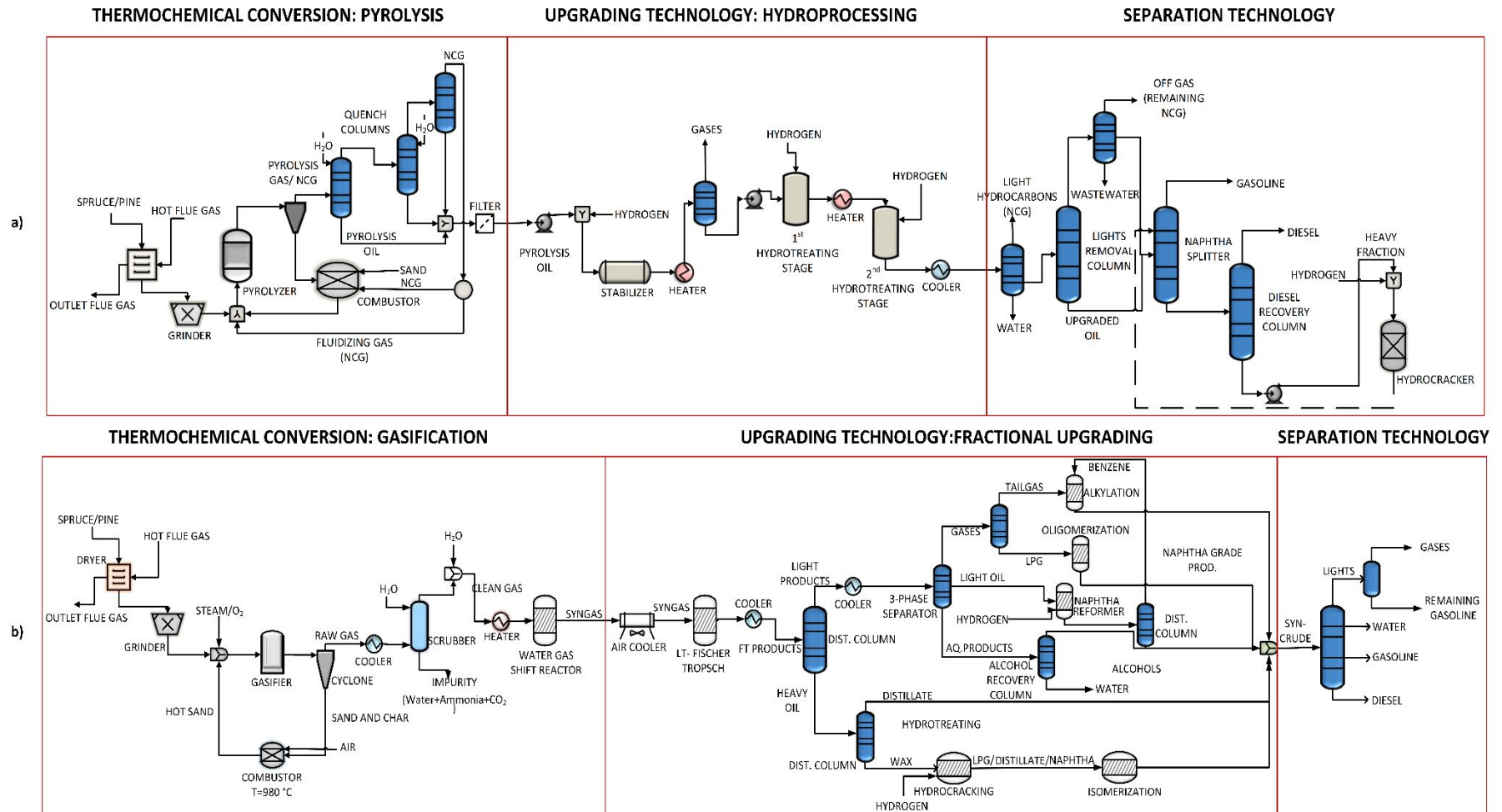**UPGRADING TECHNOLOGY:FRACTIONAL UPGRADING**

SEPARATION TECHNOLOGY

Figure 4. a) BC-PHS process flowsheet and b) BC-GLTUF process flowsheet.

5. Data and information preparation of the base cases' unit operations from Aspen™ simulation

During the preliminary stage of design and development of a biofuel production plant the conceptual design of the process routes needs to be performed. However, in order to obtain the optimal design, process simulation and analysis concerning plant economics and performance should be considered and evaluated. The process flowsheets together with the literature and experimental data (operation conditions, type of reactors, stoichiometric reactions, yields, separation needs, and so on) allow the use of computer tools to perform steady-state energy and mass balances, equipment sizing and economic calculations of the proposed BtL process routes.

In a previous study by Ibarra-Gonzalez and Rong[47], rigorous simulation of the thermochemical conversion, upgrading and separation sections was described and performed in the process simulator Aspen Plus V8.8. Therein, each technological section was treated as a separate simulation task, and thus, the simulation and economic data was collected for the entire process section, which allowed to compare each section's cost in the total process.

In this work, each individual unit operation belonging to a base case process was separately simulated. The simulation results and main task of each unit were collected and registered, which provided the original data and information of the unit operations for the construction of the superstructure, including the base cases and the interconnection among its unit operations.

For the simulations, the thermodynamic property packages Peng-Robinson and Soave-Redlich-Kwong equation of state with Kabadi-Danner mixing rules were selected for the unit operations belonging to pyrolysis-based routes and gasification-based routes, respectively. Both thermodynamic models are recommended for synthetic fuels applications, gas-processing, refinery, and petrochemical applications.[48] Moreover, the latter provides high accuracy in water-hydrocarbon systems over a wide range of temperatures and predicts the instability of the liquid phase.[49] In

addition, the electrolyte and non-electrolyte NRTL models with Redlich−Kwong equation of state were employed for the separation units.

The softwood biomass and ash were specified as non-conventional components since they are not included in the Aspen databanks. For this, their ultimate analysis including C, H, O, N, S and Ash elements and proximate analysis, given in Table 1 were entered. The biomass lower heating value (LHV) was also specified with the HCOALGEN and DCOALIGT property models chosen to estimate the biomass enthalpy of formation, specific heat capacity and density based on the ultimate and proximate analyses. The stream class MCINCPSD was selected which is used when conventional and nonconventional solids are present in the process and when the particle size distribution is known. The char product was defined as carbon and the sand was defined as silicon dioxide, which are conventional solid components available in the Aspen databanks.

The following assumptions were also taken into consideration for the setup of the simulation flowsheets. Yield, stoichiometric reactions, and conversions were fixed according to experimental data found in the literature.[47] Recovery of key components of 98% was assumed. For the complex product mixtures, model compounds were selected to represent each of the functional groups identified in chemical characterizations found in the literature. Components not participating in the reactions were defined as inert components. The system was considered as a steady-state process simulation. To model the unit operations, the Aspen Plus Yield reactor, RYield, was used to model the pyrolysis, gasification, catalytic cracking and hydrotreating reactions. The stoichiometric reactor (RStoic) was used to model the combustor, stabilizer and first hydrotreating reaction as well as the upgrading of the HTFT hydrocarbons. The separation units were model using the RadFrac block and the final fractionating column was model with a PetroFrac. Moreover, to apply rigorous stage-by-stage simulation, the columns are simulated based on the trayed towers.

Aspen Process Economic Analyzer V8.8 was used to calculate unit operations' capital costs and energy costs. These costs were calculated considering a plant capacity of 500 kg/h of softwood (spruce and pine residues) for the sole reason of technological comparison. Moreover, the capital and energy costs were calculated for fixed base-flow rates and base-residence times. For the evaluation of the base case process routes and for future applications, including the mathematical programming of the superstructure that will be addressed in Part 2, the costs must be adjusted according to the actual flowrates and residence times, as depicted in Equations 1 and 2, respectively.

$$Cost_{adj} = Cost_{base} \left(\frac{m_{adj}}{m_{base}} \right)^{0.6} \tag{1}$$

$$Cost_{adj} = Cost_{base} \left(\frac{\tau_{adj}}{\tau_{base}} \right)^{0.5} \tag{2}$$

Where $Cost_{adj}$ is the adjusted cost according to the actual flowrate (m_{adj}) and residence time (τ_{adj}), and $Cost_{base}$ is the cost calculated considering the base-flow rate (m_{base}) and base-residence time (τ_{base}) obtained from the simulations on Aspen Plus.

In Table 2, the economic results from the rigorous simulation of the unit operations for BC-PHS considering base-flow rates and base-residence times are reported. The capital and energy costs (heating, cooling and electricity) of the unit operations for BC-PCCF, BC-GHTUF, BC-GLTUF and BC-GHTH can be found in Table S1 of supplement support.

Table 2. Unit operations for BC-PHS: capital and energy cost

Process route	Unit operations' description	Capital Cost [$]	Energy Cost [$/y]
BC-PHS	Pyrolizer	23000	75944
	Cyclone	10900	39892
	Combustion	21200	39892
	Quench column 1	74100	35544
	Quench column 2	58200	35544

Filter	11500	75437
Demister	74500	30543
Stabilizer	54700	48215
Separation unit for recovery of bio-oil from NGCs	39400	35544
1st hydrotreater	90900	54446
2nd hydrotreater	170200	74890
3-Phase separator	38400	35544
Separation unit for recovery of light products from heavy products	453600	68544
Flash unit	15100	35544
Naphtha splitter	104800	46338
Separation unit for recovery of diesel from wax	47600	35544
Hydrocracking	182900	49885

Moreover, mass balances, waste streams, conversion and separation performance factors for all the unit operations were also collected and calculated from the simulation results. The data collected from the simulations allow us to proceed with the formulation of a processing superstructure to explore the distinct thermochemical-based process routes and synthesize new optimal total biofuels production processes. Since the simulations provide the data and information for sizing, costing, and economic evaluation of the unit operations, this guarantees that all the processes are compared on the same level of the converged simulation results in a consistent way. This means that the mass and energy balance information, the sizing and cost information for the unit operations are consistently calculated based on the simulation results for all the process flowsheets.

6. Integrated Superstructure synthesis

With the data and information prepared for the operation units, it is possible to define the superstructure which includes the base cases as well as new process routes defined by the

interconnection of the unit operations. The synthesis of the superstructure is performed in three main steps: (1) Definition of processing blocks by the combination of unit operations, (2) the generation of a detailed superstructure by interconnecting the processing blocks and (3) the generation of a lumped superstructure by the definition of lumped-process blocks performing major tasks. These steps are described in sections 6.1-6.3.

6.1 Step 1: Processing blocks definition

When disaggregating the five base case process routes considered for the superstructure formulation, it was found that these BtL process routes are composed of many unit operations and the modelling of the possible interconnections between them is possible but very complex. To reduce the complexity of the superstructure programming, the unit operations belonging to each process route and their individual information were grouped into processing blocks, namely *reaction blocks* and *separation blocks*. A processing block is considered as a set of units where the mass composition of the feed stream will be changed by the processing block. The blocks definition was performed by grouping mixers, pumps and heat exchangers with the reactors or separation units associated to them, and by assigning them a specific tag. The reaction blocks were tagged as *RXN(i,j)* and the separation blocks as *SEP(i,j)*. The index *i* refers to the number of processing block (1,2,3,…n) and *j* refers to the technology option. The index *j* can take value of **1** which refers to feedstock selection, **2** for a reaction block or **3** for a separation block. To exemplify the procedure, the unit operations belonging to the *Pyrolysis - thermochemical conversion section* were grouped into reaction and separation blocks as depicted in dotted-squared frames in Figure 5.
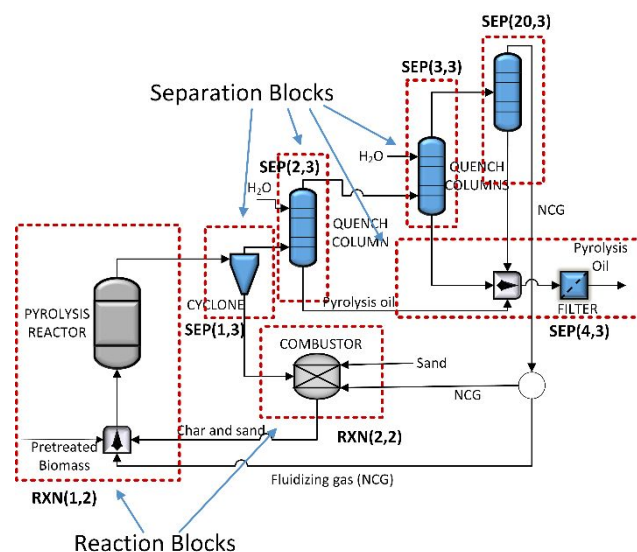
Figure 5. Formulation of reaction RXN(i,j) and separation SEP(i,j) blocks in pyrolysis

conversion section

When grouping the unit operations into reaction and separation blocks, it is very important to keep

the consistency between the unit operations and the processing blocks. To do so, data and information

of the individual unit operations (capital costs, energy costs, conversion and separation factors) are

embedded in the blocks' definition. For the reaction blocks, the data and information collected from

the simulations and required for the lumped blocks' formulation are as follows:

- Capital costs of reactors and units associated with the reactors, such as mixers, pumps and

  heat exchangers (e.g. the reaction block RXN(1,2) in Figure 5).

- Energy costs of reactors and units associated with the reactors, such as mixers, pumps and

  heat exchangers. The energy costs include heating, cooling and electricity.

- Components inlet and outlet mass flow rates. From the mass balances, conversion factors

  were calculated. The conversion factors' calculation will be described in section 7.2.

For the separation blocks, the data and information collected from the simulations and required for

the lumped blocks' formulation are as follows:

- Capital cost of distillation columns, flash drums, strippers, quench columns, solid separators and units associated with the separation unit, such as mixers, pumps and heat exchangers (e.g. the separation block SEP(4,3) in Figure 5).

- Energy costs of separation units and units associated with the separation unit, such as mixers, pumps and heat exchangers. The energy costs include heating, cooling and electricity.

- Components inlet and outlet mass flow rates. From the mass balances, separation factors were calculated for each outlet stream. The separation factors' calculation will be described in section 7.3.

After the lumped blocks, it is possible to simplify the process flowsheets by substituting the unit operations with their corresponding lumped reaction and separation blocks. The result is the formulation of processing block flowsheet, as exemplified for BC-PHS in Figure 6.
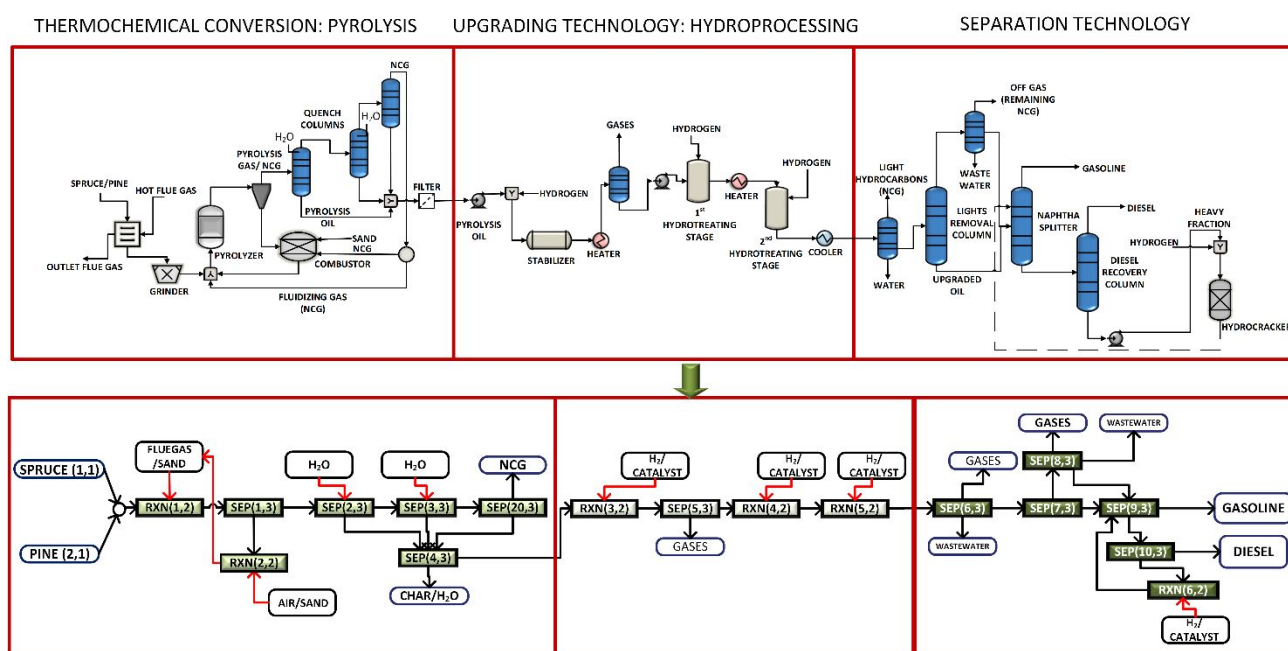

Figure 6. Formulation of the processing blocks flowsheet for BC-PHS

The definition of the processing block flowsheet is an important step for the formulation of the superstructure. These processing block flowsheets allow the creation of a network structure by identifying the possible interconnections between all the processing blocks defined. In the next section, the creation of the network structure will be described.

6.2 Step 2: Detailed superstructure generation

The network structure named as the detailed superstructure here is formulated by replacing the technological sections in the base case processes with the corresponding processing block flowsheets formulated in the previous steps. By replacing the technological sections with the processing blocks flowsheets and by detecting the possible combinations and interconnections between the blocks, a detailed superstructure is obtained which is depicted in Figure 7. The description of each individual reaction and separation block is given in Table S2. The detailed superstructure includes the numerical data collected from rigorous simulations and the structural information of the five base cases. The detailed superstructure starts from the feedstock selection, followed by the selection of the
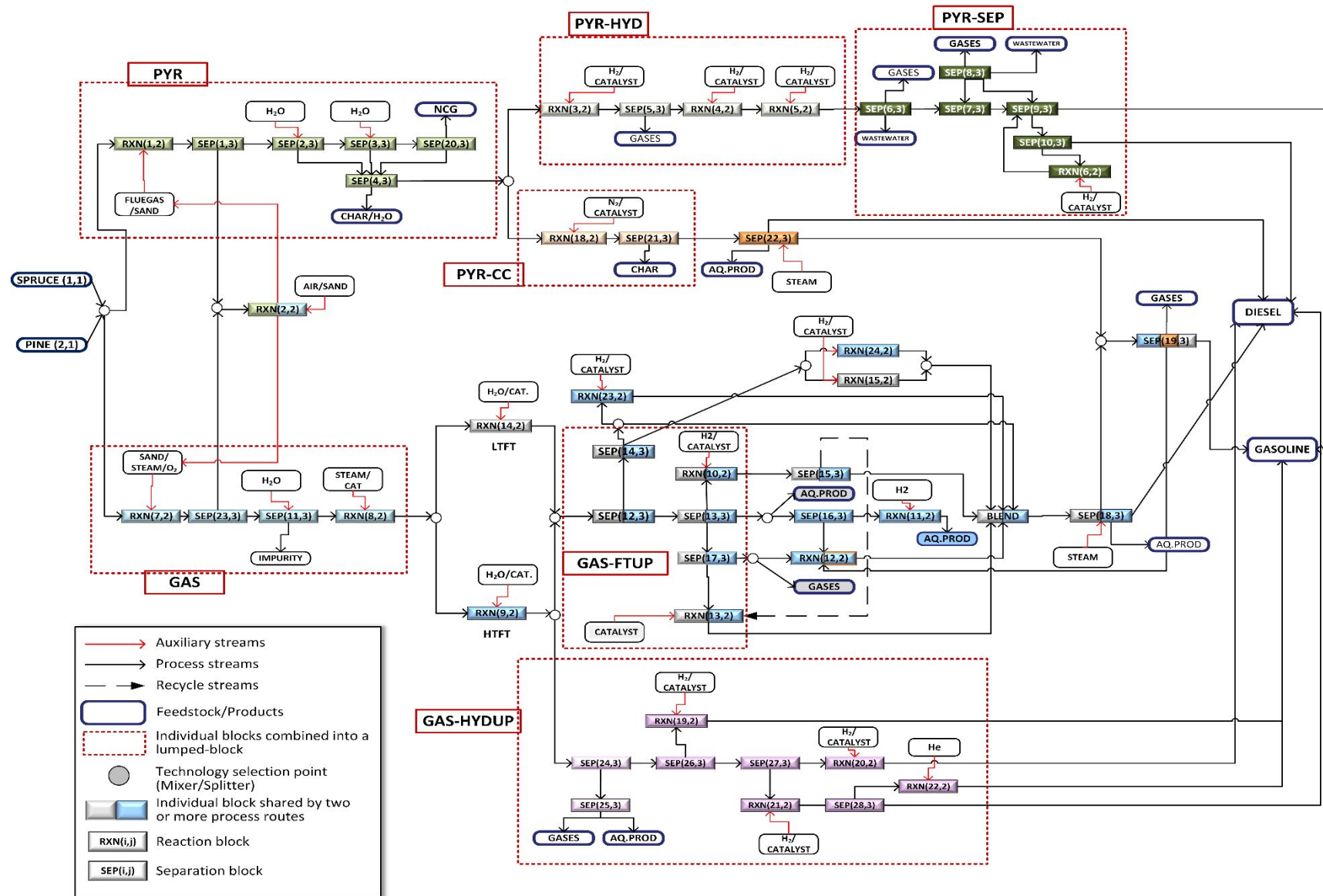
Figure 7. Softwood BtL detailed superstructure with reaction and separation blocks

thermochemical conversion technology, then the selection of the upgrading, and finally the selection of separation technologies for the biofuels production.

From Figure 7 it can be observed that different paths can be taken besides the proposed initial base case process routes. The modelling and programming of the superstructure into a GAMS algorithm will be implemented in part 2. However, it is essential that the superstructure should be reduced complexity for its modelling. There are several reasons, first it can reduce the complexity in optimization algorithm during the superstructure modelling and programming, second it can avoid errors in its structural logic interpretation during modelling, and finally it is easy to check the consistency of the data and information between the process routes.

The superstructure can reduce its interconnecting complexity by analyzing the possible grouping of the blocks between the process routes. The simplification is accomplished with the support of the numerical information (data of process units and sections) and the simulation results (energy and capital cost) presented in Table 2 and Table S1. The collected information allows the identification of blocks performing same tasks and presenting similar capital and energy costs. From this analysis, it was observed that some blocks in different process sections perform same tasks and present similar costs, thus can be considered as one shared block within the superstructure. To clarify, in Figure 7 the blocks are illustrated in two or three colors (e.g. RXN(2,2), SEP(12,3), …, etc.), which represent that these blocks are shared between the process routes.

6.3 Step 3: Superstructure simplification by definition of lumped-process blocks

For the superstructure in Figure 7, it can be observed that some blocks stand sequentially as a group which can be lumped together as a functional process section, i.e. lumped process section. For example, some consecutive reaction and separation blocks can be combined into a lumped process section. This can greatly reduce the complexity of modelling and programming of the superstructure during its optimization algorithm development. Following this observation, **lumped-process blocks**

as depicted in dotted-squared frames in Figure 7 are indicated. These lumped-process blocks perform

major tasks like:

- Biomass conversion to syngas via gasification (GAS),

- Bio-oil production via pyrolysis (PYR),

- Pyrolysis bio-oil catalytic cracking (PYR-CC),

- Pyrolysis bio-oil hydroprocessing (PYR-HYD),

- Upgraded pyrolysis product separation (PYR-SEP),

- HTFT product hydroprocessing (GAS-HYDUP),

- HTFT/LTFT product separation, catalytic reforming and alkylation (GAS-FTUP)

As observed in Figure 7 the first six lumped-process blocks are for the sequential reaction and

separation blocks, they are not shared between all the process routes. For instance, there are some

blocks that are shared only by one or two process routes. The lumped-process block (**GAS-FTUP)** is

considered for individual reaction and separation blocks which are required in the upgrading and

separation of both HTFT and LTFT syncrude fractions. Specifically, the catalytic reforming

RXN(10,2) and alkylation RXN(13,2) as well as the separation blocks SEP(12,3), SEP(13,3),

SEP(14,3), SEP(15,3), SEP(17,3) and SEP(18,3) are required for the upgrading of both syncrudes

into biofuels. These blocks perform the same tasks and present similar capital and energy costs in

both alternatives (LTFT and HTFT), therefore, they are lumped into one process block.

On the other hand, the separation blocks and reaction blocks (oligomerization RXN(12,2),

hydrogenation RXN(11,2), distillate hydrotreating RXN(23,2) and wax hydrocracking RXN(15,2)/

RXN(24,2)) were not treated as lumped-process blocks because they are quite different in capital and

energy costs.

For the superstructure synthesis, it is important to keep the consistency of the data information between the individual reaction and separation blocks and the lumped-process blocks. To do so, the performance and economic data of each lumped-process section are obtained by accounting all of the individual units within the block. For clarity, a new tag was given for the lumped-reaction and the lumped-separation in each of the lumped-process sections, namely $RXN(i,j)_{LB}$ for lumped-reaction and $SEP(i,j)_{LB}$ for lumped-separation respectively. This means that each lumped-process section has a lumped-reaction block tagged as $RXN(i,j)_{LB}$, which implies all the individual reaction blocks inside the lumped-process section including their technical and economic information. Similarly, a lumped separation block tagged as $SEP(i,j)_{LB}$ is included which implies all the individual separation blocks inside the lumped-process section. Figure 8a illustrates the lumped-process section PYR indicated as the lumped reaction and separation blocks of $RXN(1,2)_{LB}$ and $SEP(1,3)_{LB}$. Figure 8b illustrates the resulted lumped-process section PYR which appears in the simplified superstructure in Figure 9.
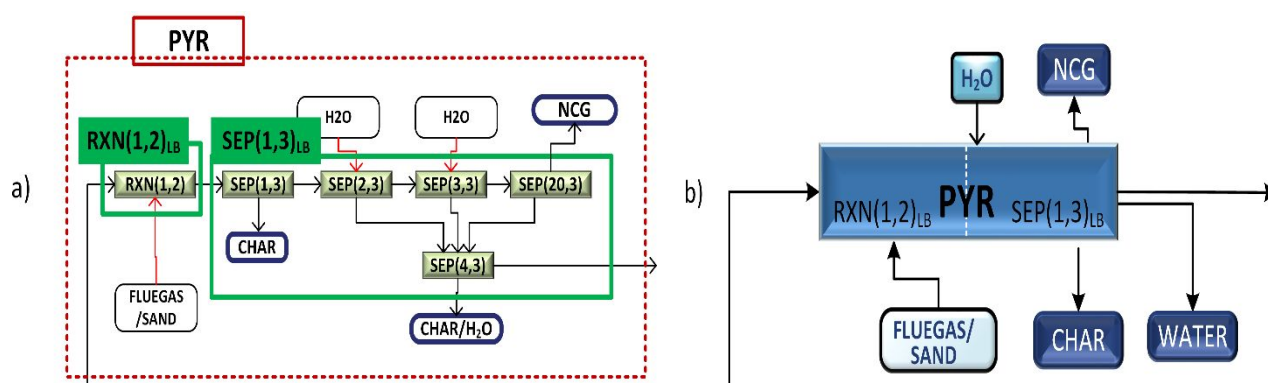

Figure 8. a) Individual reaction and separation blocks grouped into lumped-process section PYR. b) lumped-process section PYR including new reaction and separation tags.

Similar as tagging the individual blocks, the tags of the lumped-process sections follow an ascending numerical order. The index i (1, 2, 3, … n) refers to the number of processing block, while index j refers to the technology option (**1** for a feedstock selection block, **2** for a reaction block or **3** for a separation block). It is important to indicate the difference for the tagged blocks within a lumped-process section in Figure 9 from the initial lumped blocks in Figure 7. It is so that a lumped-process

section can include the data and information for one or more individual blocks. For instance, the **lumped-separation block SEP(1,3)$_{LB}$** is not equal to the **individual separation block SEP(1,3)**, because the lumped-separation block includes all the data of the individual separation blocks SEP(1,3), SEP(2,3), SEP(3,3), etc. A lumped-process block can be equal to the individual block only when it is conformed by a single individual block, for instance the lumped-reaction block RXN(1,2)$_{LB}$ in Figure 8a.

Following these treatments, the **simplified superstructure** considering the definition of the lumped-process sections is presented in Figure 9. The blocks in the superstructure have been assigned new tags for their block names which are the logical interconnection information for developing optimization algorithm in part 2. The reaction and separation lumped-process blocks in the simplified superstructure of Figure 9 are tagged as follows: bio-oil production via pyrolysis (PYR): RXN(1,2)-SEP(1,3); pyrolysis oil hydroprocessing (PYR-HYD): RXN(3,2)-SEP(2,3); pyrolysis oil catalytic cracking (PYR-CC): RXN(5,2)-SEP(4,3); conversion of biomass to syngas via gasification (GAS): RXN(6,2)-SEP(7,3); upgraded pyrolysis product separation (PYR-SEP): RXN(4,2)-SEP(3,3); HTFT hydroprocessing (GAS-HYDUP): RXN(15,2)-SEP(10,3); HTFT and LTFT hydrocarbons upgrading section (GAS-FTUP): RXN(10,2)-SEP(8,3). After the new tags to the lumped-process blocks, the remaining reaction and separation blocks are retagged continuing with the next block number *(i)* following an ascending numerical order from left to right (Figure 9). For example, from Figure 7, the individual separation block SEP(22,3) was retagged as SEP(5,3) and the SEP(19,3) was retagged as SEP(6,3), as presented in Figure 9. The same was done with the other individual blocks.

FEEDSTOCK

TECHNOLOGICAL
CONVERSION
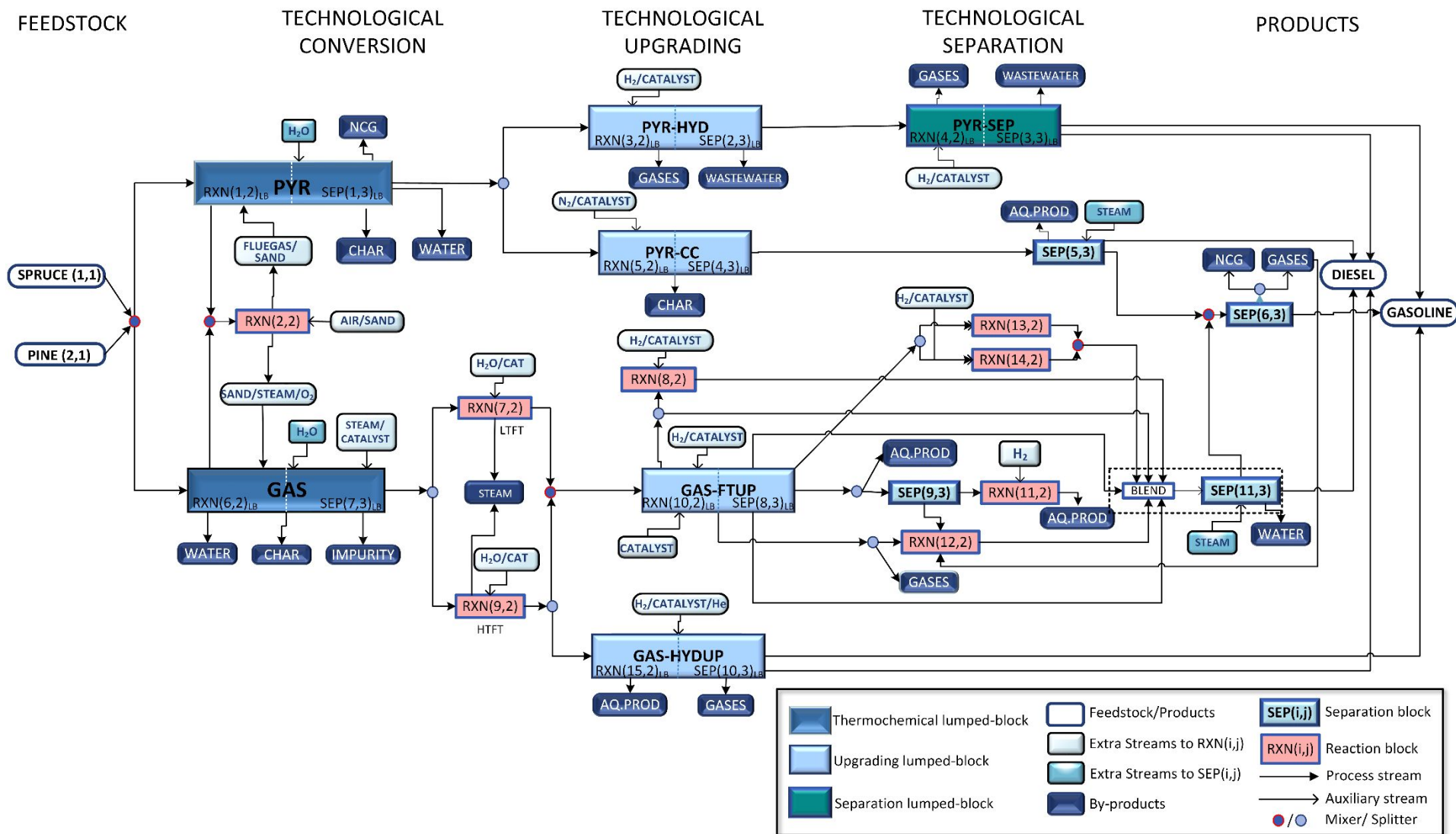
TECHNOLOGICAL
UPGRADING

TECHNOLOGICAL
SEPARATION

PRODUCTS

Figure 9. Softwood BtL simplified superstructure with lumped process sections

The lumped-process blocks definition has the advantage to reduce the complexity for the superstructure modelling while keeping the same accuracy of their numerical information including costs through the superstructure. However, as mentioned, it is necessary to keep the consistency between the individual blocks' information and the final lumped superstructure, which means that the performance and economic parameters should not be affected. This is assured by considering the mass balances, conversion factors, capital and energy costs of the individual reactions blocks when defining the lumped-reaction blocks so that the combined blocks have the consistent information. Similarly, the mass balances, separation factors, capital and energy costs of the individual separation blocks must be considered for the lumped-separation blocks. The superstructure's performance and cost parameters are introduced in the following section.

The superstructure with lumped process sections which will facilitate the programming and development of the optimization algorithm for synthesizing the optimal network for given feedstock specifications, product portfolios and optimization objective.

7.   Performance parameters of the lumped blocks in the superstructure

7.1 Lumped-process blocks capital and energy costs

As introduced in section 6, Aspen Process Economic Analyzer V8.8 was used to calculate the unit operations' capital and energy costs. These unit operations' costs were then used in the calculation of the capital and energy costs of the individual reaction and separation blocks. Following the same reasoning, the individual reaction and separation blocks (depicted in Figure 7) information was used to calculate the capital and energy costs of the lumped-process blocks (presented in Figure 9). For example, the capital cost (CC) calculation of the lumped-separation block $SEP(1,3)_{LB}$ (presented in Figure 8) is given in Equation 3.

$$CC_{SEP(1,3)_{LB}}$$
$$= \sum CC_{ind}[SEP(i,j)] = CC_{ind}[SEP(1,3)] + CC_{ind}[SEP(2,3)] + CC_{ind}[SEP(3,3)] + CC_{ind}[SEP(4,3)] + CC_{ind}[SEP(20,3)]$$

(3)

Where $CC_{SEP(1,3)_{LB}}$ is the total capital cost of the lumped-separation block $SEP(1,3)_{LB}$ and it is equal

to the sum of the capital cost of the individual separation blocks $CC_{ind}[SEP(i,j)]$ that were combined

into that specific lumped-process block (Figure 8).

The capital and energy cost calculations of all the lumped-reaction and lumped-separation blocks are

performed following the same procedure. For example, Equation 4 presents the energy cost

calculation for the lumped-separation block $SEP(1,3)_{LB}$.

$$EC_{SEP(1,3)_{LB}} = \sum EC_{ind}[SEP(i,j)]_{(electricity,\ heating,\ cooling)} = EC_{ind}[SEP(1,3)] + EC_{ind}[SEP(2,3)] + EC_{ind}[SEP(3,3)] + EC_{ind}[SEP(4,3)] + EC_{ind}[SEP(20,3)]$$

(4)

Where $EC_{SEP(1,3)_{LB}}$ is the total energy cost of the lumped-separation block $SEP(1,3)_{LB}$ and it is equal

to the sum of the energy costs of the individual separation blocks $EC_{ind}[SEP(i,j)]$ conforming the

lumped-process block. The energy costs include the electricity, heating and cooling consumed by

each block.

7.2 Reaction blocks' performance parameters

From the reaction units' rigorous simulations and mass balances, conversion factors were

calculated to accurately describe the performance of the reaction blocks. These performance

parameters are defined in the algorithm for modeling and programming of the superstructure, which

will be addressed in Part 2. The conversion factors $Conv_f$ were calculated based on the reactors' inlet

and outlet component mass flow rates. The $Conv_f$ term represents the conversion of reactants to

products. In addition, for the calculation of the conversion factors of the lumped-reaction blocks

containing 2 or more individual reaction blocks, mass balances were calculated considering the total reactants inlet flowrate and the total products outlet flowrate of all the reaction blocks included in the lumped-reaction block. For instance, in Figure 10, the inlet and outlet streams of the reaction blocks $RXN(1,2)_{LB}$ and $RXN(6,2)_{LB}$ are presented. Moreover, in Table 3, the inlet and outlet component mass flow rates and the conversion factors calculated for the lumped-reaction blocks $RXN(1,2)_{LB}$ and $RXN(6,2)_{LB}$ are given. The reactants' conversion factors are presented with a minus sign, which means that they are being consumed, and the positive values represent the products' factors.
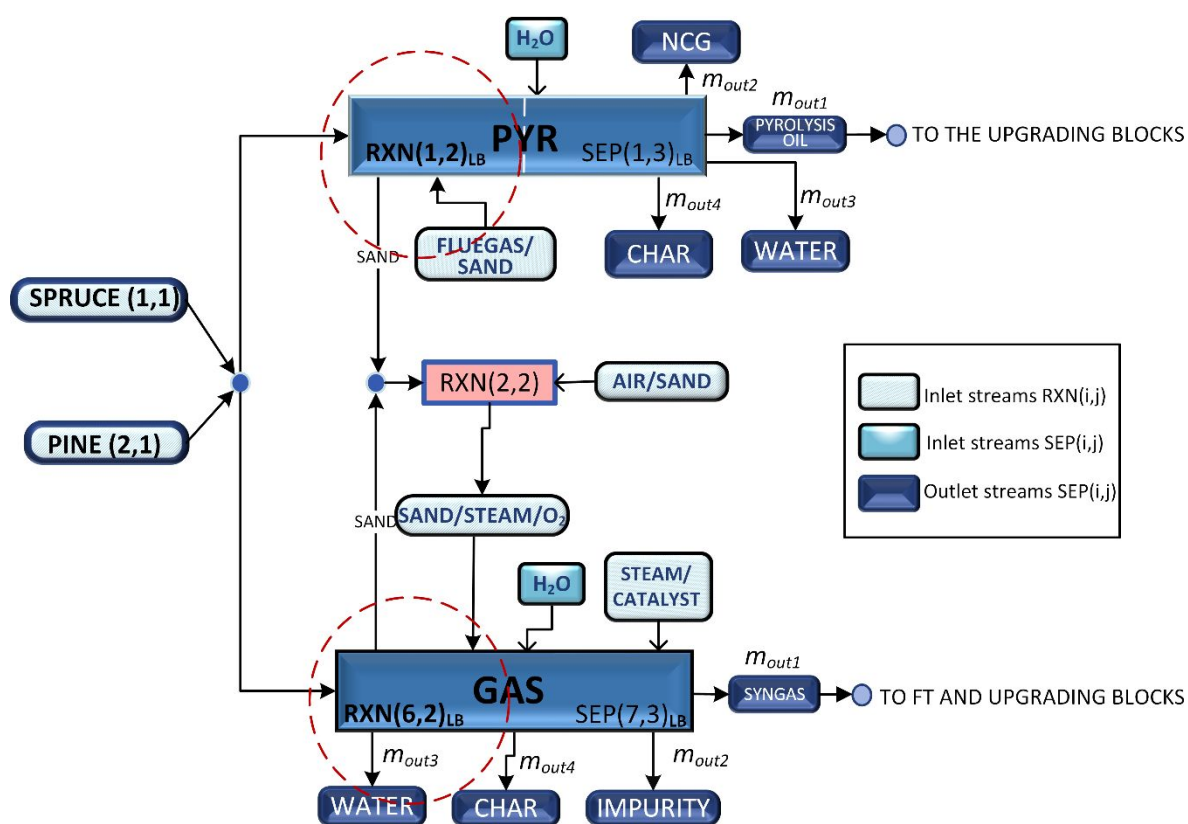

Figure 10. Inlet and outlet streams from $RXN(1,2)_{LB}$ and $RXN(6,2)_{LB}$

Table 3. Mass balances and conversion factors for $RXN(1,2)_{LB}$ and $RXN(6,2)_{LB}$ in Figure 10

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Inlet Components	Inlet flow (kg/h)	$Conv_f$	Outlet Components	Outlet flow (kg/h)	$Conv_f$
			Block RXN(1,2)$_{LB}$		
Spruce/Pine	500	-1.00	CO	110.40	0.22
Fluegas composition		-3.00	CO_2	103.09	0.21
CO	690		CH_4	14.40	0.03
CO_2	645		H_2	2.40	0.00
CH_4	90		C_2H_4	9.60	0.02
H_2	15		H_2O	240.00	0.48
C_2H_4	60		Alcohols	56.32	0.11
			Aldehydes	32.00	0.06
			Ketones	283.26	0.57
			Acids	288.26	0.58
			Furans	122.24	0.24
			Phenols	358.40	0.72
			Anhydrosugar	92.16	0.18
			Esters	47.36	0.09
			Char	240.11	0.48
			Block RXN(6,2)$_{LB}$		
Spruce/Pine	500	-1.00	CO	112.18	0.22
Oxygen	155	-0.31	CO_2	168.21	0.34
Steam	250	-0.50	H_2	182.35	0.36
Extra Steam	300	-0.60	N_2	0.27	0.00
			CH_4	44.53	0.09
			C_2H_2	0.35	0.00
			C_2H_4	12.97	0.03
			C_2H_6	4.18	0.01
			NH_3	88.90	0.18
			H_2O	574.78	1.15
			Char	16.29	0.03

7.3 Separation blocks' performance parameters

From the separation units' rigorous simulations and mass balances, separation or recovery factors **Sep$_f$** of the lumped-separation blocks were calculated for their performance, which will enable the superstructure modeling and programing similar as for the reaction blocks. The separation factors

stand for the components' mass flow rate that is being recovered in each of the separation blocks'

outlet streams. In this case, the inlet flow rate of the separation block is equal to the outlet flow rate

of the immediate upstream reaction block. In Figure 10, the outlet streams from the separation blocks

$SEP(1,3)_{LB}$ and $SEP(7,3)_{LB}$ are presented and, in Table 4, mass balances and calculated separation

factors for the lumped-separation block $SEP(1,3)_{LB}$ are presented.

Table 4. Mass balances and separation factors for SEP(1,3)$_{LB}$ in Figure 10

Block SEP(1,3)$_{LB}$					Outlets								
Inlet Components	Inlet flow (kg/h)	m_{out_1}	kg/h	Sep_f	m_{out_2}	kg/h	Sep_f	m_{out_3}	kg/h	Sep_f	m_{out_4}	kg/h	Sep_f
		Pyrolysis oil			NCGs			Aqueous product			Solids		
CO	110.40	CO	0.01	0.00	CO	110.39	1.00	H_2O	18700.58	1.00	Char	240.11	1.00
CO_2	103.09	CO_2	0.26	0.00	CO_2	102.84	1.00	Alcohols	0.96	0.02			
CH_4	14.40	CH_4	0.01	0.00	CH_4	14.39	1.00	Aldehydes	0.03	0.00			
H_2	2.40	H_2	0.00	0.00	H_2	2.40	1.00	Ketones	2.20	0.01			
C_2H_4	9.60	C_2H_4	0.02	0.00	C_2H_4	9.58	1.00	Acids	4.76	0.02			
H_2O	240.00	H_2O	39.40	0.00	H_2O	0.02	0.00	Furans	0.53	0.00			
Alcohols	56.32	Alcohols	55.36	0.98	Aldehydes	0.38	0.01	Phenols	0.14	0.00			
Aldehydes	32.00	Aldehydes	31.59	0.99	Esters	0.00	0.00	Anhydrosugars	3.92	0.04			
Ketones	283.26	Ketones	281.07	0.99				Esters	0.02	0.00			
Acids	288.26	Acids	283.50	0.98									
Furans	122.24	Furans	121.71	1.00									
Phenols	358.40	Phenols	358.26	1.00									
Anhydrosugars	92.16	Anhydrosugars	88.24	0.96									
Esters	47.36	Esters	47.34	1.00									
Char	240.11												
Extra Stream H_2O	18500.00												

8.   Discussion

The developed methodology describes the required steps for the superstructure formulation and provides the conceptual structures and numerical data for the synthesis of new BtL process systems. Following the step-by-step methodology described in Section 6 and supported by the data and performance parameters presented in sections 5 and 7, the final BtL superstructure depicted in Figure 9 was developed, from which it is possible to observe that besides the initial process routes, different paths connecting the feedstocks, the thermochemical conversion methods, upgrading, and separation technologies can be taken, and different process alternatives can be generated during the search of the technological routes. However, this is an initial approach that provides the conceptual analysis of the different processing networks that can be considered. For a detailed implementation and application of the final superstructure, a mathematical optimization model and procedure should be developed and performed. Therefore, in Part 2 of this study, the superstructure modelling is formulated and defined as a Mixed Integer Non-Linear Programming (MINLP) problem coded in GAMS 24.5.6, which sets the objective to minimize the total cost of manufacturing (TCOM) of BtL fuels systems under different feedstock compositions, product profiles and mass and energy integration scenarios.

9.   Conclusion

In this work, a step-by-step approach was proposed for synthesis of a softwood BtL transportation fuels superstructure supported by the structural formulation and numerical information of the processing units and their process sections. Multiple processing routes including softwood thermochemical conversion via gasification or pyrolysis, FT hydrocarbons synthesis, upgrading and separation units were simulated to generate the information that supports the analysis of their interconnection into a superstructure formulation. Rigorous simulations and experimental data allowed the prediction of mass balances, reaction and separation performances, capital and energy

costs of the selected technologies, which provide the consistent information and data for the final superstructure formulation and its further implementation and optimization, as is presented in Part 2 of this work.

The resulting superstructure, presented here in Part 1, was developed through conceptual structure development and numerical data preparation from rigorous simulations. First, the unit operations in the base cases are simulated and rigorous technical and economic data are prepared. Then the processing blocks flowsheets are formulated from the base cases along with technical and economic data for the defined processing blocks. Thereafter, the detailed superstructure is defined by interconnecting the separation and reaction blocks of the processing blocks flowsheets, which includes not only the base cases, but also new process routes through different interconnecting of the conversion, upgrading and separation sections. Finally, to simplify the modelling and programming of the superstructure (presented in Part 2), the lumped-process blocks are formulated, which resulted in a lumped superstructure with reduced input-output interconnectivity between individual units. The lumped superstructure reduces the complexity for the logical modelling of the superstructure in terms of both structural interconnection and data transferring among the units and the streams between the different process routes. All the technical and economic data are rigorously prepared and registered for the structural changes of the process units and blocks during the superstructure development.

In conclusion, the methodology simultaneously developed the process structures and their rigorous numerical data and information within the superstructure, which provides a framework for modelling and optimization to explore and synthesize optimal conversion pathways and total production processes for BtL fuels.

   ▪   **ASSOCIATED CONTENT**

Supporting Information

The Supporting information is available free of charge via the Internet at http://pubs.acs.org/.

Detailed information regarding the capital and energy costs of unit operations and their description, as well as reaction and separation blocks performing tasks description.

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10. ABBREVIATIONS

τ_{adj} = adjusted residence time

τ_{base} = base residence time

BC = Base case

BC-GHTH = Gasification- HTFT Hydrocarbon Production-FT Hydrocarbon Hydroprocessing

BC-GHTUF = Gasification- HTFT Hydrocarbon Production-FT Hydrocarbon Upgrading-Fractionation

BC-GLTUF = Gasification- LTFT Hydrocarbon Production-FT Hydrocarbon Upgrading-Fractionation

BC-PCCF = Pyrolysis-Catalytic Cracking-Fractionation

BC-PHS = Pyrolysis-Hydroprocessing-Separation

BtL = Biomass to liquid

CC = Capital cost

$CC_{ind}[SEP(i,j)]$ = Capital cost of individual separation blocks

$CC_{SEP(i,j)_{LB}}$ = Total capital cost of lumped separation block

$Conv_f$ = Conversion factor

$cost_{adj}$ = adjusted capital cost

$cost_{base}$ = base capital cost

db = dry base

EC = Energy cost

$EC_{ind}[SEP(i,j)]$ = Energy cost of individual separation blocks (electricity, heating and cooling)

$EC_{SEP(i,j)_{LB}}$ = Total energy cost of lumped separation block

FT = Fischer-Tropsch

GAS = Gasification

GAS-FTUP = FT products fractional upgrading

GAS-HYDUP = HTFT products hydroprocessing

GHG = Greenhouse gas

HHV = higher heating value

HTFT = High temperature Fischer-Tropsch

LHV = lower heating value

LPG = Liquefied petroleum gas

LTFT = Low temperature Fischer-Tropsch

MINLP = Mixed Integer Non-Linear Programming

MJ = megajoule

m_{out_n} = Separation stream' outlet flow rate from SEP(i,j)

NCGs = Non-condensable gases

NREL= National Renewable Energy Laboratory

PYR = Pyrolysis

PYR-CC = Pyrolysis oil catalytic cracking

PYR-HYD = Pyrolysis oil hydroprocessing

PYR-SEP = Pyrolysis upgraded product separation

RXN(i,j) = Individual reaction block

RXN(i,j)$_{LB}$ = Lumped reaction block

SEP(i,j) = Individual separation block

SEP(i,j)$_{LB}$ = Lumped separation block

Sep$_f$ = Recovery factor

SPA = Solid phosphoric acid

TCOM = total cost of manufacturing

WGSR = Water gas shift reactor

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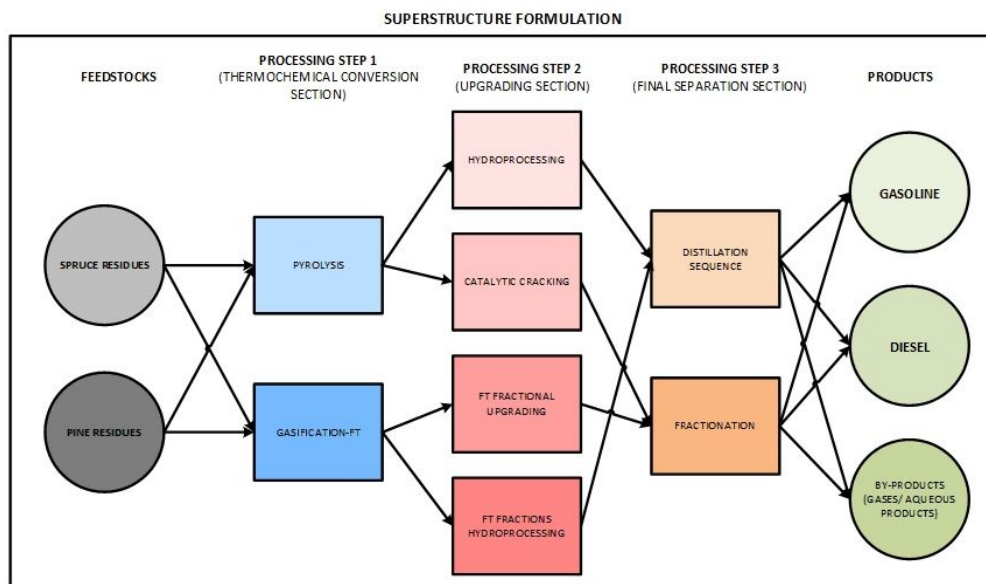
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