# Assessment of co-processing hydrodeoxygenated fast pyrolysis oil and vacuum gas oil in a fluid catalytic cracking unit

by

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# Abstract

The production of liquid biofuels from lignocellulosic biomass feedstock (e.g. forest biomass) has received special attention because these biofuels are carbon neutral, have flexible production and upgrading processes, and can be produced from feedstock that is widely available. The major challenge in the direct substitution of bio-crude or bio-oil for petroleum fuels is their physical properties and compatibilities with existing infrastructure. The potential to use them is limited due to their high water and oxygen contents, thermal instability, and high corrosiveness and viscosity. To improve the quality and physical properties of biomass-based oil, hydroprocessing and hydrocracking into liquid fuels is an option, but these processes require a large capital investment to build standalone units. One way to resolve the challenges in the upgrading of bio-oil is to co-process it with crude oil in a petroleum refinery and take advantage of existing facilities. Suitable biomass-based oil can be mixed with conventional crude oil and processed at the same facility. This offers several advantages, including reducing capital costs (i.e., compared to building a standalone bio-refinery) and blending at a several co-processing ratios, depending on the refinery unit's ability to handle the bio-oil and the physical properties of the bio-oil.

In this study, processing hydrodeoxygenetaed bio-oil from biomass fast pyrolysis with vacuum gas oil in a refinery's fluidized catalytic cracking (FCC) unit was considered as the co-processing pathway. There have been many studies on the technical feasibility of this co-processing method, and the physical properties of hydrodeoxygenated bio-oil (HDO) show promising results for co-processing operations. A conceptual framework was developed to understand the associated costs of co-processing bio-oil with conventional crude and its effect on the FCC unit economics. A rigorous simulation model was developed to analyze the effects of adding new feedstocks to the refinery's FCC units. The refinery operating conditions before and after co-processing operations were based on the developed simulation model and was used to analyze the cost effects of co-processing in a refinery operation.

The simulation results show that by mixing 10 wt.% hydrodeoxygenated pyrolysis oil with vacuum gas oil, overall FCC unit $CO_2$ emissions can be reduced by 4% with almost the same gasoline yield. The developed cost model shows that as a result of co-processing, gasoline and diesel production costs will increase by 6.8 ¢/litre and 2.7 ¢/litre, respectively, while almost the same amounts of these products are produced. Co-processing HDO with vacuum gas oil (VGO) is technically feasible based on earlier experimental studies and will introduce renewable content to refinery transportation fuels at the time of production. The information developed in this study could be used as a preliminary assessment of co-processing of bio-oil with conventional crudes.

## Preface

This thesis is original work by Ali Alizadeh under the supervision of Dr. Amit Kumar. Chapter 2 will be submitted as Alizadeh, A., Kurian, V., Oyedun, A., Biswas, D., Kumar, A., "Co-processing biomass-derived oils with petroleum feedstocks: A review" to a peer-reviewed journal. Chapter 3 is prepared for submission to a peer-reviewed journal as Alizadeh, A., Oni, A.O., Kurian, V., Oyedun, A., Kumar, A., "Simulation study and economic analysis of coprocessing hydrodeoxygenated fast pyrolysis oil and vacuum gas oil in an FCC unit." I was responsible for the concept formulation, data collection, analysis, model development, and manuscript composition for each. Dr. Adetoyese Oyedun, Dr. Vinoj Kurian and Dr. Abayomi Olufemi assisted in model development and manuscript edits. Dr. Amit Kumar was the supervisory author and was involved with concept formulation, evaluation, assessment of results, and manuscript edits.

To my lovely wife and son,

Ali Alizadeh

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# Abbreviations

| | |
|---|---|
| API | American Petroleum Institute |
| bbl | Barrel |
| bpd | Barrels per day |
| CAT/OIL | Catalyst to oil ratio |
| $CO_2$ | Carbon dioxide |
| CPO | Catalytic pyrolysis oil |
| FCC | Fluid catalytic cracking |
| GHG | Greenhouse gas |
| HDO | Hydrodeoxygenation |
| HHV | High heating value |
| HPTT | High-pressure thermal treatment |
| HTL | Hydrothermal liquefaction |
| LCO | Light cycle oil |
| LHV | Lower heating value |
| LPG | Liquefied petroleum gas |
| MAT | Micro-activity test reactor |
| MCRT | Micro carbon residue test |
| MFSP | Minimum fuel selling price |
| MW | Megawatt |
| NL | Normal litre |
| ROT | Riser outlet temperature |
| RVP | Reid vapour pressure |
| SLM | Standard litre per minute |
| TAN | Total acid number |
| TCR | Thermo-catalytic reforming® |
| VGO | Vacuum gas oil |
| WHSV | Weight hourly space velocities |

# Chapter 1: Introduction

## 1.1. Background

An increase in global energy demand combined with new climate change policies has resulted in a continued push for renewable energy sources. The production of liquid fuels from non-food biomass feedstocks is receiving special attention because these biofuels are nearly carbon neutral, has flexible production and upgrading processes, and uses low-value feedstock that is widely available [1]. First-generation biofuels, e.g. bioethanol or biodiesel, are produced from edible energy crops, including sugar, starch and oil crops [2]. Corn produced for ethanol would use the same land, water, and fertilizer used by the agricultural industry to grow crops for food production, and thus first-generation biofuels compete directly with the food chain and increase food prices [2-7]. Hence there is a need for second-generation biofuels which is produced from non-food-based feedstock (e.g., agricultural and forestry residue, algae) that is either waste material (e.g. waste vegetable oils and fats) or can be produced in marginal lands. These biofuels have several advantages over the first-generation biofuels. There is a large potential of producing the second-generation fuels in a more sustainable and economical production way without competing with food crops [2].

Second-generation biofuels can be produced through the thermochemical conversion of biomass and further upgrading of the produced bio-oil or bio-crude. Bio-oil from fast pyrolysis is mainly produced from biomass residues at a temperature of 450-550 °C in the absence of air, a high heating rate, and a residence time less than 2 seconds [8-11]. Bio-crude, on the other hand, can be produced from the hydrothermal liquefaction (HTL) of wet biomass feedstocks. The process takes place at an operating temperature of 300-350 °C at 5-20 MPa for 5-60 minutes with water in the liquid phase [12]. The major challenge of the direct substitution of bio-crude or bio-oil for petroleum fuels is the cost of hydroprocessing and hydrocracking into liquid fuels [13]. The potential of their use, without any upgrading, is limited due to their high water and ash contents, instability, and high corrosiveness and viscosity [13].

One of the ways to overcome this limitation is to process the produced fuels in a standalone bio-refinery and to produce bio-diesel or bio-gasoline as final products. Although this approach is technically feasible, it is not viable to produce biofuels this way given the high capital investment needed to build a new bio-refinery. Thus, using existing infrastructures, refineries, and distribution facilities has received attention recently. Many researchers around the world are working to understand the advantages and disadvantages of co-processing bio-oil in a conventional oil refinery with petroleum crude oil. This co-processing operation has the advantage of using the existing infrastructure, and therefore reduces the capital cost. However, there is a need to understand the possible effects of adding bio-oil (or bio-crude) to a refinery feedstock from a technical and economical perspective. This research analyzes co-processing bio-oil in a refinery FCC unit and the associated economic effects.

## 1.2. Literature review and research gap

One of the ways to decrease the cost of second-generation biofuel production, compared to producing biofuel in a standalone bio-refinery, is to co-process with crude oil in an existing petroleum refinery facility. Co-processing bio-crude with crude oil helps in using the existing infrastructure and hence could help in producing biofuel as lower cost than the conventional method of producing biofuels.

Some studies focus on co-processing bio-oil or bio-crude with petroleum crude oil and examine the parameters and feasibility of co-processing operations [1, 14-21]. Mante et al. summarized some physical properties of bio-oil that are required to introduce it to the refinery, mainly to the fluid catalytic cracking (FCC) unit [19]. The authors briefly explained why properties such as the acidity, API gravity, viscosity, storage stability, distillation curve, composition, miscibility, and carbon residue of bio-oil should be monitored and, in most cases, improved before being blended with crude oil.

Mercader et al. studied the effects of upgrading technologies and operating conditions on bio-crude properties that are essential for successful FCC co-processing of pyrolysis oil [14]. Based on their findings, despite high oxygen content (17-28 %), hydrodeoxygenated bio-oil derived from pyrolysis could be successfully blended and co-processed with petroleum crude oil up to 20 wt.% without causing a significant increase in coke or light gas formation. Hoffmann et al. focused on the chemical and thermophysical analysis of bio-crude from the hydrothermal liquefaction unit to determine the bulk and fractional properties that will be required for downstream processing [1]. Their results suggested that only minor upgrading is needed to achieve the necessary co-processing properties.

Co-processing raw biomass-based oil with crude oil usually results in significant coke or light gas formation [14, 16]. For this reason, Fogassy et al. conducted further research to establish and understand the reason for the production of more coke and more aromatic gasoline fractions during co-processing [16]. They used the carbon-14 method to discriminate fossil carbon from bio-carbon and found that not all FCC products receive bio-carbon content equally. Their results revealed that oxygenated molecules of bio-oil are processed more easily than crude oil hydrocarbons, resulting in more coke and light gas production inside the FCC reactor. Thegarid et al. examined the possibility of eliminating the intermediate upgrading process (mainly hydrodeoxygenation) to lower the capital cost of the plant [21]. It has been shown that thermal pyrolysis oil cannot be co-processed directly, but instead some moderate upgrading (e.g., hydrodeoxygenation) is needed. They tested the possibility of co-processing catalytic pyrolysis oil (CPO), instead of thermal pyrolysis oil, with vacuum gas oil (VGO) and found that CPO can be directly co-processed with VGO if it is mixed with more than 80 wt.% VGO. However, some differences in product distribution and quality between the co-processing of both HDO (hydrodeoxygenated oil) and CPO have been observed. The authors suggested that a new catalyst for both FCC and pyrolysis may solve the problems and eliminate the need for an intermediate upgrading process. A more detailed review is included in Chapter 2 of the thesis.

In light of these studies, it is clear that the technology is still under development, and studies need focus on the feasibility of upgrading or co-processing bio-oil and bio-crude in existing refineries without operational problems. Moreover, there are no economic assessment or environmental analyses of the co-processing of bio-oil with crude oil. An economic assessment is essential to examine the overall cost and additional expenses of the process, and carbon change assessment is necessary to understand the environmental impact of the entire process. There is no comprehensive study that focuses on and summarizes the effects of the different bio-oil production processes (thermal pyrolysis, catalytic pyrolysis, and HTL) and upgrading routes (HDO, HTT) on the properties of the produced bio-crude and its co-processing possibilities. These gaps need to be assessed.

## 1.3. Research objective

The overall objective of the current research is to understand the effect of co-processing hydrodeoxygenated bio-oil with vacuum gas oil in a fluidized catalytic cracker unit of a conventional oil refinery through development of process models. Replacing VGO with HDO (up to 10%) in the FCC unit may affect the FCC reactor operation and cause some operational challenges like polymerization, excessive coking, and off-gas formation. Also, this change in feedstock composition may change the total gasoline, diesel, and liquefied petroleum gas (LPG) yields and therefore the costs. Another important effect will be the bio-carbon content of the final products. This parameter should also be monitored to make sure produced transportation fuels meet mandated regulatory requirements. The specific objectives are to:

- Develop a detailed process simulation model to analyze the effects of co-processing HDO on the refinery's FCC unit operation
- Develop a cost model with inputs from the process simulation model to perform an economic analysis for the co-processing
- Perform a bio-carbon content analysis to demonstrate transportation fuels' compliance with current (and potential future) mandated regulatory requirements.
- Conduct sensitivity analysis to understand the impact of various input parameters on the results

## 1.4. Limitation of this study

This study was performed to develop a framework to understand the effects of co-processing biomass-based intermediate products with vacuum gas oil in a standard refinery's operation. The main assumptions and inputs of this study are based on publicly available experimental research data. Therefore no experimental research was performed to independently analyze all the effects of co-processing in FCC reactor operation, performance, catalyst activity and any potential operational challenges. The bio-carbon content of the final products was calculated using the mass balance method as using any experimental method (e.g. $^{14}C$) was not feasible.

## 1.5. Organization of the thesis

This is a paper-based thesis and organized in 4 chapters as follows. Chapter 2 is the literature review and summary chapter. In this chapter, processes for the production of bio-oil from biomass feedstock are summarized and the advantages and drawbacks of each process are examined. Also, as the main objective of this research is the co-processing of bio-oil with petroleum-based feedstocks, available research data on bio-oil upgrading options and co-processing are reviewed and presented in the chapter.

Chapter 3 presents the main method and results of the current research in co-processing hydrodeoxygenated bio-oil produced from the fast pyrolysis of biomass in a refinery FCC unit. In this chapter, the developed simulation model for co-processing is discussed . This also discusses the cost of transportation fuel production through co-processing.

Chapter 4 summarizes the key results of this research and makes recommendations for future work are discussed.

# Chapter 2: Co-processing biomass-derived oils with petroleum feedstocks: A review

## 2.1. Introduction

An increase in global energy demand combined with new climate change policies has led to a continued push for renewable energy sources. The production of liquid fuels (second-generation biofuel) from non-food biomass feedstocks (e.g., wood chips, straw) is receiving special attention because these biofuels are nearly carbon neutral, have flexible production and upgrading processes, and can be produced from low-value feedstock [1]. As summarized by Naik et al., first-generation biofuels like biodiesel, corn ethanol, and sugar alcohol offer some benefits; these are environmentally friendly and is also a safe source of fuel [3]. The main disadvantage of these fuels is their limited feedstock availability (some are also required as food). Second-generation fuels, i.e., hydrodeoxygenated oil, bio-oil, lignocellulosic ethanol, butanol, and mixed alcohols, offer the same advantages compared to first-generation biofuels as these do not compete with the food chain.

Liquid fuels can be produced through the thermochemical conversion of biomass and upgrading the produced bio-oil or bio-crude. The primary thermochemical conversion processes are pyrolysis and hydrothermal liquefaction. In fast pyrolysis, biomass is heated rapidly in an oxygen-free atmosphere. This process generates a vapour product that contains all the volatile components and can be liquefied in subsequent operations to make liquid products. In case of high initial moisture content of the biomass, hydrothermal liquefaction is another thermochemical conversion method that can be used to produce liquid products. High temperature and pressure operating conditions of this process help to break organic components of the biomass to smaller molecules [22]. Decompositions of biomass and re-polymerizations reactions to form bio-crude take place in a highly reactive environment in the presence of a solvent, water in most cases [23].The major challenge with the direct substitution of bio-crude or bio-oil for petroleum fuels is the need for hydroprocessing and hydrocracking to improve the qualities of the raw bio-oil or bio-crude [13]. The potential to use them is limited due to their high water and ash contents, instability, and high corrosiveness and viscosity [13]. Separate upgrading can by avoided by co-processing the bio-oil with crude oil in existing standard refinery and distribution facilities. Blending and co-processing biomass-derived intermediate oils with petroleum feedstocks has several advantages such as minimizing capital cost by using existing infrastructures, the ability to blend at various co-processing ratios, and operational flexibility [24, 25].

When identifying possible co-processing options, decisions should be made regarding feedstock source, bio-oil production process, required upgrading process, and mixing point in the refinery operation.

Figure 2.1 illustrates all the options for each step. Theoretically, every combination of these options can be a co-processing route that needs to be investigated.

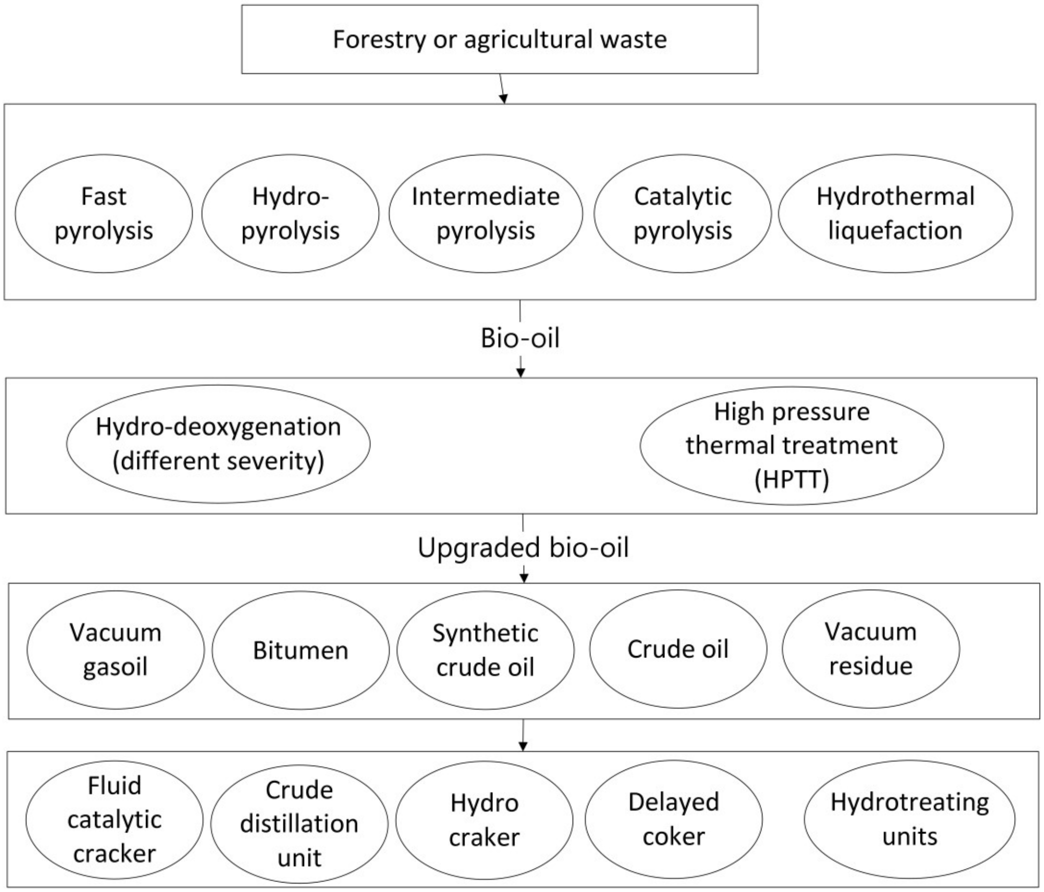


**Figure 2.1 Co-processing options**

In section 2.3, the methods of producing bio-oil from agricultural and forestry residues is described. The differences in process, quality, and quantity (yield) of the liquid product as the source for transportation fuels are also summarized in this section. Many researchers have suggested that directly feeding bio-oil to refinery units is not possible and could cause problems such as corrosion, excessive coke formation, and instability in product quality [26-31]. Therefore, upgrading is necessary before co-processing. In section 2.3, the available upgrading options and their advantages and drawbacks are summarized. In section 2.4, the physical properties of bio-oil produced from different production and upgrading methods and compare them to petroleum feedstocks are summarized. The physical properties required by the refinery for a successful co-processing is also described. The potential mixing point in the refinery for co-processing is described in more detail and the findings of other research on co-processing are illustrated at the end of section 2.4.

## 2.2. Production processes for biomass-derived oils

Biomass can be processed in thermochemical, biological, chemical, and physical conversion processes depending on the final product sought [3]. Thermochemical conversion is one of the oldest methods and has been used over a long time to make bio-coal. Thermochemical processes can be categorized into production methods based on the main product. Pyrolysis and hydrothermal liquefaction (HTL) lead to more liquid products that can potentially be converted into transportation fuels [32]. Torrefaction and gasification give more solid (char) and gas products, respectively[32]. As this work is mainly focused on transportation fuels, pyrolysis and HTL are the production methods considered. Gasification of biomass material followed by Fischer-Tropsch reactions to convert the extracted gas to liquid fuels (like methanol) is another option[23, 33]. The high capital cost of this process is a big disadvantage, and research is still needed to find new production methods and to reduce the required capital cost[4].

Fast pyrolysis is a well understood process for biomass processing that mainly produces liquid products. To improve the quality of the liquid product, some modifications have been suggested by many research groups. In in situ or ex situ catalytic pyrolysis, the catalyst was used to change the reaction mechanism from solely thermal to thermal and catalytic to produce more desirable products[34, 35]. Intermediate pyrolysis is another type of modification that changes the heating rate and residence time to produce liquids with lower oxygen content[36]. In a newly proposed method, hydrogen was added to the pyrolysis reactor to have thermal cracking and upgrading at the same time[37-40]. Hydrothermal liquefaction is another production method that is different from pyrolysis; it offers significant advantages and makes liquid products with acceptable yield and quality[6, 18, 23, 41, 42]. All these production methods will be described in detail in the following sections.

### 2.2.1. Fast pyrolysis

Fast pyrolysis of biomass is the main process considered for bio-oil production because its operation is relatively simple and it has been demonstrated at large pilot/pre-commercial scale [43-45]. In this process, biomass decomposes in a thermo-chemical process by rapid heating in the absence of oxygen. The product is a solid that is rich in carbon and a vapour stream that contains all the volatile matter. The solid (biochar) can be burned to provide the required heat and energy for the process or used for other applications. The vapour from the process is condensed to make a liquid fraction called tar or bio-oil with non-condensable gas that can be used to produce chemicals (olefins) or burned to provide the energy [46]. The most important features and steps of this process are summarized by Bridgwater as [32]:

- Drying the feed to less than 10% water content to minimize the water content of the final liquid product;

- A very small biomass particle size (less than 3 mm) is required to provide enough surface area for heat transfer to occur;
- A controlled reaction temperature of around 500 °C to maximize the liquid yield;
- A short vapour residence time (around 2 seconds) to minimize over cracking and excess off-gas formation;
- Rapid cooling of the vapour to prevent subsequent polymerization reactions.

Varying the heating rate and residence time leads to a different type of pyrolysis and different product yields. Figure 2.2 shows the product distribution based on the pyrolysis type.

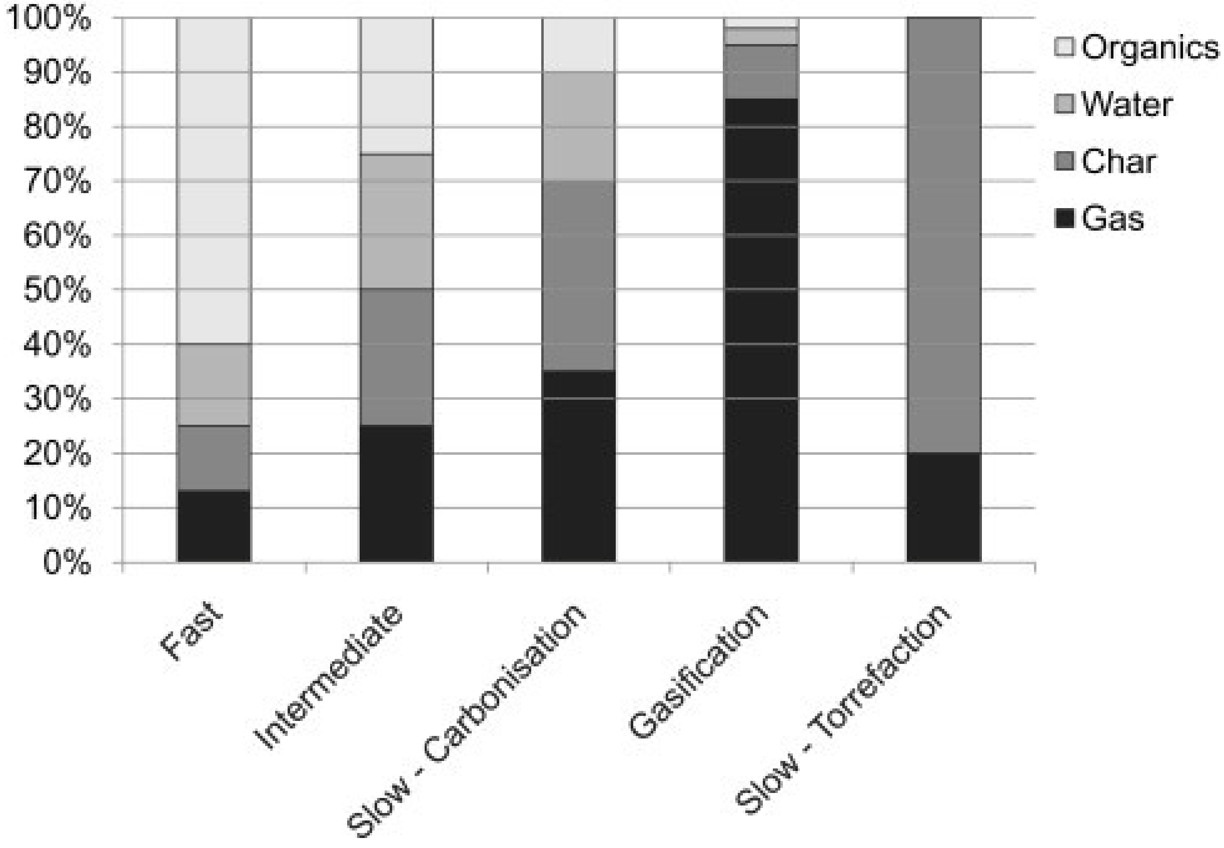


**Figure 2.2 Product yields of different pyrolysis processes, from Bridgwater** [32]

High liquid yield, up to 70-80 wt.%, makes fast pyrolysis a very suitable candidate for transportation fuels. The produced oil is a multi-component mixture from the depolymerization of cellulose, hemicellulose, and lignin. The physical properties of this oil are summarized in Table 2.1 and compared with typical heavy fuel oil. Bio-oil has a high water content (15-30%) that makes its heating value almost 50% less than a petroleum feedstock [9]. The presence of oxygen in more than 300 components in the bio-oil makes it immiscible with hydrocarbon fuels and leads to low pH values of around 2-3 [9]. The low pH value makes bio-oil very corrosive and thus all the processing equipment (for example to upgrade the bio-oil to biofuel) be made of a special material type to resist corrosion [9]

**Table 2.1 Properties of pyrolysis oil, heavy fuel oil, and crude oil [9, 47]**

| **Physical property** | **Bio-oil** | **Crude oil** | **Heavy fuel oil** |
|---|---|---|---|
| Density (g/cm$^3$) | 1.05-1.25 | 0.86-0.92 | 0.94 |
| Viscosity (cP) | 40-100 | 180 | 180 |
| Water content (wt.%) | 15-30 | <0.1 | 0.1 |
| pH | 2.8-3.8 | - | - |
| Nitrogen (wt.%) | 0-0.2 | <1 | 0.3 |
| Hydrogen (wt.%) | 5-7 | 11-14 | 11 |
| Carbon (wt.%) | 54-65 | 83-86 | 85 |
| Oxygen (wt.%) | 28-40 | <1 | 1 |
| Higher heating value (MJ/kg) | 16-19 | 44 | 40 |

### 2.2.2. Intermediate pyrolysis

Intermediate pyrolysis, in most studies, is defined as a process whose heat transfer rate is between those of slow and fast pyrolysis processes, typically in the range of 200-500 °C/min, and solid residence times of 10 minutes [48, 49]. It has been claimed that the liquid fractions produced through intermediate process are around 34% [48] and 75% from the fast pyrolysis for woody feedstock. In this review, intermediate pyrolysis has been reviewed developed by the Fraunhofer Institute for Environmental, Safety, and Energy Technology, UMISCHT [50]. Thermo-catalytic reforming® (TCR) is the main aspect of this technology and comprises a multi-zone horizontal auger screw reactor[51-53]. In TCR, pretreated biomass is heated in an inert environment and converts to bio-oil, char, and gases. Produced gas passes through a catalytic reformer at 700 °C where reforming takes place and eventually condenses to form bio-oil, permanent gases, and moisture [50, 52, 54]. These product gases have a higher percentage of hydrogen, which can be exploited for fuel synthesis and the production of green chemicals like methanol [50, 54]. Studies show that the content of the product gases differs depending on the biomass feed composition. Neumann et al. report a yield of 31% char, 8% bio-oil, 41% permanent gases, and 20% aqueous when digestate from anaerobic digestion plant is used as the feedstock [51]. The produced bio-oil typically has 7-11% oxygen content, less than 2% water content, a higher heating value greater than 36.7 MJ/kg, and a total acid number less than 5g KOH /kg [55]. Product gas has up to 55% hydrogen, up to35% carbon dioxide, up to 25% carbon monoxide, and trace amounts of methane and volatile hydrocarbons [55]. One of the advantages of TCR is its flexibility in handling various feedstock types, which has led to focus on various waste streams and municipal sludge as a potential feedstock. However, the feedstock must go through different pre-treatment stages like drying, sorting, shredding, and pelletizing [53]. Ouadi et al. carried out TCR experiments on household residual waste, which was treated to produce pellets and then fed into the reactor, producing 44 wt.% gas, 31 wt.% char, 19 wt.% aqueous phase, and 6 wt.% bio-oil phase  [53]. The bio-oil has 6.7% oxygen, a total acid number of 2.9 mg KOH/g, and a higher heating value of 38.2 MJ/kg and is thus comparable to biodiesel [53]. Also, there are different studies on upgrading this TCR oil to be used as a transportation fuel. Neumann et al. report an oxygen content lower than 0.8% when they subjected TCR oil to catalytic hydrodeoxygenation; water content decreased from 2.2% to 0.003%, the total acid number (TAN) fell from 2.1 mg KOH/g to below the detection level, and the lower heating value (LHV) increased from 34.0 MJ/kg to 42.3 MJ/kg making this oil comparable to that of gasoline and diesel [55].

### 2.2.3. Catalytic pyrolysis

The catalytic pyrolysis of biomass is an effective means of using bio-oil as a transportation fuel. This process eliminates oxygen content through a series of simultaneous dehydration, decarboxylation, oligomerization, aromatization, alkylation, and decarbonylation reactions with the help of a catalyst, typically zeolites[56]. Studies show that the cumulative approach of pyrolysis and catalyst use, resulting in high-quality bio-oils, is the biggest advantage of this process. Catalysts like synthetic zeolites (e.g., ZSM-5, HZSM-5) have been explored for yield enhancement with all possible reactor combinations, for in situ,/ex situ systems, and different temperature and pressure conditions [35, 56, 57]. The reactors that have been studied widely for catalytic pyrolysis are fixed-bed, fluidized bed, and auger reactors [35, 57]. Hu et al. report an increase of bio-oil yield from 19.7-42.3% in a non-catalytic process to 64.1-68.8% with NaY zeolite catalysts for catalytic pyrolysis of different species of bamboo in a fixed bed reactor [58]. A study by French and Czernik reports that the choice of catalyst for a specific biomass is the most important parameter in enhancing bio-oil yield, but no strong agreement between these two parameters has been developed, and therefore a range of bio-oil yields results [35]. However, the factor that most affects bio-oil yield's commercial adaptability is the deposition of coke (which is roughly 30% of the carbon [40]) on active catalyst sites, which quickly deactivates the catalyst.

### 2.2.4. Hydropyrolysis

Hydropyrolysis is one of the oldest studied techniques for coal thermal decomposition and has recently been used to produce bio-oils from biomass in the presence of hydrogen [40, 59]. In this process the hydrogen radicals generated by the hydrogen gas react with the volatiles from the biomass, producing carbon monoxide, carbon dioxide, and water. Studies claim that the percentage of oxygen in the bio-oils is lower than in the bio-oils generated from pyrolysis because of the presence of hydrogen. Also, as an exothermic process, hydropyrolysis naturally generates heat that fuels the reactions and thus there is no need for an external heating medium, unlike an endothermic pyrolysis process. Fast hydropyrolysis reduces residence times through high heating rates of 500 °C/s in fluidized bed reactors [40]. Although hydropyrolysis has been studied for different feedstocks – from lignin to woody feedstock to sugarcane bagasse under different temperature and hydrogen pressure conditions

– some studies report no significant progress over non-catalytic pyrolysis or processes using lower hydrogen pressures than pyrolysis does [59]. Catalytic hydropyrolysis has garnered attention recently because it uses a lower hydrogen pressure (20-35 bar) than non-catalytic hydropyrolysis (150-700 bar) [40, 59]. A major study in this area was conducted by the Gas Technology Institute; the study comprised an integrated catalytic hydropyrolysis process coupled with hydroconversion in a 2 kg/hr plant that eventually ran at pilot scale at 50 kg/day. The process achieved a 28 wt.% yield of hydrocarbons in the gasoline and diesel range and 35-40% water produced in a separate phase, which the researchers claim is carbon-free [40, 60]. The researchers also anticipate that reforming the C1-C3 hydrocarbons and CO will provide the hydrogen internally, thereby making the process more economical [40, 60]. There has been no testing done to prove the feasibility of this approach.

### 2.2.5. Hydrothermal liquefaction

Hydrothermal liquefaction (HTL) is one of the popular methods of producing liquid fuels from biomass apart from pyrolysis [7]. Biomass with moisture content less than 20% can be liquefied via pyrolysis; with a moisture content above 20%, a drying stage is required, and thus the process is less economical. Hydrothermal liquefaction can handle water-rich biomass feedstocks since water acts both as a reactant and catalyst and facilitates the decomposition process [7]. HTL is normally carried out at lower temperatures and lower heating rates than pyrolysis. The operating temperature and pressure are in the range of 523-647K and 4-22MPa, respectively, [61]. Depending on the operating conditions (i.e., temperature, pressure, catalyst, reaction time), the desired products – biochar, bio-oil or product gases like hydrogen, methane, etc. – can be obtained [62]. The bio-oil produced by HTL has lower oxygen content (<2% oxygen) than that produced by fast pyrolysis, and the overall process proved to be energy efficient as it was carried out at lower temperatures than pyrolysis [7, 62]. Main properties of the bio-crude from HTL are listed in Table 2.2 [7]. Catalytic hydrothermal liquefaction was developed in large part to reduce the formation of char and tar through homogenous and heterogeneous catalysts. Some studies report the use of alkali salts, which have been seen to reduce the formation of char, thereby increasing the yield of the desired product. However, the use of a homogenous catalyst is energy-intensive due to the recovery of the catalyst. A study by Kumar et al. reports using heterogenous catalysts like platinum, nickel, and metal oxides and shows improvement in bio-oil yield [62].

**Table 2.2: Properties of stabilized bio-crude through hydrothermal liquefaction (derived from [63, 64] )**

| Physical property | Bio-crude | Bio-crude |
|---|---|---|
| Density ($g/cm^3$) | 0.761 | 0.7747 |
| Total acid number (mg KOH/g oil) | <0.01 | n/a |
| Viscosity (cP) | 1.29 | 1.96 |
| Carbon (wt.%) | 83.4 | 84.2 |
| Hydrogen (wt.%) | 13.5 | 13.9 |
| Oxygen (wt.%) | 0.07 | 1.7 |
| Nitrogen (wt.%) | <0.05 | 0.1 |
| Sulphur (wt.%) | <0.005 | 0.0063 |

Cao et al. report in their review paper on the hydrothermal liquefaction of agricultural and forestry wastes that biomass feedstock type is one of the most important parameters in the HTL process [65]. Studies conducted on the hydrothermal liquefaction of beechwood biomass in a 0.6 L stirred batch reactor at 300 °C for a holding time of 60 mins give a bio-oil yield of 14% and 28% without and with sodium hydroxide [41]. The authors concluded that the presence of a strong base favours the conversion to bio-oil and inhibits the production of biochar [41]. Feng et al. report the yields of HTL from three different lignocellulosic feedstocks, white spruce bark, birch bark, and white pine bark, under the same operating conditions as 58%, 67%, and 36%, respectively [66]. The authors attribute the results to lignin, the most stable component in nature, and therefore resistant to the coking process in liquefaction, whereas cellulose and hemicellulose degrade faster in the liquefaction process as their physical structure is relatively simpler than lignin [66]. Zhu et al. conducted a techno-economic assessment and estimated the minimum fuel selling price (MFSP) for hydrotreated HTL oil to be 1.29$/L for a single standalone HTL and upgrading plant [67].

## 2.3. Upgrading options

Biomass-derived oil is composed of a complex mixture of oxygenated hydrocarbons. For example, there are 300+ components in pyrolysis oil. The main components of bio-oil are acids, aldehydes, ketones, alcohols, glycols, esters, ethers, phenols, and phenol derivatives, as well as carbohydrates and lignin-derived oligomers [31]. Because of the high oxygen content, 30-55 wt. % depending on the biomass source, bio-oil has some properties (i.e., low heating value and immiscibility with hydrocarbons, chemical and thermal instability, high viscosity, and corrosiveness) that should be addressed before any attempt is made to introduce it in a conventional refinery [31]. Several upgrading routes have been proposed to date to lower the oxygen content of the bio-oil and thereby improve its quality for processing in a refinery unit operation. These methods are categorized as hydrodeoxygenation (HDO) and high-pressure thermal treatment [25].

Hydrodeoxygenation uses high-pressure hydrogen to remove the oxygen as water using mixed oxides and supported metal catalysts. Although this method has been successful for upgrading the bio-oil and even producing bio-gasoline and bio-diesel, an obvious disadvantage is the high amount of hydrogen required and associated costs. Since hydrogen is in high demand in refinery operations, research is underway into alternative upgrading methods[25, 68, 69]. High-pressure thermal treatment, the other main method, has not been proven commercially and technically feasible.

### 2.3.1. Hydrodeoxygenation

The hydroprocessing of bio-oil is the main upgrading path currently being considered by many researchers. Hydrodeoxygenation is normally performed in two steps, stabilization and upgrading, to prevent excessive coke formation. The first step is carried out at a relatively low temperature (150-170 °C) to stabilize the oil and the second step at higher temperatures (350 -380 °C), when deoxygenation (> 95%) occurs [25].

Recent research on hydroprocessing has been focused on optimizing the operating conditions of the two-step upgrading process, reducing hydrogen consumption, and developing new catalysts solely for biomass-derived oil hydroprocessing [70]. Most of the research focuses on hydrotreating the bio-oil to produce renewable fuel (as a final product), but French et al. attempted to upgrade the bio-oil just enough to be able to co-process the product in a refinery [71]. They processed the bio-oil in two-step hydrotreatment at 150/360 °C and 2500 PSIG hydrogen pressure and a hydrogen flowrate of 4.087 Nl/minute/kg of bio-oil (1.5 slm for oil charge of 400g) for 1 hour on each step [71].

Depending on the hydrotreating operating conditions, the final product's physical properties will differ. Gueudre et al. examined the function of hydrotreating severity, in terms of hydrogen consumption and operating temperature, on conversion, yield, and naphtha or gasoline composition in co-processing with vacuum gas oil (VGO) in a fluid catalytic cracking (FCC) reactor [28]. In their experiment, the pyrolysis oil was first hydrotreated on the Ni-based catalyst (at a hydrogen pressure of 200 bar and temperature of 250 °C) and the resulting oil was treated at different temperatures (80-320 °C) to find the optimum operating conditions. The authors found that an optimum naphtha quality can be achieved by the mild hydrotreating of bio-oil corresponding to 200 Nl of hydrogen per kg of pyrolysis oil (this corresponds to a maximum hydrotreating bed temperature of 320 °C). At these operating conditions, the authors observed a reduction of 25% in MCRT (micro carbon residue test), 50% in TAN, and 50% in O/C compared to the initial pyrolysis oil [28] .

### 2.3.2. High-pressure thermal treatment (HPTT)

To reduce the operating costs of bio-oil upgrading, the Biomass Technology Group (BTG) in the Netherlands and the University of Twente developed a method to reduce the oxygen and water content and thereby increase the energy content of bio-oil (from 14.1 to 28.4 MJ/kg) [30]. In this process, pyrolysis oil was thermally treated at 140 bar and 300-340 °C for several minutes. High pressure is required to prevent the water from evaporating and extensive charring of the oil. The researchers found that the oxygen content decreased from 40 wt.% to 23 wt.%, because of the formation of gaseous $CO_2$. This method is a cheap upgrading method that does not need a catalyst or hydrogen for upgrading. It produces refinery-ready bio-oil that can be directly (or with mild hydrodeoxygenation and little hydrogen) processed in refinery units. Although it is an attractive method, more research is required to overcome some polymerization problems that were observed [30].

## 2.4. Identified co-processing opportunities

As discussed earlier, the use of biomass-derived oils as transportation fuels is limited due to their high water and ash contents, instability, and high corrosiveness and viscosity [43]. One way to resolve the challenges faced by upgrading bio-oil is to co-process it with crude oil in an existing standard refinery, production, and distribution facilities. In selecting a specific pathway for co-processing, the potential effects on the refinery and general process chain (from biomass to transportation fuels with renewable contents) should be examined from technical, financial, regulatory compliance, refinery operation, and supply chain views.

From a process perspective (on the individual refinery unit level), the effects of adding a new feedstock to the process and possible operation upsets, changes in the yield and quality of a product (that still needs to comply with regulatory requirements), and catalyst deactivation should be tested based on the added bio-oil physical properties. From a financial view, the added cost of making transportation fuels with renewable content should be examined based on yield differences (after and before co-processing), bio-oil and petroleum feedstock cost difference, upgrading cost, and other utility costs. Another important consideration is the renewable content of the final products. This parameter should be calculated to determine what mixing ratio satisfies the mandated amount of renewable content. Finally, the co-processing option should be examined in a general refinery operation context and changes to process flow should be considered.

### 2.4.1. Physical properties of produced oil

Biomass-derived oils may have very different physical properties depending on the feedstock source, production and upgrading processes, and storage conditions. These properties that are different from petroleum feedstocks are summarized in Table 2.3. One of the most important parameters is the number of oxygenated components in the biomass-derived oils. Petroleum feedstocks normally do not have oxygen components. Biomass-derived oils, on the other hand, are normally a complex mixture of oxygenated components. This oxygen-rich composition leads to the lower heating value, immiscibility with hydrocarbon fuels, and high viscosity and corrosiveness [26].

Another difference between biomass and petroleum-derived feedstocks is the amount of nitrogen and sulphur. Fuel standards mandate very low sulphur content on the final products and both nitrogen and sulphur are considered a catalyst poison on downstream processing units. As can be seen in Table 2.3, biomass-derived oils normally have less nitrogen and sulphur based on biomass and crude oil sources. Therefore the bio-oil will not increase the sulphur level of the final product and can be used to control the sulphur content with appropriate blending [72].

Depending on the processing technology, biomass-derived oils have a water content in the 1.7-25 wt.% range [25, 42, 73, 74] . This is much higher than crude oil's water content and is one of the main reasons for the low heating value of biomass-based oils. Another parameter of concern is the amount of hydrogen and its ratio to the carbon. The effective H/C ratio is a parameter that is normally used to estimate the amount of upgrading (deoxygenation) needed. The lower this parameter, the more severe the upgrading [42].

Coking tendency is the parameter that any refinery operators will be interested in examining before blending bio-oil with their feedstock. Coking tendency can be measured by the standard micro carbon residue test (MCRT) to measure carbonaceous residue formed after evaporation. For example, the MCRT of normal FCC feed is less than 0.5 wt.% [25], while biomass-derived oils have a very wide range.

Despite the different physical properties of different bio-oils, some properties are considered problematic in almost all refinery units and need to be addressed before any co-processing operation. To avoid the negative effect of introducing new feedstock in a refinery, parameters such as acidity, density (API gravity), and thermal stability should be examined and improved if needed [73].

**Table 2.3 Physical properties of different biomass-derived oils and petroleum feedstocks for comparison**

| Property | Units | HTL | Catalytic pyrolysis oil | Intermediate pyrolysis oil | Fast pyrolysis oil | HDO pyrolysis oil | Crude oil | Heavy fuel oil | VGO |
|---|---|---|---|---|---|---|---|---|---|
| Feedstock | | Hardwood | Pine | Digestate | Forest residue | | | | |
| Water | wt.% | 3.65 | 5 | 1.7 | 25 | 2.1 | < 0.1 | 0.1 | |
| Solids | wt.% | | | | 0.04 | | | | |
| Nitrogen | wt.% | | 0.2 | 2.2 | 0.2 | | < 1 | 0.3 | 0.07 |
| Sulphur | wt.% | BDL | BDL | 0.6 | 0.01 | | < 4 | | 2 |
| Carbon | wt.% | 83.9 | 74 | 76.6 | 40.7 | 73.3 | 83-86 | 85 | 85 |
| Oxygen | wt.% | 5.3 | 19 | 11.2 | 45-50 | 16.9 | < 1 | 1 | |
| Hydrogen | wt.% | 10.4 | 6 | 7.7 | 8.04 | 9.8 | 11 - 14 | 11 | 12 |
| ASH | | 0.069 | | <0.05 | | | | | |
| Kinematic viscosity | cSt | 11.97 | 30 | 40 | 16 | | | | |
| Dynamic viscosity | cP | | 33.2 | | | | 180 | 180 | |
| Density | kg/l | 0.97 | 1.1 | 1.063 | 1.196 | 0.93[75] | 0.86-0.92 | 0.94 | 0.89 |
| HHV | MJ/kg | 40 | | 33.9 | 16.8 | 35.1 | 44 | 40 | |
| pH | | | 3.71 | | 2.6 | | | | |
| MCRT or carbon residue | wt.% | 3.37 | | | | 2.2 | | | |
| API | | 14.21 | -2.9 | 1.51 | -131 | 20.51 | 22-32 | 19 | 27 |
| TAN | (mg KOH /gr) | 36.8 | | 4.9 | 70 [5] – 100 [72] | | | | |
| Main reference | | [42] | [73] | [74] | [25] | [25] | [47] | [9] | [31] |

### 2.4.1.1. Acidity

Bio-oil's acidity presents one of the biggest challenges in co-processing. Pyrolysis oil has a pH range of 2-3 and a TAN of 100-200 [40]. Given that crude oils with a TAN higher than 0.5 are normally considered acidic in the oil industry [73], pyrolysis bio-oil cannot be mixed directly with petroleum feedstocks. Although bio-oil will have different TANs based on the production process, all biomass-derived oils have high acid numbers, mainly because of the oxygenated components. This issue can be addressed either through upgrading or using appropriate construction material to minimize corrosion in the equipment. As co-processing is normally considered for low mixing ratios (5-15 wt.%), the dilution benefit with petroleum streams should also be considered [73].

### 2.4.1.2. Density

Density (or API gravity) is one of the metrics used by a refinery operation in qualifying and pricing different crude oils. Petroleum crude oils have an API in range of 19-50, and higher API crudes are considered to be light and to have more value [73]. Most of the biomass-derived oils have an API lower than 10 (and even negative) and therefore the petroleum industry considers them extra heavy for fast, intermediate, and catalytic pyrolysis oil and heavy for hydrothermal liquefaction and hydrodeoxygenated (upgraded) oils. These low API values will affect pricing and valuation of biomass-derived oils by the industry as it sees this kind of oil as difficult and more energy-intensive to refine.

### 2.4.1.3. Stability

Due to the short residence time in the pyrolysis reactor, neither the produced vapour nor the resulting bio-oil, from the rapid quenching of the vapour, is in thermodynamic equilibrium [9, 72].

As bio-oil is a mixture of many oxygenated components, during storage its composition changes toward the equilibrium, and this results in molecular weight and viscosity changes in the oil [72]. This thermal and storage instability is an indicator of oil behaviour during refining operations. It usually polymerizes during distillation, which could result in the formation of solid residue. Also, in the FCC operation, normal FCC feedstock (e.g., VGO) is preheated to around 229 °C before entering the riser [73]; this limits the direct injection of bio-oil due to thermal instability. To address these issues, further upgrading of the bio-oil and optimization of the pyrolysis reactor and/or modification of the FCC (or other refinery unit operations) have been suggested [5, 76, 77]. For example, in the fast or catalytic pyrolysis reactor, short residence time is required to avoid secondary reactions (e.g., condensation, oligomerization, and polymerization) of the produced volatile components. By optimizing the residence time, it is possible to balance the time required to complete desired reactions and avoid unwanted secondary reactions and therefore produce more stable bio-oil [76]. On the refinery operation side, it is possible to consider different operation strategies, as suggested by Pinho et al. [5, 77], such as using different injection points for the bio-oil and VGO in the FCC reactor (riser). This will lead to one more flexibility in operation and each feedstock can have different preheating temperatures.

## 2.4.2. Potential co-processing routes

### 2.4.2.1. Co-processing of hydrodeoxygenated pyrolysis oil in an FCC unit

This co-processing route is the path that most studies currently focus on and appears to be the most promising method to produce fuels with renewable content. In this method, fast pyrolysis oil goes through hydrodeoxygenation upgrading to decrease oxygen content and increase its processability in an FCC reactor. The resulting HDO is then mixed with vacuum gas oil at 10-20 wt.% at the FCC reactor inlet. The parameters that need to be adjusted include mixing percentage, FCC reactor operating conditions (including riser outlet temperature, catalyst-to-oil ratio, etc.), and the FCC reactor catalyst.

##### *2.4.2.1.1. Effects on product distribution, quality, and overall conversions*

One of the most important parameters is the effect of co-processing HDO with normal FCC feedstocks. Fogassy et al. mixed 20% hydrodeoxygenated pyrolysis oil (hydrogenated at 290 bar and 330 °C) with vacuum gas oil and processed the mixture in a fixed bed reactor [26]. The experiment was done in 3 different catalyst-to-oil (cat/oil) ratios (2.9, 4.5, and 5.9, corresponding to weight hourly space velocities (WHSV) of 20 $h^{-1}$, 13 $h^{-1}$, and 10 $h^{-1}$) [26] . The authors found negligible catalyst deactivation because of the co-processing and almost the same total conversion, especially for a high catalyst/oil ratio. The overall conversion increases with a catalyst/oil increase for pure VGO and co-processing. The co-processing yields a higher conversion than just VGO cracking, but the difference decreases with a catalyst/oil increase. The higher conversion of co-processing can be justified by the fact that HDO already contains components in the product range [26] .

In an another study, Mercader et al. upgraded the bio-oil from woodchips in a one-step HDO process [25]. The final temperature of the HDO was varied from 230-340 °C to find the optimum temperature. The resulting HDO oils were co-processed with VGO. Although it was a one-step upgrading process, because the authors observed a strong hydrogen consumption between 150 and 200 °C, it can be concluded that an integrated stabilization process was occurring too. In the experiment on the effect of the HDO operating temperature, the authors found that hydrogen consumption increased from 232 to 326 NL H2/kg of feed. On the other hand, if hydrogen consumption is expressed in NL/HHV product oil, it remains constant around 22 NL/MJ even with final reaction temperature increases from 230 to 340 °C.

The authors did not observe a big difference in product yield distribution at fixed (60 wt. %) conversion among HDO oils at different temperatures despite an oxygen content in the oils of 16.9 to 28.0 wt. %. This finding suggests that much less severe HDO conditions, just as much as needed to reduce the highly reactive functional groups, might be enough. On the other hand, HDO processing at lower temperatures leads to less carbon recovery (from the original biomass) in the oil phase and therefore less carbon efficiency. It was observed that co-processing 20 wt.% HDO oil leads to an average 20% higher cat/oil ratio (to have the same overall conversion) compared to pure VGO processing. The effect of this higher cat/oil ratio on FCC plant operation was not considered in this work and needs to be investigated. Optimizing HDO reaction operating conditions, therefore, is required to achieve the lowest hydrogen consumption, lowest FCC reactor operating cost, and highest renewable content in the final products [25].

###### *2.4.2.1.2. Coke and light gas formation*

To introduce new feedstocks to an FCC plant, it is important to consider coke and light gas formation tendencies. Coke formation leads to many operational problems and decreases the catalyst lifetime. Light gas formation reduces overall conversion as the carbon goes to low-value light gases instead of being transferred to the final product. Fogassy et al. observed much higher coke formation tendency and dry gas production for co-processing [26]. The higher production of light gas may be due to the thermal cracking of HDO, which forms more methane and ethane, as well as $CO_2$ formation through the deoxygenation reactions.

#### 2.4.2.2. Co-processing raw fast pyrolysis oil in an FCC plant

As discussed earlier, the co-processing of mildly hydrotreated bio-oil in an FCC unit has been proven to be technically feasible. The disadvantage of this method is the added cost of the hydrotreatment operation and relatively high hydrogen demand [25, 68, 69] . Some researchers have tried to test the possibility of processing raw bio-oil in the FCC reactor. Pinho et al. co-processed bio-oil from pine woodchip fast pyrolysis with VGO at 5/95 and 10/90 ratios and tested it on a demonstration-scale (200 kg/hr) FCC unit [77]. The authors found this to be a technically feasible process that produces a product in the gasoline and diesel range. They observed a drop in dry gas (C1, C2, and hydrogen) and liquefied petroleum gas (LPG) yields and increases in C3 and C4 olefinicity. The gasoline yields were nearly identical, and the highest yield occurred at the same conversion rate (68-69%) for all feedstocks. They also observed similar LCO yields for pure VGO and 5% co-processing but a slightly lower yield for a 10/90 ratio co-processing. Coke formation was the same for pure VGO and 10% bio-oil, but it was lower in the 5% bio-oil case. These findings are contrary to the results of other research, which found that co-processing raw bio-oil leads to excessive dry gas and coke formation as well as lower quantity and quality fuels.

Pinho et al. attributed this difference in results to the difference in the lab-scale and pilot plant units [77]. In almost all other experiments, researchers have used small-scale reactors with a single feed line. Bio-oil is thermally unstable and will be polymerized and plug the feedline if heated above 50 °C. This forces the VGO and bio-oil to be mixed and fed to the reactor at around 50 °C [77]. VGO is a heavy fossil feed that is normally heated to 180-320 °C to reduce its viscosity and vaporize heavy components to get a good dispersion. Injecting bio-oil and VGO from different feed nozzles helps to optimize both temperatures independently and form the least amount of coke [77].

Another difference in industrial (or pilot plant) operations with lab-scale equipment is the temperature profile difference between the riser and reactor tube. In pilot plant operations, a hot catalyst returns from the regenerator at a very high temperature (around 700 °C). This hot catalyst contacts liquid bio-oil (a very small amount) at the bottom of the riser, causing a thermal shock and vaporizing and breaking the heavy components. This temperature is much higher than the riser outlet temperature (ROT) (around 540 °C), at which most lab-scale reactors have been set to operate isothermally [77].

Another parameter that can explain the differences between results is the local catalyst-to-oil ratio. Pinho et al., in their study, injected bio-oil first and from a separate feed nozzle; this small portion of the total feed (5% or 10%) came in contact with the whole catalyst, causing a very high local catalyst/oil ratio, as much as 10 times higher than the average value [77]. This high volume of catalyst (at high temperature) helped bio-oil break into smaller molecules thermally and catalytically. By using $^{14}C$ isotopic analysis, Pinho et al. found a 1% renewable source of carbon in the final products (for a 5% co-processing ratio) [77]. This value is in good agreement with another study by the same authors, which found 2 wt.% and 5 wt.% of the renewable content for 10 wt.% and 20 wt.% co-processing, respectively [5]. It should be mentioned that the accuracy of the $^{14}C$ method for co-processing below 10% was recently challenged as it did not account for the carbon (with a fossil source) that goes to the fuels in co-processing and would have gone to the dry gas for VGO (alone) processing [78]. When we consider this factor, the produced fuels can get a credit for mixing biofuels at around 2.5% instead of 1% for 5% co-processing, and the C-efficiency (the percentage of carbon that goes to the fuel) for bio-oil increases to 76% from the 32% calculated using the $^{14}C$ method.

### 2.4.2.3. Co-processing opportunity for catalytic pyrolysis oil

Catalytic pyrolysis oil (CPO) seems a better candidate than fast pyrolysis bio-oil for co-processing with petroleum feedstocks in refinery plants as it produces higher quality oil. The research on catalytic pyrolysis mainly compares CPO and hydrodeoxygenated fast pyrolysis oil co-processing in FCC in terms of the quality and quantity of produced transportation fuels and the effect of feedstock on final oil physical properties.

Lappas et al. used the FCC catalyst for the catalytic pyrolysis of forestry residue biomass (beechwood) at 450 °C and 500 °C and compared the results with a no catalyst case (silica sand was used as the heat carrier) and kept the other parameters fixed [79]. They found that catalytic pyrolysis yields less oil with better quality than fast pyrolysis. CPO has lower oxygenated components, density, viscosity, and Conradson carbon residue. This process also produces an oil with higher water content and therefore a much lower HHV. The authors concluded that although this process has great potential, the FCC catalyst is very active and not suitable for catalytic pyrolysis; research to find a suitable catalyst is needed.

In another study, Thegarid et al. compared the co-processing of HDO or CPO with VGO (in a 10% / 90% ratio) in an FCC unit simulated by a MAT reactor [31]. The authors concluded that CPO, unlike fast pyrolysis oil, does not need prior upgrading to be co-processed with VGO if the ratio remains below 20%. They also estimated the overall carbon efficiency to be around 30 wt. % for the catalytic pyrolysis compared to 24 wt. % for combined pyrolysis and hydrodeoxygenation steps.

#### 2.4.2.4. Co-processing opportunity for hydrothermal liquefaction bio-crude

The hydrothermal liquefaction process, as mentioned in the above sections, can handle high moisture feedstock and works at near-critical water conditions that produce more stable bio-oils in a cost-effective way [7, 62]. The bio-oil produced by HTL for co-processing with fossil fuels should, therefore, be explored. Studies in this area are oriented towards HTL bio-crude characterization and assay analysis in a format like conventional petroleum crude oil and comparison between different crudes for increased adaptation at existing refineries. Fractional distillation of HTL bio-crude using a 15:5 theoretical plate column was done following the ASTM D1160 method to evaluate the bulk properties as well as to understand the physical and chemical properties of each fraction, which will help design the co-processing model according to the quality of every fraction [42]. Studies have found the presence of oxygenates in every fraction of HTL bio-crude in the form of phenols, cyclic ketones, esters, and ethers, which ensures a lower hydrogen requirement through hydrotreating. Jensen et al. hydrotreated the bio-crude with a nickel molybdenum catalyst supported on aluminum oxide and evaluated the process with respect to temperature in the range of 150 °C and 350 °C and pressure between 55 and 140 bar [18]. The effect of temperature on the conversion process was concluded to have a more pronounced effect than pressure.

## 2.5. Research gaps

Second-generation biofuels can be produced from different production and upgrading methods, each of which offers different quantities and qualities of products. To compare second-generation biofuel production via co-processing with first generation biofuels (drop-in biofuels from corn), a complete life cycle assessment of these processes in terms of total GHG emissions and added cost for the refinery should be developed. Further details and literature review on cost assessment is given in Chapter 3. Also, as was mentioned, the catalytic pyrolysis offers a good quality product that can potentially be mixed directly with petroleum feedstock without upgrading. This operation will reduce the bio-oil price substantially, but it will require specific catalyst development for biomass pyrolysis. In analyzing a co-processing operation, it is essential to consider all the effects of co-processing for a refinery operation in terms of product quality and quantity, bio-carbon content of final transportation fuels, and refinery economics.

# Chapter 3: Assessment of co-processing of hydrodeoxygenated fast pyrolysis oil and vacuum gas oil in an FCC unit

## 3.1.Introduction

The greenhouse gas (GHG) emissions effects of fossil fuels have driven the move to renewable energy use. Moreover, governments around the world have mandated a minimum amount of renewable content in transportation fuels. This led to the production of first generation of a biofuel mainly from corn or other food grains such as wheat, barley and rapeseed. Because these are used for food purposes, using these as feedstocks for production of biofuel result in increase food price [2-7]. As Path D in Figure 3.1 shows, first-generation biofuel is produced and processed separately from the fossil fuel and blended at the end to the conventional transportation fuel as a drop-in fuel to meet government mandates. However, second-generation biofuel, bio-oil is produced from non-food-based biomass and with some intermediate upgrading is mixed with petroleum refinery feedstock as shown in Paths A, B, and C (Figure 3.1). The advantage to this approach of adding bio-content to a transportation fuel is that it uses existing infrastructure (vs. building a separate biorefinery) and lignocellulosic biomass. In this study, the effects of processing bio-oil/biocrude with petroleum intermediates in the refinery fluid catalytic cracking (FCC) unit were examined through development of process models.

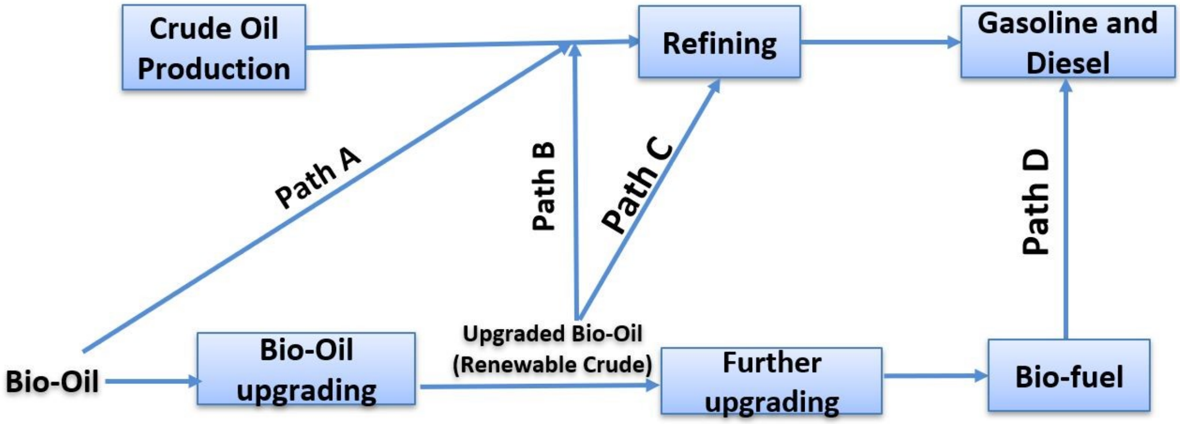


Figure 3.1: First- and second-generation biofuels with petroleum feedstocks

The FCC units have some operational limitations that should be addressed before changes in feedstock are introduced. The most important limitation is catalyst sensitivity and deactivation. FCC catalysts are sensitive to certain atoms in the feedstock and can be poisoned in less than a second [32, 80]. Other limitation is related to the riser and regenerator temperatures. Higher temperatures normally yield higher conversion, but there is a limitation based on riser and regenerator construction materials [81, 82]. The pressure difference between the riser and the regenerator is another key parameter of the FCC unit operation. This difference in pressure dictates the catalyst circulation rate between the riser and the regenerator and is an important factor in overall unit operation. These mechanical limitations should be considered before making any changes in the FCC unit operation.

The approach to determine the most suitable lignocellulosic biomass feedstock for the co-processing operation is explained in section 3.2, and the physical properties of different bio-oils/bio-crudes are compared. Because of the flexibility of the FCC unit, this unit is selected as the point of blending for co-processing. The physical properties of hydrodeoxygenated bio-oil (HDO) is examined in section 3.2.1. The FCC unit operation is also explained. The simulation model for FCC was developed and used in this research. This has been described in sections 3.2.2 and 3.2.3. The economic analysis and advantages of the co-processing operation are described in section 3.2.4. The main goal of co-processing is to add bio-content to conventional transportation fuels. In section 3.2.5, two different approaches are described to calculate the bio-content of final products. The results of this research are summarized in sections 3.3 and 3.4. These sections discuss the overall yield and operation of the FCC unit with respect to co-processing, bio-content of the final product, and economic effects, along with the comparison between drop-in and co-processing pathways.

## 3.2. Methods

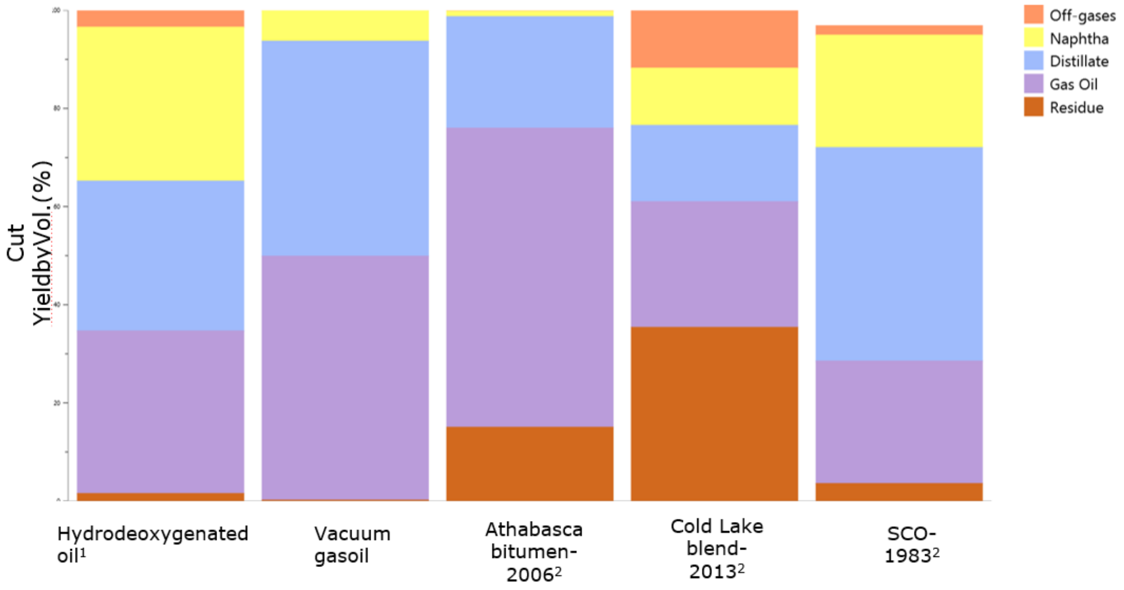
In selecting the best route to integrate biofuels into an existing refinery, decisions should be made on biomass feedstock source, bio-oil production process, bio-oil upgrading processes and mixing point in the refinery. These factors affect the quality and quantity of bio-oil and refinery operations. Figure 2.1 shows different potential paths for co-processing operations.

Once the lignocellulosic biomass feedstock (e.g., agricultural and forestry residues) has been selected, a process to produce liquid fuel from the feedstock needs to be chosen. The level of upgrading required is directly related to the physical properties of the produced bio-oil (i.e., production method) and the requirements of the selected mixing point in the refinery for co-processing. Earlier studies mainly show that direct integration of raw bio-oil into the refinery will cause operational challenges such as polymerization, excessive coke formation, feed line plugging, rapid catalyst deactivation, etc. [26-31]. Because of the physical properties of hydrodeoxygenated bio-oil, it was selected as the biomass-based oil for this research.

The mixing refinery intermediate (or feedstock) and the mixing point in the refinery have a big impact on the refinery's ability to process a new feedstock. Because of the FCC unit's flexibility in handling feedstock and product demand, this unit is considered the main refinery operation for co-processing and has been analyzed by many research groups [5, 15, 16, 26, 28, 31, 47, 79, 83-85]. A steady-state Aspen HYSYS® simulation model was developed to assess the effects of adding HDO to an FCC unit operation and to analyze the impact from the refinery point of view. This study includes a refinery economic analysis and regulatory compliance review for the minimum bio-content of gasoline and diesel.

### 3.2.1. Physical properties of HDO

Given the complexity of refinery unit operations and their sensitivities to new feedstock, and operating conditions in general, the physical properties of any new feedstock should be carefully analyzed before any attempt is made to introduce it to the refinery. The hydrodeoxygenation of pyrolysis oil is considered as one of the promising upgrading methods for making bio-oil compatible with refinery operations [26]. Figure 3.2 compares the assay results of HDO with other main types of oil. The HDO assay characteristics are comparable to the vacuum gas oil's (VGO) assay in terms of product yield. The HDO assay contains slightly more products in the gasoline (naphtha) and off-gas range than VGO and fewer in the diesel ranges. These product distributions and yields will change as the HDO (or VGO) go through catalytic cracking in the FCC reactor. As shown in Table 3.1, HDO has less sulphur and nitrogen than VGO, and this may lead to better quality final products and increase catalyst life in downstream operations.



1. Simulated using Aspen HYSYS®. Source data adapted from Fogassy et al. [26]
2. Simulated using Aspen HYSYS® database[86].

**Figure 3.2: Assay characteristics of HDO and some petroleum feedstocks**

**Table 3.1. Properties of HDO and VGO [26, 87, 88]**

| **Properties** | **HDO** | **VGO** |
|---|---|---|
| Density (g/cm³) | 0.93 | 0.89 |
| Sulphur (wt.%) | 0 | 2.02 |
| Nitrogen (wt.%) | 0 | 0.07 |
| Hydrogen (wt.%) | 10 | 12.4 |
| Carbon (wt.%) | 69 | 85.4 |
| Oxygen (wt.%) | 21 | 0 |
| Conradson C (wt.%) | 0 | 0.26 |
| Higher heating value (MJ/kg) | 42.3-45.3 | 42 |

## 3.2.2. FCC unit description

### 3.2.2.1. Riser-regenerator configuration

The FCC is the heart of the petroleum refinery. It uses a catalyst to break heavier components into gasoline and diesel range fuels in a fluidized bed reactor. Breaking heavier molecules leaves coke deposits on the catalyst surface and deactivates the catalyst in few seconds. For this reason, continuous catalyst regeneration is required to burn the coke from the catalyst and reactivate it. The activated catalyst is re-injected into the reactor (riser) and the cycle continues. Burning the coke from the catalyst surface provides the energy required to break the high molecular weight molecules and produces a great amount of $CO_2$ at the same time. FCC units are the biggest emitter of $CO_2$ of all refinery operations and the main contributor to the refinery gasoline pool [89]. Figure 3.3 is a schematic diagram of an FCC reactor.

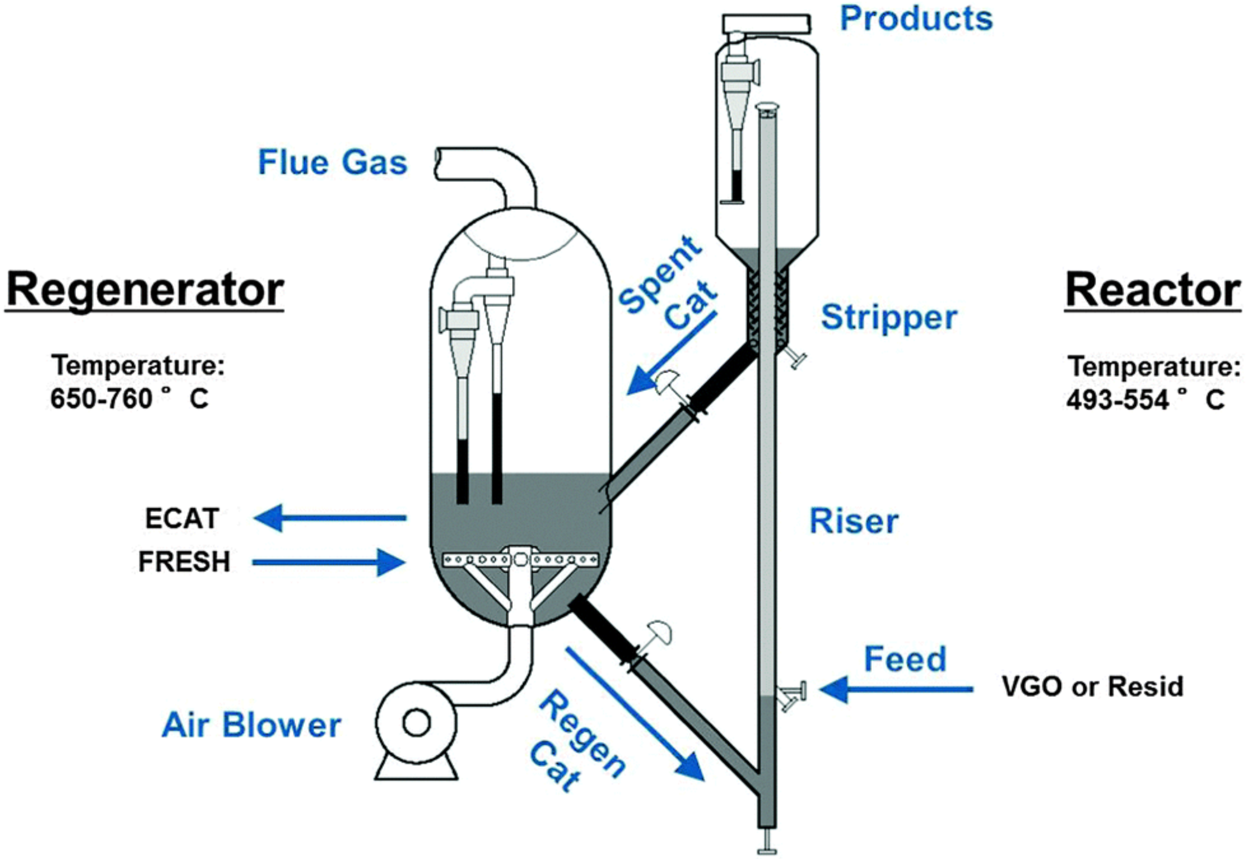


**Figure 3.3: Fluidized catalytic cracker (FCC) unit schematic operation [90]**

### 3.2.2.2. Downstream distillation

In the FCC reactor operation, a cyclone separates the riser effluent hot gas mixture from the deactivated catalyst. The effluent gas stream contains all the reaction products and goes directly to the main distillation column for the preliminary separation. Figure 3.4 (and Figure A.1) shows the overall configuration of a typical FCC unit's downstream fractionation used in this research for process simulation development. The main distillation column separates the feed stream (FCC effluent) into the bottom slurry and the top light gas products that contain most of the gasoline- and liquefied petroleum gas (LPG)-range products. Another side stream from the column gives the diesel range product as light cycle oil (LCO). The column overhead vapour goes to the wet gas compressor for two-stage compression and then to a flash drum for maximum recovery of the heavy components. The gas stream leaving the compressor contains all the LPG, gasoline, and light gas (off-gas) components in the FCC effluent, which should be separate from each other. This stream enters a cooler and then a flash drum (V-101) for the final separation of light gases and a liquid stream. The liquid stream enters the reboiled stripper (T302) for the final removal of any trace amounts of $H_2S$. This is an important step as all the remaining $H_2S$ will go to the LPG product and can make the product quality out of acceptable range. The bottom product of the stripper enters the gasoline stabilizer for the separation of LPG from gasoline. This column controls the amount of C4 components in the gasoline (one of the metrics for gasoline quality) through Reid vapour pressure (RVP) specification and controls LPG quality with a controller on the maximum allowable C5+ concentration [91] .

The vapour stream from the stripper flash drum (V-101) contains light gases produced in the FCC riser plus some C5-range components that should be separated for maximum recovery. To accomplish this, this stream is sent through the secondary absorber where it releases trapped C5 components while absorbing all the trace amounts of light components from the liquid stream of the compressor interstage flash drum. The resulting gas stream, which is mainly $H_2$, methane, and ethane, goes to the primary absorber for the final removal of any heavier components using LCO drawn from the main distillation column [91].

### 3.2.3. Simulation model description

Refinery product yield and quality as well as economics should be analyzed for normal and co-processing operations for a good understanding of the potential advantages of co-processing. A simulation model is the best tool for this analysis, and it also provides insight into the refinery operation. In this research, Aspen HYSYS® software [86] was used to develop a simulation model of the refinery FCC plant. The model includes the FCC reactor, main distillation column, overhead wet gas compression system for maximum diesel and LPG recovery, primary and secondary absorber, and gasoline stabilizer (debutanizer) columns. The main data used for this sample FCC unit is from typical FCC plant simulation examples from Aspen HYSYS® and a typical refinery (UOP design) with a capacity of 800,000 tonnes per year, is taken from chapter 4 of Chang et. al [91].

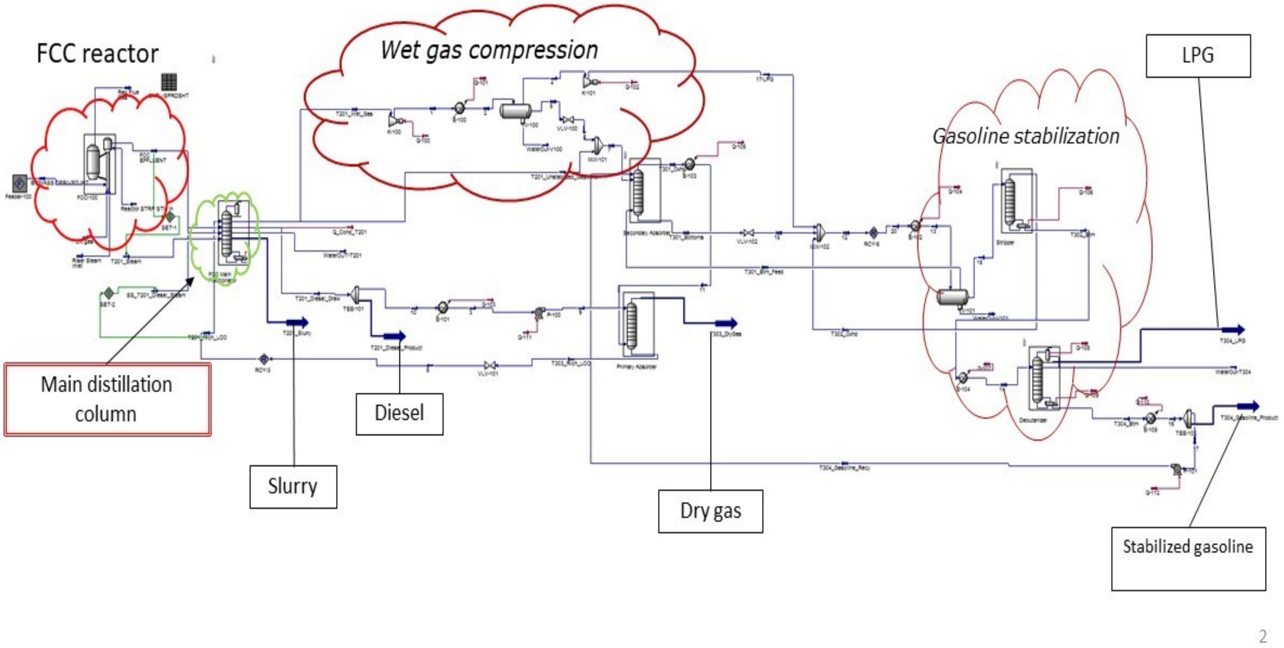


**Figure 3.4: Overall snapshot of the process simulation model for HDO co-processing**

In this FCC simulation model, a hot catalyst from the regenerator enters the bottom of the riser alongside VGO feedstock and HDO. The hot catalyst will vaporize the feed for the reactions to start on the catalyst surface. Riser effluent stream directly goes to the main distillation column, where heavier components and diesel are separated from the bottom and side streams, respectively. The column has 5 pump-arounds to control the column temperature profile and enhance product separation. To compare overall unit operations during normal and co-processing operations, all the pump-around parameters are kept constant between the two modes of operation.

The main parameters used in this simulation model are summarized in Table 3.2. To compare the results of normal operation with co-processing, the aim was to keep the same product quality value by changing plant operating conditions. To accomplish this, the model operating parameters were tuned (by changing utility demand) to meet plant specifications.

**Table 3.2. Main parameters use in FCC unit modelling**

| Property | Unit | Value | Unit operation |
|---|---|---|---|
| Condenser temperature | °C | 41 | Main distillation column |
| Stage 17 (below feed stage) temperature | °C | 345 | Main distillation column |
| Reflux ratio |  | 0.5 | Main distillation column |
| Diesel 90% cut point (ASTM D-86) | °C | 355 | Main distillation column |
| Riser temperature | °C | 518 | FCC reactor |
| Riser pressure | Bar-g | 2.4 | FCC reactor |
| Inter-stage cooler temperature | °C | 35 | Wet gas compressor |
| Gasoline RVP | kPa | 54.5 | Stabilizer column |

| Property | Unit | Value | Unit operation |
|---|---|---|---|
| Max $H_2S$ content | Mole % | 0.005 | Stripper |
| LPG max C5+ | mole% | 5 | Stabilizer column |

### 3.2.4. Simulation model validation

In this research, a typical FCC unit with a complete downstream fractionation unit was simulated using Aspen HYSYS® . A typical FCC unit configuration from a UOP design for a refinery was used as the reference plant for the model development [91]. Following an initial model run, the FCC reactor was calibrated using the Aspen FCC reactor calibration tool with the reference plant product's distribution details. Figure 3.5 shows the results of the simulation after the calibration. It can be seen that the model makes a good prediction of the product's distribution for LPG and naphtha. The slightly higher difference in product distribution for LCO and bottom products, lower yield prediction for LCO and higher for bottoms, is due to the differences in the defined range between the simulation model and plant data for those two products. In the current research, the main focus is to understand the relative difference in the FCC unit product's yields for normal operation (VGO processing) and co-processing operation (10 wt.% HDO with VGO) and not the product's absolute rate. Considering this target, the results obtained from the model calibration, using typical plant data, are considered accurate for this research. Further tuning of the model will need specific plant data for model development and tuning and therefore will help to understand the operation of that specific plant in the co-processing operation.

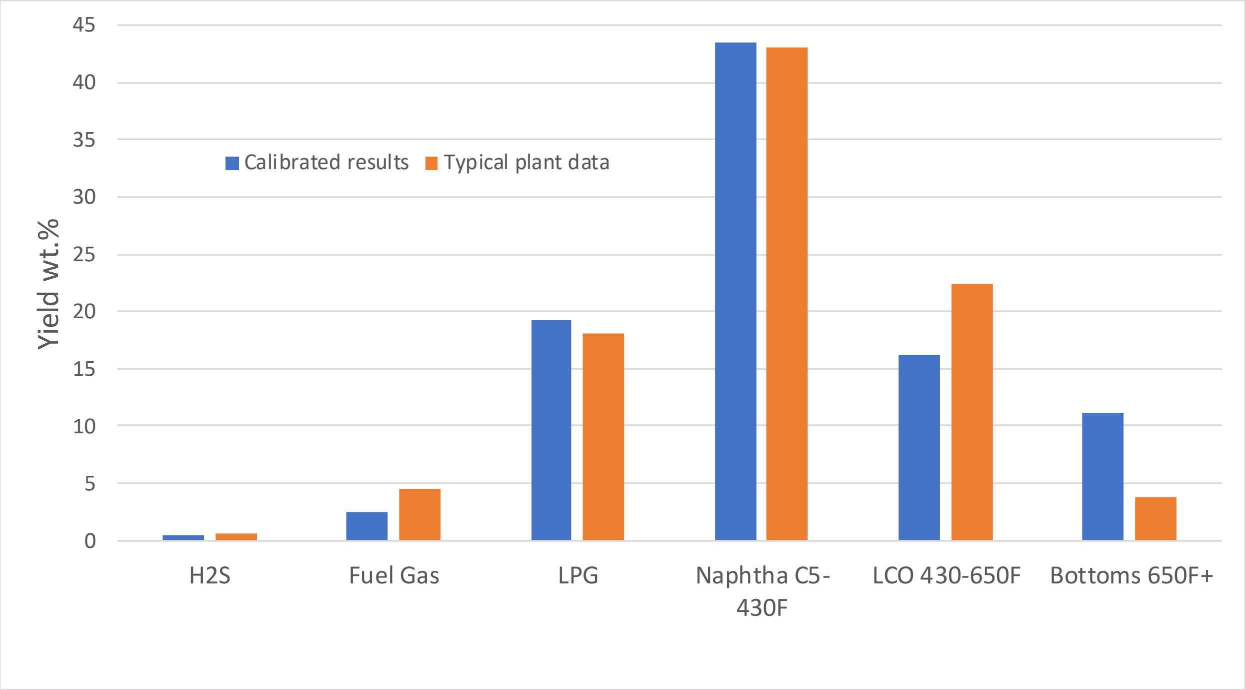


**Figure 3.5: FCC reactor product distribution comparison**

To examine the simulation model in the co-processing operation, the model trend was verified in relation to available experimental data from Fogassy et al. [26]. There is very limited publicly available data for co-processing HDO in a pilot plant or at industrial scale for calibration of the model. Also, Pinho et al. suggested that heavy feed and coke will behave and form differently in laboratory-scale batch operation apparatuses than in an industrial-scale FCC unit operation [5, 77]. There are fundamental differences in the operation of fixed bed apparatus and pilot-plant fluidized bed operations in temperature and residence (contact) time control. The Aspen HYSYS® FCC reactor model uses steady state modelling equations to develop a rigorous simulation of an industrial FCC unit. As a result the laboratory-scale data could not be used for the calibration of the model in co-processing operations. In the current research, the simulation model was calibrated using typical industrial plant data and then the model was used to examine the trends in co-processing. Figure 3.6 shows the comparison of results between experimental data and simulations for VGO cracking and 20 wt.% HDO co-processing with VGO. The conversion is defined as the sum of the yields of dry gas, LPG, gasoline, and coke. The simulation model was run at three different total inlet flow rates, and the conversion and products' yields were calculated for each flow rate. The yields were plotted against the total conversion and presented in Figure 3.6, to compare the simulation and experimental (lab-scale) results. The simulation model predicts the products' yields with operating conditions changing in the same way as the experimental data, and the absolute yield values are in the acceptable range.

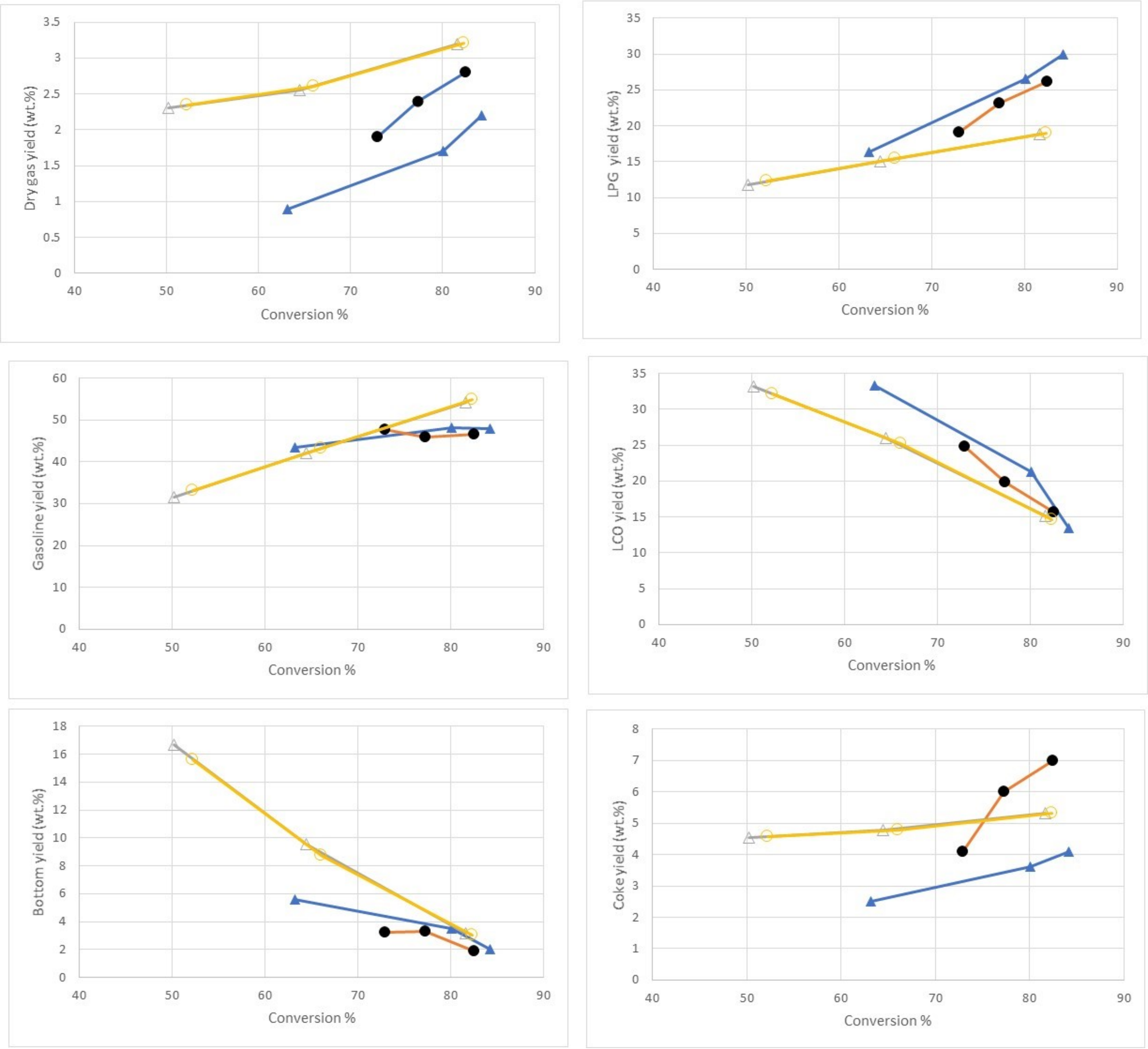


**Figure 3.6: Comparison of FCC reactor products' yields at different conversion rates**

Experimental VGO cracking (▲), experimental HDO/VGO co-processing (●), simulation output of VGO cracking (△), and simulation output of HDO/VGO co-processing (○)

## 3.2.5. Description of the economic assessment

The focus of the economic assessment is to understand how co-processing bio-oil in the FCC unit affects final product cost. Hence incremental costs for the refinery related to co-processing operation are considered. Figure 3.7 shows the methodology and parameters considered in this assessment. It was assumed that co-processing will not require any capital investment. This assumption is valid if the bio-oil does not require upgrading. Thus, a hydrodeoxygenated bio-oil was considered as the feedstock. This will increase feedstock cost and therefore the overall added co-processing cost in the current study. If the FCC reactor can process raw bio-oil, as suggested by Pinho et al. [5, 77, 92], this can reduce the feedstock cost substantially with a small amount of capital investment to modify the FCC riser arrangements.

Also, because this study is a general overview of the FCC unit operation, it was assumed that the new bio-based feedstock will replace the petroleum-based feed by a pre-determined percentage (e.g., 10% wt.). Based on HDO assay analysis and FCC unit simulation results, it is known that the FCC units will have some extra capacity if they take HDO oil because of its assay characteristics. This means refinery operations can add some bio-oil without reducing the amount of petroleum-based feedstock. This extra capacity, which will increase gasoline and diesel production, has an important role in economic assessment of the refinery. In the current work, this approach was not chosen as it requires a detailed capacity analysis of a specific FCC plant.
The main cost factor is the cost of the feedstocks (bio-oil and VGO) and the most important revenue for the refinery operation is from gasoline, diesel, and liquified petroleum gas (LPG). Since the amount of transportation fuel produced by the FCC unit can differ because of co-processing, the cost-effectiveness of co-processing should be included in any financial analysis. As mentioned above, the idea of a co-processing operation is to take advantage of existing infrastructure and thereby avoiding the capital cost of building new refinery units. It should also be mentioned that refineries may benefit from taking raw bio-oil (i.e., without any upgrading) and

saving substantially on feedstock cost. This will need some modification to the FCC reactor riser, which has some capital cost factors. Pinho et al. found this co-processing method technically feasible [5, 77], but further research on a pilot plant-scale is required.

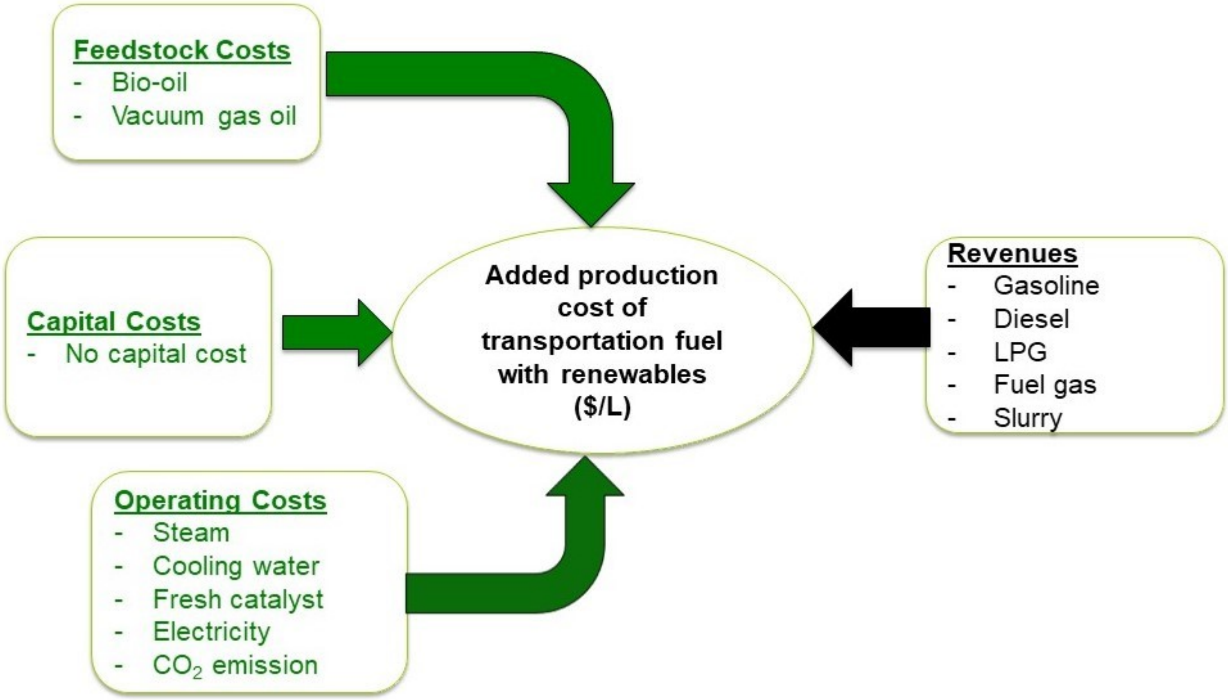


**Figure 3.7: Economic analysis model main parameters**

As a result of co-processing, the FCC plant's utility demand changes, which in turn changes the refinery's operating costs. In this study, steam and electricity consumption were monitored during and after co-processing, and the associated cost was considered in the economic assessment model. Also, because HDO has a different assay than the original VGO feedstock, the amount of coke formed on the catalyst surface is different and hence the fresh catalyst the FCC reactor needs change. Therefore, the cost of providing a fresh catalyst for the refinery is accounted for in the model.

Another important impact of the changes in riser coke formation is the amount of $CO_2$ produced from coke burning on the catalyst surface. The FCC regenerator is the biggest $CO_2$ producer in the refinery operation and any changes in its operation has a big impact on the plant's overall GHG emissions. Because of the penalties (or caps) currently mandated in most jurisdictions, this cost factor was considered in the model.

The unit production also affect the economic assessment and was therefore considered as the revenue source for the FCC plant in this cost model. Other than gasoline, diesel, and LPG (propane and butane), FCC produces some off-gas and slurry. Off-gas is mainly used as fuel in a refinery, so it was considered a utility for other refinery units. The slurry stream from the main distillation column bottom was modelled as the low-quality burning oil in this model. Equation 1 was used and the parameters are summarized in Table 3.3 to calculate the added cost for the refinery unit.

$$FCC\ unit\ added\ cost = \left(F_i \times C_i - F_j \times C_j\right)_{co-processing} - \left(F_i \times C_i - F_j \times C_j\right)_{Base\ case} \quad (1)$$

F: Stream flowrate (unit mass/hr)

C: Material cost (price) (USD/unit mass)

i, j: stream index

i= VGO, Bio-oil, riser process steam, fresh catalyst, regenerator emitted $CO_2$, distillation process steam

j= Dry gas, LPG, gasoline, diesel, slurry

**Table 3.3. Cost analysis model inputs (2018 average)**

| Cost parameter | Unit | Cost (USD) | Source |
|---|---|---|---|
| VGO | USD/litre | 0.4 | [93] |
| Bio-oil | USD/litre | 0.72 | [94] |
| LPG | CAD/litre | 0.735 | [95] |
| Gasoline | CAD/litre | 0.7753 | [95] |
| Diesel | CAD/litre | 0.855 | [95] |
| Slurry | CAD/litre | 0.7875 | [95] |
| steam | USD/tonne | 8.7 | [81] |
| Catalyst | USD/tonne | 3750 | [81] |
| $CO_2$ penalty (tax) | CAD/tonne | 30 | [96] |
| Electricity | USD/MW.hr | 40 | [94] |
| Exchange rate | USD/CAD | 1.2957 | [97] |

### 3.2.6. Bio-carbon content analysis

The main purpose of the co-processing operation is to transfer the biomass-based carbon to transportation fuels. To assess the success of this operation and to demonstrate regulatory compliance, the bio-carbon content of the final gasoline and diesel should be measured. The $^{14}C$ isotope method is a standard method for measuring the age of carbon atoms. Carbon with a fossil fuel origin ages millions of years while carbon from biomass-based feedstock ages 20-50 years. Therefore, these can easily be distinguished using the $^{14}C$ experimental method.

Although the $^{14}C$ method provides insight into the carbon source for transportation fuels, it does not consider any bio-carbon transferred to other products, coke, or regenerator $CO_2$. During the processing of VGO (or other fossil-based fuels), LPG, light gas, and cycle oil are produced alongside gasoline and diesel. Although there are no regulatory requirements for these byproducts in terms of bio-carbon content, transforming bio-carbon to them offsets their GHG emission impact. This should be considered (and credited to the co-processing operation) when analyzing co-processing. Another important factor is the $CO_2$ produced when the coke deposited on the regenerator is burned. The FCC regenerator is the biggest emitter of $CO_2$ in the refinery operation, and any changes in the quantity and source of this $CO_2$ emission should be captured. During co-processing, some bio-carbon goes to coke (and regenerator $CO_2$ ultimately), which reduces the overall FCC unit GHG emission effect.

With these considerations the following equations were developed based on Talmadge et al.'s work to calculate the bio-carbon content of transportation fuels [78].

$$Bio\ oil\ \%\ in\ gasoline = \left(\frac{overall\ gasoline\ yield - VGO\ only\ processing\ gasoline\ yield}{Overall\ gasoline\ yield} \times 100\right) \tag{2}$$

$$Gasoline\ yield = \frac{Total\ \ gasoline\ produced}{Total\ VGO\ inlet} \tag{3}$$

A critical assumption of this method is that during the co-processing operation, the bio-oil processing does not affect VGO processing, and the VGO part of the fuel (90% in most cases) has the same yield factor as in normal operations. Given the low percentage of the co-processing operation (5%-10%), this assumption is reasonable. To calculate the overall gasoline yield of the co-processing operation, the total gasoline produced was divided by the total VGO added to the reactor; the bio-oil weight was not considered. This assumption can be justified by bio-oil carbon neutrality.

## 3.3. Results and discussion

### 3.3.1. The co-processing operation

The FCC unit operation was analyzed for both normal and co-processing operations. Vacuum gas oil is the main feedstock to the unit. The effects of replacing 10% of the feed with hydrodeoxygenated bio-oil on unit performance was studied.

Table 3.4 shows the main results for the products and feedstock for a 0% (normal operation) and a 10% co-processing operation. The results show that co-processing does not have a big impact on overall product flowrate. As a result of co-processing, the flowrate of the produced dry gas, slurry, and coke decreased by 9%, 6%, and 4%, respectively, and the gasoline flowrate increased by 4%. The small change in flowrate is mainly because HDO has similar assay characteristics to VGO, as can be seen from Figure 3.2. This is one of the reasons this bio-oil has been chosen by many research groups for the co-processing operation in the FCC reactor. Also, as mentioned in section 3.2.3, the simulation specifications were set to ensure that the minimum required qualities for gasoline, diesel, and LPG are always achieved. This will make the two operations comparable.

**Table 3.4. Overall FCC unit product yield (tonne/hr) from the developed simulation model**

| Properties | Base case | 10% HDO |
|---|---|---|
| Bio-oil (HDO oil) | 0 | 10.8 |
| VGO flowrate | 108.2 | 97.4 |
| Total input flow | 108.2 | 108.2 |
| Dry gas | 4.3 | 3.9 |
| LPG | 21.8 | 20.9 |
| Gasoline | 36.1 | 37.6 |
| Diesel | 34.9 | 35.2 |
| Slurry | 4.7 | 4.4 |
| Coke | 7.5 | 7.2 |

To make sure that the FCC unit can operate in the co-processing operation with new utility demands and new operating conditions, the important parameters of the FCC unit were monitored for VGO-only and co-processing operations and are presented in Table 3.5. The regenerator air flowrate was chosen to consider air compressor capacity limitations. The riser outlet temperature was set at a fixed temperature of 518 °C to consider all the metallurgical limitations of the reactor. Also, the catalyst circulation rate was compared in the co-processing and base case operations to make sure it does not cause more pressure drop between the riser and the regenerator; the reactor can circulate this amount of catalyst in new operating conditions. Because less coke is generated in the riser during co-processing, the air flowrate required to burn the coke from the catalyst surface in the regenerator is lower in co-processing than in the base case operation. Thus it was considered that the air compressor will be able to handle co-processing operations and therefore no additional capital investment is needed for the new air compressor. The FCC unit demands for process steam (i.e., the steam added to the main distillation column) is another important parameter that was compared in the two modes of operation to account for the utility demand and to make sure the new mode of operation will not need any extra utility that may not be available at the refinery.

**Table 3.5. FCC unit performance before and after co-processing (tonne/hr)**

| Property | Base case | 10% HDO |
|---|---|---|
| Regenerator airflow | 161.8 | 147.8 |
| Catalyst circulation | 1148 | 1122 |
| Reg $CO_2$ emission | 25.2 | 24.2 |
| Process steam | 13.04 | 13.04 |
| Electricity (MW) | 7.32 | 6.7 |

The plant performance analysis in terms of utility (steam and electricity consumption) shows that the FCC units use almost the same amount of steam and that less electricity is consumed during co-processing than during normal operation, mainly due to the lower regenerator air flowrate. Since co-processing leads to less coke formation, burning the accumulated coke on the catalyst surface generates less $CO_2$ during co-processing. Considering the penalties (or the $CO_2$ emission cap) most jurisdictions apply for $CO_2$ production, this can be another advantage for the co-processing operation.

### 3.3.2. Bio-carbon content analysis of the co-processing operation

Apart from the quality and quantity of transportation fuels produced via co-processing, bio-carbon content is another important parameter in co-processing. As explained in section 3.2.5, there are two methods of determining the value of this parameter. The $^{14}C$ method is a completely experimental method. Other studies on co-processing 10-20% HDO found 2-5% bio-C content on the final gasoline [5, 77].

The mass balance method for the calculation of the total bio-carbon content of transportation fuels has received some attention [78]. The $^{14}C$ method does not account for the fossil-based carbon that would have gone directly to the atmosphere as a result of coke or dry gas formation but is captured in transportation fuels. This a direct result of co-processing, as some bio-carbon replaces fossil-based carbon in coke or dry gas. This disadvantage of $^{14}C$ contradicts the main idea of blending biofuel to lower overall refinery GHG emissions. Thus the mass balance method was used to analyze the overall effect of co-processing (through Equations 2 and 3).

The results of normal operations (base case) and co-processing based on the simulation model are summarized in Table 3.6. The mass balance method of calculating bio-carbon content and yield shows that gasoline and diesel yields increase by 18% and 12%, respectively, in co-processing compared to normal operations. The method also shows that co-processing has the potential for up to 11% bio-carbon content with 10% hydrodeoxygenation bio-oil.

**Table 3.6. Bio- C analysis for the base case and co-processing operations**

| Property | Unit | Base case | Co-processing (90% VGO, 10% HDO) |
|---|---|---|---|
| VGO flowrate | tonne/hr | 108.2 | 97.4 |
| Bio-oil flowrate | tonne/hr | 0 | 10.8 |
| Gasoline flowrate | tonne/hr | 36.11 | 37.65 |
| Diesel flowrate | tonne/hr | 34.9 | 35.2 |
| Gasoline yield | | 0.33 | 0.39 |
| Diesel yield | | 0.32 | 0.36 |
| Bio-C content in gasoline | wt.% | 0 | 15 % |
| Bio-C content in diesel | wt.% | 0 | 11 % |

### 3.3.3. Economic assessment

Adding a new feedstock to a refinery operation can change refinery economics. The added cost was assessed for an FCC unit to replace 10% of its normal feedstock (VGO) with hydrodeoxygenated bio-oil through the methods explained in section 3.2.4 and the parameters listed in Table 3.3.

Table 3.7 shows the results from this analysis. The overall cost of producing gasoline for the refinery was calculated using the parameters listed in Table 3.3. The FCC unit performance before and after co-processing obtained from Tables 3.4 and 3.5. During co-processing, the refinery (FCC unit) production cost to produce the same quantity of products will increase by 4,734

USD/hr for a refinery of size 80,000 bpd capacity. The added cost for gasoline and diesel production (with bio-content) will increase the final price of transportation fuels. Although all refinery products, including LPG and slurry, will have some bio-carbon content, there are no regulatory requirements for these products to have any bio-content. For this reason, the added cost was distributed between gasoline and diesel only, based on their regulatory requirement to have bio-content. Currently, refineries are required to mix bioethanol with gasoline and diesel at a yearly average amount of 5% and 2%, respectively. Since gasoline has a higher bio-content requirement, a higher percentage of the overall refinery processing cost increase was allocated to gasoline than to diesel, based on their bio-content regulatory requirements. Another approach would be to distribute the added cost based on total production volume, which would lead to different added costs for the gasoline and diesel, but the overall refinery-added cost per barrel of feed would be the same.

**Table 3.7. Main cost analysis results for co-processing 10% HDO (USD)**

| **Cost parameter** | **Unit** | **value** |
|---|---|---|
| Refinery added cost | USD/hr | 4,734 |
| Refinery added cost | USD/bbl. | 13.45 |
| Increased cost of Gasoline production | USD/litre | 0.068 |
| Increased cost of diesel production | USD/litre | 0.027 |

Figure 3.8 shows the results of sensitivity analysis for gasoline- and diesel-added costs by changing different parameters. The added costs for both gasoline and diesel are sensitive to the feedstock price. As Figure 3.8 shows, if HDO price decreases by 50%, through, technology

advancement, economies of the scale, or modification of the FCC unit to process raw bio-oil, there would not be any added cost for the refinery to process bio-oil and to get bio-content in transportation fuels (i.e., there will be a 100% reduction in added cost). A ±50% change in other parameters will change the refinery's added cost only by ±5%.

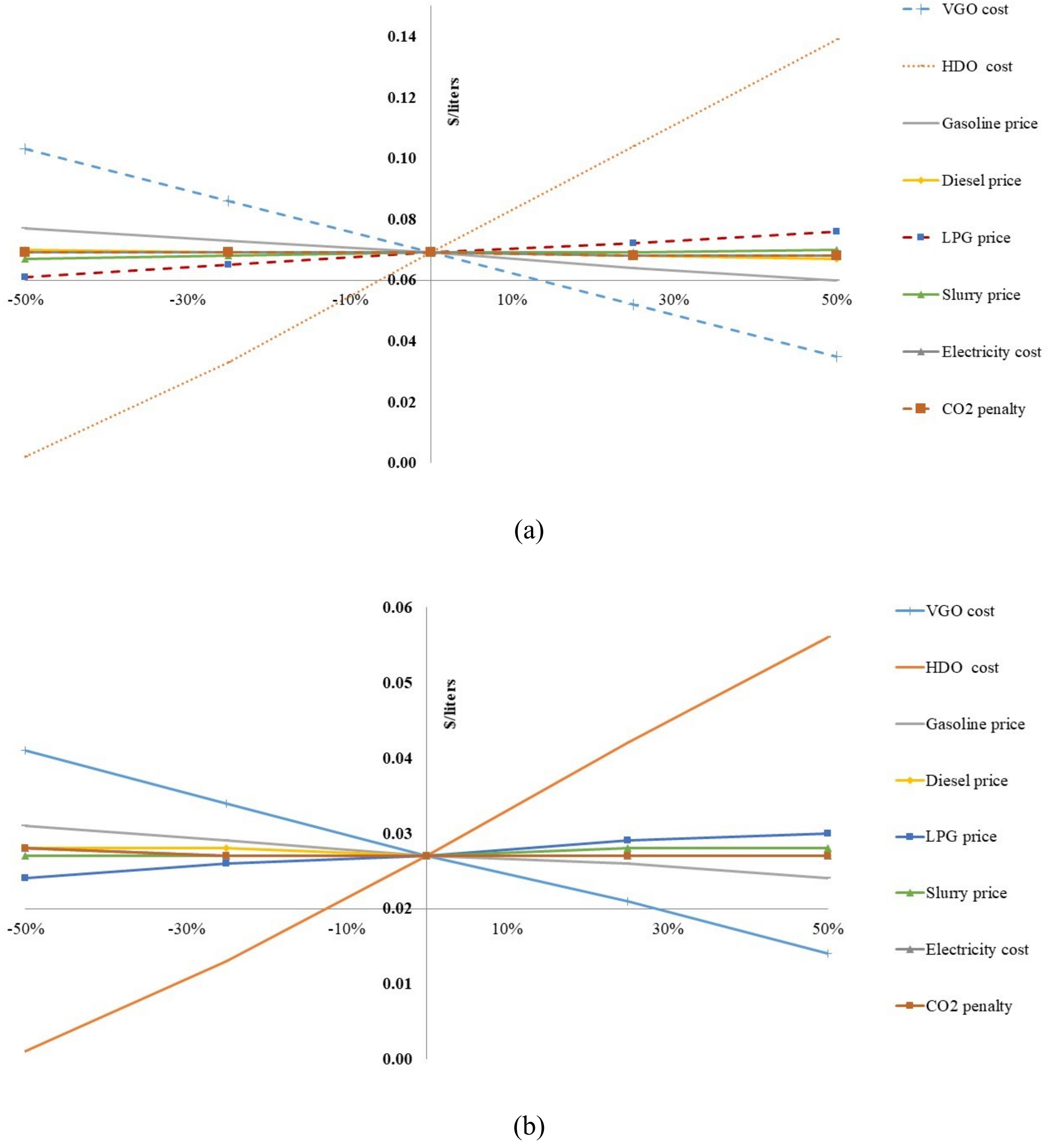


**Figure 3.8: Added production cost sensitivity analysis for (a) gasoline (b) diesel**

## 3.4. Comparison of cost of drop-in fuels and incremental cost of co-processing

Currently, refineries and fuel distribution companies are mandated by the government to blend an average (yearly) 5% vol. bioethanol with gasoline and 2% vol. with diesel. Co-processing is an approach to meet these requirements. Currently, the price of ethanol (2018 average) is in the range of 1.51 $/gallon (0.4 $/litre) [98].

Equations 4 and 5 show that for every litre of gasoline a refinery sells, it needs to buy 0.0526 litres of ethanol. The costs for the refinery to buy ethanol are shown in Table 3.8.

$$\frac{Ethanol}{Ethanol+Gasoline} = 5\% \tag{4}$$

$$\frac{Ethanol}{Gasoline} = 5.26\% \tag{5}$$

**Table 3.8. Drop-in bioethanol added cost for the refinery (2018 USD)**

| Cost parameter | Unit | Value |
|---|---|---|
| Added cost of gasoline production | USD/litre | 0.02 |
| Added cost of diesel production | USD/litre | 0.008 |

Because of high demand and government incentives for bioethanol production, ethanol production capacity is increasing rapidly around the world. This capacity expansion has lowered the price in recent years. There are now concerns about this industry's sustainability and outlook due to limited capacity and demand increase as government mandates become stricter. In light of these concerns, the US Annual Energy Outlook 2019 predicted an ethanol price increase from 1.5$/gallon in 2018 to 5$/gallon in 2050 [98].

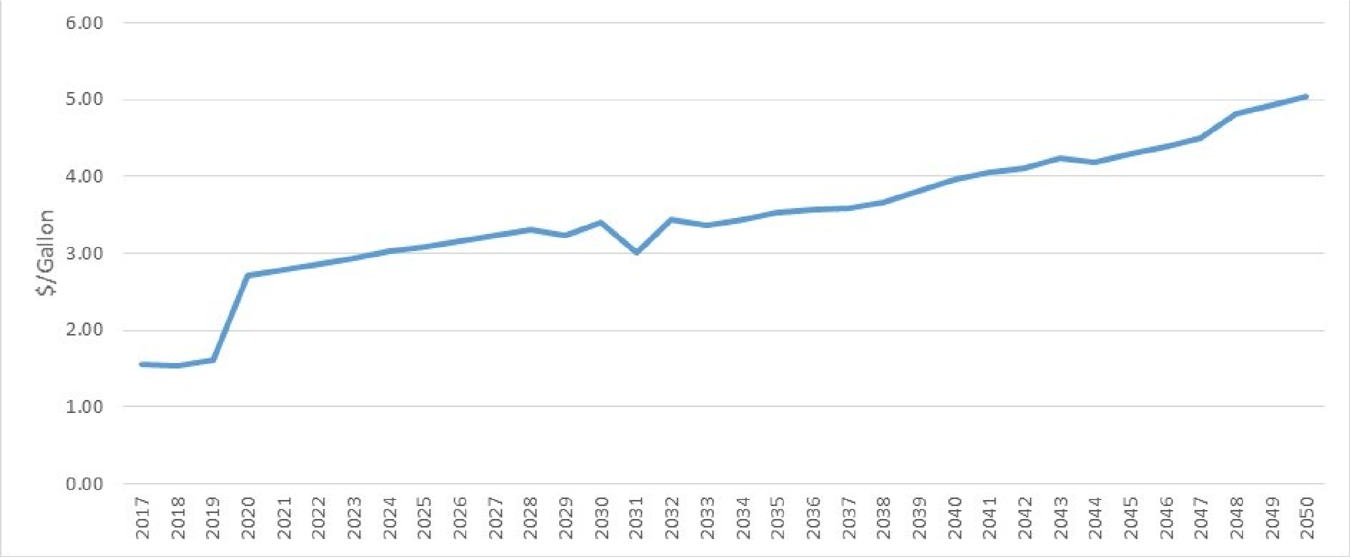


**Figure 3.9: Ethanol price outlook**

In addition to ethanol production costs, producing ethanol as the first generation biofuel competes with the requirement of grains as food source. Co-processing can be an alternative approach to adding bio-content to transportation fuels.

## 3.5. Conclusion

In this study, the effects of replacing 10% of the FCC unit's petroleum-based feedstock (VGO) with biomass-based oil were studied from operational and economic points of view. Co-processing has the advantage of using existing infrastructure and refinery units with very low need for capital investment while meeting mandated bio-carbon content on transportation fuels. Adding bio-content to final transportation fuels is technically feasible and, based on the calculations, up to 11% bio-content in final products can be expected. This will reduce GHG emissions in the transportation sector. The co-processing operation will increase refinery operating costs and may therefore increase fuel final price.

# Chapter 4: Conclusions and Recommendations for Future Work

## 4.1. Conclusion

Processing biomass-based oil in conventional oil refineries is receiving special attention because it is carbon neutral, has flexible production and upgrading processes, and uses low-value feedstock that is widely available. In this study, a detailed process simulation model was developed using Aspen HYSYS® to examine the effects of replacing 10% of the FCC unit's feedstock with a biomass-based oil. The simulation model integrates the Aspen HYSYS® FCC unit model with a downstream product fractionation unit. The co-processing operation has the advantage of using existing infrastructure and refinery units with almost no need for capital investment while meeting government-mandated bio-carbon content on final transportation fuels. In addition, a cost model was developed to examine the effects of co-processing on the FCC unit's economics. Co-processing will change the refinery operating cost and therefore have some effects on the production cost of transportation fuels. The cost model considers the main factors in refinery operating costs, that is, the feedstock cost, product sale revenue, and catalyst and utility cost. The process simulation indicates that co-processing yields slightly more gasoline and diesel. Coke deposition on the catalyst surface was reduced and thus catalyst circulation rate fell by 2.3% . Also, reduced coke formation in the FCC riser produces less $CO_2$ in the regenerator and less air is required to burn this coke. Therefore, regenerator $CO_2$ emissions and regenerator compressor airflow rates decreased by 4% and 8.6%, respectively.

The final goal of the co-processing operation is to convert the biomass-based carbon to a transportation fuel. To determine whether this can be achieved, the bio-carbon content of the final gasoline and diesel was examined. The literature review showed that, depending on the co-processing percentage ratio, gasoline and diesel produced via co-processing have 1%-2% bio-carbon content when tested by the $^{14}C$ method. On the other hand, the carbon mass balance shows that the rest of the bio-carbon was transferred to coke, $CO_2$, or other products. This analytical method proves that co-processing transfers some fossil-based carbons to transportation fuels rather than coke or $CO_2$. From the overall refinery $CO_2$ production perspective, this carbon can be credited to the co-processing operation. As Table 4.1. shows, it was observed that by co-processing, it is possible to get up to 15% and 11% bio-content in gasoline and diesel through the mass balance method calculation.

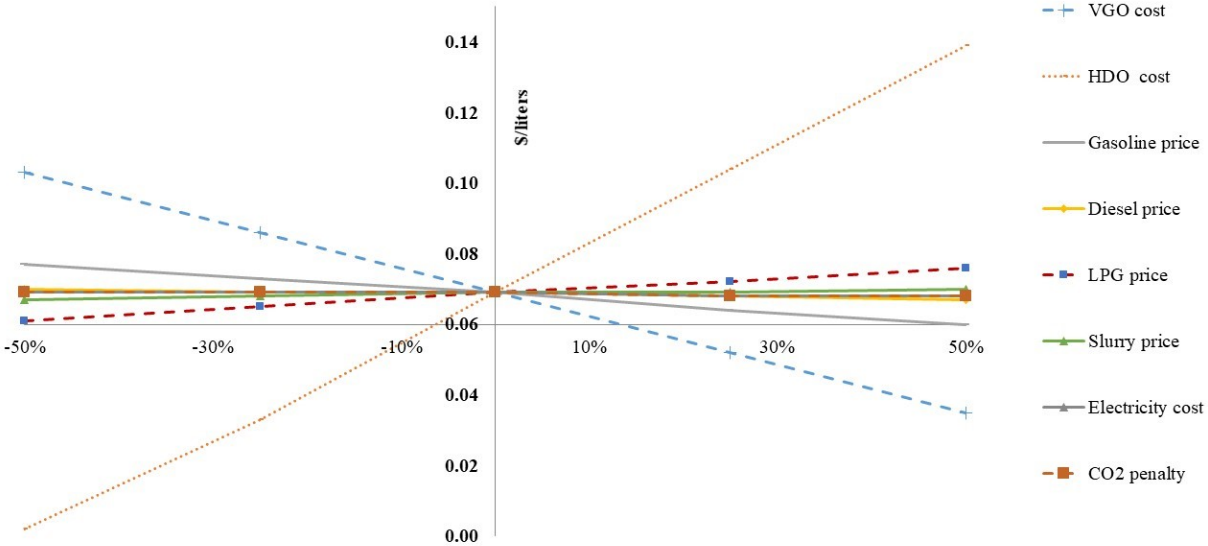
**Table 4.1. Bio- C analysis for the base case and co-processing operations**

| Property | Unit | Base case | Co-processing (90% VGO, 10% HDO) |
|---|---|---|---|
| Gasoline yield | | 0.33 | 0.39 |
| Diesel yield | | 0.32 | 0.36 |
| Bio-C content in gasoline | wt.% | 0 | 15 % |
| Bio-C content in diesel | wt.% | 0 | 11 % |

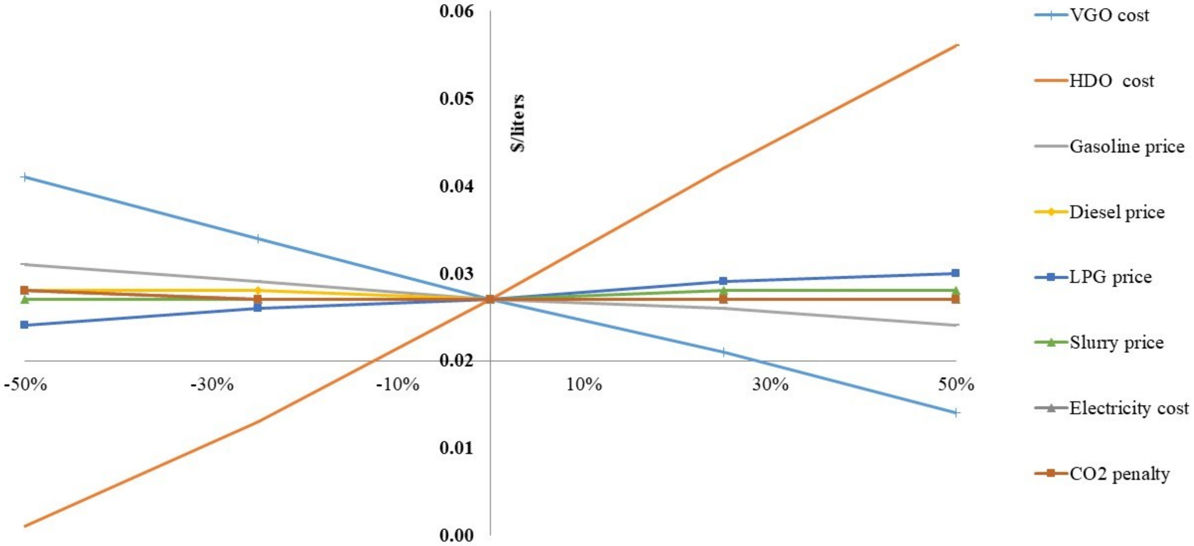
As Table 4.2. shows, from the refinery operating cost perspective, it was observed that replacing 10% of the VGO with HDO in the FCC reactor feedstock will change the refinery's economic balance. As a result of co-processing, gasoline and diesel production costs will increase by 6.8 ¢/litre and 2.7 ¢/litre, respectively, while producing almost the same amount of product. The added cost of the refinery, in general, is very sensitive to feedstock (VGO and HDO) price. For example, Figure 4.1. presents that a 50% reduction in HDO price will make the co-processing operation economically neutral without any added cost to the refinery.

**Table 4.2. Main cost analysis results for co-processing 10% HDO (USD)**

| **Cost parameter** | **Unit** | **value** |
|---|---|---|
| Increased cost of Gasoline production | USD/litre | 0.068 |
| Increased cost of diesel production | USD/litre | 0.027 |



(a)



(b)

**Figure 4.1: Added production cost sensitivity analysis for (a) gasoline (b) diesel**

## 4.2. Recommendations for Future Work

Upgrading raw bio-oil to hydrodeoxygenated oil in refinery units can be the next step in integrating biomass-based oils into existing refinery units. This will reduce the HDO costs for the FCC unit and thereby improve overall co-processing economics. The flexibility of FCC units in taking new feedstocks and this study's economic analysis show a promising approach to transferring biomass-based carbon to transportation fuels. This transfer of carbon will require both further study and modification of the FCC unit's catalyst to improve the performance of the units and their ability to transfer more bio-based carbon to final products (rather than to coke or off-gas).

From the overall GHG-effects perspective, the production of first-generation biofuels (from corn) produces $CO_2$ during plant construction and operation. Thus a comprehensive study and comparison of overall GHG effects of first- and second-generation biofuels will help government agencies and policymakers in assigning the right amount of GHG credit for the co-processing operation. During co-processing, some biomass-based carbon will be transferred to LPG, off-gases, and low-value fuels. A comprehensive GHG-effects study will also be able to account for total refinery GHG emissions reduction as the final goal of government-mandated blending operations and be able to identify the right approach for accounting for bio-based carbon content.

In summary, the following research gaps were identified during the current study that will help to fully understand and improve the co-processing operation.

1. Exploring the option of upgrading raw bio-oil to hydrodeoxygenated oil in the refinery's hydrotreating or hydrocracking units.

2. Further study and modification of the FCC unit catalyst and riser configuration. The new catalyst will improve the overall performance of the units such that bio-based carbon can be transferred to final products rather than to coke or off-gas.
3. Comprehensive study and comparison of overall GHG effects of first-generation biofuels and co-processing that also considers $CO_2$ production during ethanol or bio-oil production. The results of this comprehensive comparison will help government agencies and policymakers in assigning the right amount of GHG credit for these two different methods of producing bio-based transportation fuels.

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# Appendix A.

Main stream results of the process simulation are summarized in Table A.1 and Table A.2 for VGO and VGO+HDO cases, respectivly. Figure A.1 shows the developed process simulation flowsheet.

**Table A.1. Simulation results of process main stream (VGO only case)**

| | Unit | BIOMASS DERIVED INT. | FCC EFFLUENT | T201_ Steam | SS_T201_ Diesel_Steam |
|---|---|---|---|---|---|
| Vapour Fraction | | 0.72 | 1.00 | 1.00 | 1.00 |
| Temperature | C | 175.00 | 517.36 | 240.00 | 240.00 |
| Pressure | kPa | 300.00 | 300.13 | 1,351.33 | 1,351.33 |
| Molar Flow | kgmole/h | 0.00 | 1,756.83 | 153.06 | 15.62 |
| Mass Flow | kg/h | 0.00 | 110,297.87 | 2,757.45 | 281.45 |
| Liquid Volume Flow | m3/h | 0.00 | 153.69 | 2.76 | 0.28 |
| Heat Flow | kJ/h | 0.00E+00 | -1.47E+08 | -3.60E+07 | -3.67E+06 |

| | | T201_Slurry | T201_Wet_ Gas | T201_Diesel_ Product | T301_Ovhd |
|---|---|---|---|---|---|
| Vapour Fraction | | 0.00 | 1.00 | 0.00 | 1.00 |
| Temperature | C | 345.00 | 41.00 | 175.03 | 43.53 |
| Pressure | kPa | 301.73 | 255.03 | 272.54 | 1,300.33 |
| Molar Flow | kgmole/h | 13.72 | 790.68 | 188.15 | 284.36 |
| Mass Flow | kg/h | 4,683.35 | 34,031.98 | 34,900.20 | 6,707.10 |
| Liquid Volume Flow | m3/h | 4.57 | 62.31 | 38.83 | 16.37 |
| Heat Flow | kJ/h | -6.94E+06 | -4.21E+07 | -6.60E+07 | -1.14E+07 |

|  | **Unit** | **T301_Bottoms** | **T303_DryGas** | **T302_Ovhd** | **T302_Btm** |
|---|---|---|---|---|---|
| Vapour Fraction |  | 0.00 | 1.00 | 1.00 | 0.00 |
| Temperature | C | 56.70 | 38.23 | 48.34 | 152.06 |
| Pressure | kPa | 1,322.33 | 1,200.33 | 1,266.33 | 1,301.33 |
| Molar Flow | kgmole/h | 5,822.02 | 230.13 | 2,599.17 | 4,541.12 |
| Mass Flow | kg/h | 425,719.89 | 4,297.91 | 98,875.17 | 382,922.90 |
| Liquid Volume Flow | m3/h | 626.01 | 11.86 | 175.34 | 548.60 |
| Heat Flow | kJ/h | -7.99E+08 | -7.81E+06 | -7.72E+07 | -6.51E+08 |

|  |  | **T304_LPG** | **T304_Gasoline_ Product** |
|---|---|---|---|
| Vapour Fraction |  | 0.00 | 0.00 |
| Temperature | C | 46.83 | 35.00 |
| Pressure | kPa | 1,171.33 | 1,202.33 |
| Molar Flow | kgmole/h | 437.67 | 410.35 |
| Mass Flow | kg/h | 21,791.89 | 36,113.10 |
| Liquid Volume Flow | m3/h | 39.33 | 50.93 |
| Heat Flow | kJ/h | -2.38E+07 | -7.36E+07 |

**Table A.2. Simulation results of process main stream (VGO + HDO case)**

| | Unit | BIOMASS DERIVED INT. | FCC EFFLUENT | T201_ Steam | SS_T201_ Diesel_Steam |
|---|---|---|---|---|---|
| Vapour Fraction | | 0.72 | 1.00 | 1.00 | 1.00 |
| Temperature | C | 175.00 | 517.37 | 240.00 | 240.00 |
| Pressure | kPa | 300.00 | 300.13 | 1,351.33 | 1,351.33 |
| Molar Flow | kgmole/h | 94.31 | 1,738.87 | 153.35 | 15.63 |
| Mass Flow | kg/h | 10,820.80 | 110,502.94 | 2,762.57 | 281.59 |
| Liquid Volume Flow | m3/h | 11.72 | 152.99 | 2.77 | 0.28 |
| Heat Flow | kJ/h | -1.73E+07 | -1.48E+08 | -3.60E+07 | -3.67E+06 |

| | | T201_Slurry | T201_Wet_ Gas | T201_Diesel_ Product | T301_Ovhd |
|---|---|---|---|---|---|
| Vapour Fraction | | 0.00 | 1.00 | 0.00 | 1.00 |
| Temperature | C | 345.00 | 41.00 | 175.02 | 43.82 |
| Pressure | kPa | 301.73 | 255.03 | 272.54 | 1,300.33 |
| Molar Flow | kgmole/h | 12.93 | 742.21 | 191.33 | 265.53 |
| Mass Flow | kg/h | 4,382.42 | 32,064.34 | 35,194.60 | 6,273.13 |
| Liquid Volume Flow | m3/h | 4.26 | 58.50 | 39.10 | 15.22 |
| Heat Flow | kJ/h | -6.52E+06 | -3.94E+07 | -6.66E+07 | -1.06E+07 |

|  | Unit | T301_Bottoms | T303_DryGas | T302_Ovhd | T302_Btm |
|---|---|---|---|---|---|
| Vapour Fraction |  | 0.00 | 1.00 | 1.00 | 0.00 |
| Temperature | C | 57.29 | 38.25 | 47.76 | 153.70 |
| Pressure | kPa | 1,322.33 | 1,200.33 | 1,266.33 | 1,301.33 |
| Molar Flow | kgmole/h | 6,110.14 | 211.47 | 2,812.02 | 4,701.44 |
| Mass Flow | kg/h | 445,240.08 | 3,910.68 | 106,941.56 | 397,381.43 |
| Liquid Volume Flow | m3/h | 651.44 | 10.80 | 184.66 | 568.41 |
| Heat Flow | kJ/h | -8.32E+08 | -7.13E+06 | -7.87E+07 | -6.76E+08 |

|  |  | T304_LPG | T304_Gasoline_ Product |
|---|---|---|---|
| Vapour Fraction |  | 0.00 | 0.00 |
| Temperature | C | 47.08 | 35.00 |
| Pressure | kPa | 1,171.33 | 1,202.33 |
| Molar Flow | kgmole/h | 418.35 | 428.31 |
| Mass Flow | kg/h | 20,859.60 | 37,652.18 |
| Liquid Volume Flow | m3/h | 37.61 | 53.08 |
| Heat Flow | kJ/h | -2.25E+07 | -7.68E+07 |

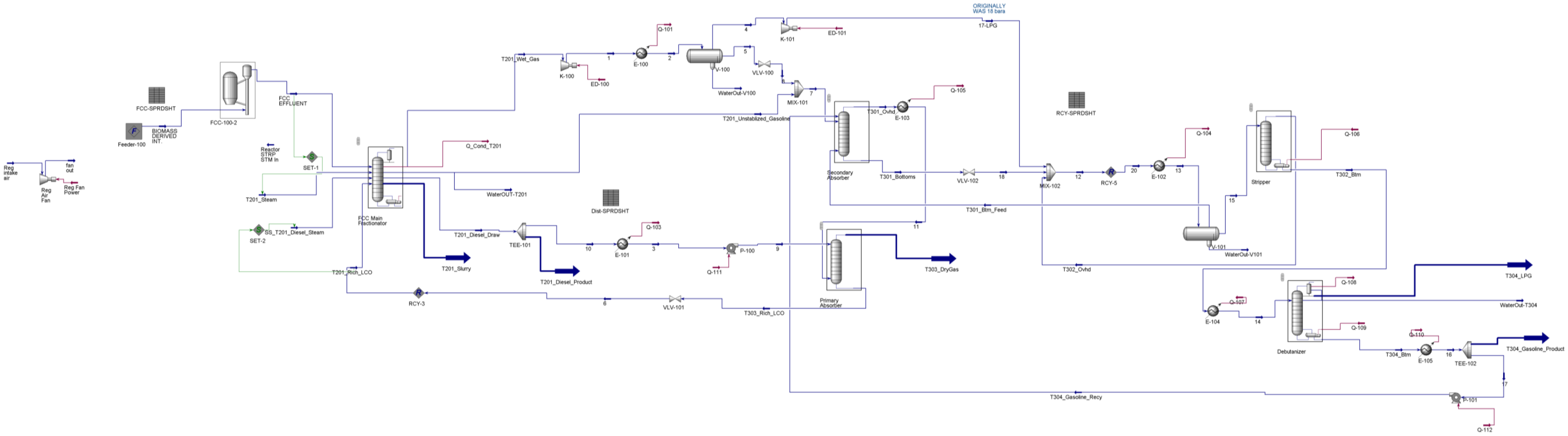

**Figure A.1: Simulation model main flowsheet**