![IEA Bioenergy logo]

IEA Bioenergy
Technology Collaboration Programme

Recent progress in the production of low carbon-intensive drop-in fuels –

Standalone production and coprocessing

IEA Bioenergy: Task 39

Recent progress in the production of low carbon-intensive drop-in fuels –
Standalone production and coprocessing

Susan van Dyk, Jianping Su, Jack Saddler

IEA Bioenergy: Task 39

February 2022

Key take home messages

The production and use of drop-in biofuels will be essential if the world is to meet its carbon reduction targets. Hard-to-decarbonise sectors such as aviation and marine will need these lower carbon intensive (CI) fuels. However, the production of lower-carbon-intensive (CI) fuels must rapidly increase if targets, such as those outlined in COP26, are to be met.

- Development of drop-in biofuels has been slow and only limited volumes are currently available. The only fully commercial process that is currently used to produce drop-in biofuels is via the hydrotreatment of lipids, using the oleochemical pathway (hydrotreated vegetable oils, HVO, or hydrotreated esters and fatty acids, HEFA).

- However, other drop-in biofuel technologies are moving towards commercialisation, with many facilities under construction or planned.

Co-processing biogenic feedstocks (lipids, biocrudes, etc.) within existing petroleum refineries can provide an alternative, fast and effective way to rapidly increase the volumes of drop-in, lower carbon-intensive fuels.

- Two main feedstocks can be used for co-processing: lipids (fats, oils and greases (FOG's)) and biomass derived biocrudes produced via technologies such as fast pyrolysis and hydrothermal liquefaction. The most likely insertion points of these feedstocks within refineries will be at the hydrotreater or the fluid catalytic cracker, depending on the desired products and risk mitigation.

- Lipids are currently co-processed at a commercial scale in various locations around the world. This will likely expand as lipids are relatively easy to upgrade. In the longer term, feedstock availability, cost and sustainability will place a limitation on the growth lipid co-processing. Thus, it is likely that, biocrude liquid intermediates will become significant co-processing feedstocks.

- However, co-processing biogenic feedstocks in a refinery poses some risks for the refiner in terms of operational challenges, fuel quality issues, corrosion of metallurgy, inactivation of catalysts, increased hydrogen demand, etc. Risk mitigation requires an understanding of the potential impacts of biogenic feeds and the steps that need to be taken to reduce and overcome risks. At this time, several companies are developing technologies to facilitate co-processing while mitigating associated risks. These include reactor modification, the use of pretreatment processes and guard beds, dedicated catalysts, upgraded metallurgy, etc.

- Commercial experience has indicated that co-processing lipids at low ratios (e.g. 5%) has a relatively minor impact on refinery operations and the associated risks can be managed with limited investment in new and modified infrastructure. However, as co-processing ratios increase, as demonstrated by companies such as PREEM, it is likely that much greater investment will be required and more extensive refinery modifications will be needed.

- Although some infrastructure and operational modifications will be required to facilitate co-processing at an existing refinery, the cost is likely to be significantly lower than building dedicated standalone biorefinery. However, the cost will be influenced by the type of feedstock, the insertion point, the blend ratio, etc. It should be noted that biocrudes are complex, variable and distinct from lipids and it is very likely that more extensive steps will be required to mitigate refinery risk with biocrude characteristics such as the oxygen content, TAN, etc., all influencing the ease of co-processing.

- Co-processing can allow petroleum refineries to produce lower carbon-intensive fuels to more readily meet policy obligations while earning credits. It also provides refineries with the opportunity to meet longer-term climate commitments.

Co-processing has the potential to produce large volumes of drop-in, lower-CI fuels but will require significant volumes of biogenic feedstocks.

If a 10% blend was currently inserted in the FCCs, hydrotreaters and hydrocrackers of the world's refineries, a total of 6.04 mb/d (~ 350 billion litres per year) of biogenic feedstocks would be required.

The methods used to track the biogenic content (green molecules) of co-processed fuels need to be refined

- Better tracking of the "green molecules" (biogenic content) in the finished fuels is needed, to determine the impact of co-processing on the carbon intensity of the final fuels, overall emission reductions and to better quantify any credits refiners might receive from enabling policies.

- Although the quantification of the carbon intensity of feedstocks is relatively well-established, the life cycle assessment (LCA) of the co-processed fuels is more complex. Typically, life cycle analysis is not carried out for the whole refinery, but rather only for the processing unit where the co-processing takes place. Although for the case of insertion at the hydrotreating units, the LCA can be relatively straight-forward, when co-processing at the fluid catalytic cracker, the situation is significantly more complex.

- Although carbon 14 measurements are considered to be the "gold standard" way of determining renewable carbon content, this assessment requires expensive equipment, skilled technicians, etc., and is usually done offsite. As it only provides a percentage renewable content, an accurate mass balance for the processing unit is still necessary.

- The carbon 14 method has been successfully used by companies that are co-processing lipids in a hydrotreater. However, at low biofeed concentrations, the carbon 14 (ASTM D6866) method has a high uncertainty. It is likely that carbon 14 measurements when co-processing biogenic feeds in an FCC will be more challenging.

- Other methods, such as the mass balance based on observed yields, (also known as the step-change mass balance method), can be used to assess the effectiveness of co-

3

processing compared to fossil feedstock baseline. Although this method is cheaper and easier for refiners to carry out using existing equipment, it has several shortcomings such as the need for a stable baseline and an accurate closure of the mass balance. It also assumes that no interaction occurs between fossil and biogenic molecules.

- One of the biggest challenges in using this method is establishing a stable baseline. Refinery operations vary due to changes in the crude oil feedstock, refinery targets, seasonal variabilities, emergency shutdowns, etc. These variations can be more significant than the influence of co-processing biogenic feedstocks at low percentages. Flow meters may also be subject to error which make it difficult to establish a baseline and subsequent determination of changes resulting from co-processing at low blends.

- When co-processing at low blend ratios (5%) at the FCC, the baseline "noise" made it difficult to distinguish any changes associated with co-processing biogenic feedstocks. Forced closure of the mass balance resulted in high standard deviations which affected the accuracy of measurement. However, a combination of methods, with periodic C14 measurements, was successfully used to track the green molecules after co-processing at the FCC.

Table of Contents

5

List of figures

List of tables

Abbreviations

AEM   Anion Exchange Membrane

AMS   Accelerated Mass Spectrometry

ATAG   Air Transport Action Group

BETO   Bioenergy technologies office

CAN   Carboxylic acid number

CAPEX   Capital expenditure

CARB   California Air Resources Board

CCUS   carbon capture and utilisation or storage

CHP   Combined heat and power

CI   Carbon intensity

CPO   Catalytic pyrolysis oil

DCO   Decarboxylation/decarbonylation

FCC   Fluid catalytic cracker

FOG   Fats, oils and greases

FPO   Fast pyrolysis oil

FT   Fischer-Tropsch

HAGO   Heavy atmospheric gas oil

HCO   Heavy cycle oil

HDO   Hydrodeoxygenation

HDS   Hydrodesulfurization

HDT   Hydrotreating

HEFA   Hydrotreated esters and fatty acids

HFO   Heavy fuel oil

HHV   Higher heating value

HTL   Hydrothermal liquefaction

HVGO   Heavy vacuum gas oil

HVO   Hydrotreated vegetable oils

IPCC   Intergovernmental Panel on Climate Change

IRENA   International Renewable Energy Agency

IRMS   Isotope Ratio Mass Spectrometry

ISCC   International Sustainability and Carbon Certification

LAGO   Light Atmospheric gas oil

LCA   Life cycle assessment

LCFS   Low carbon fuel standard

LCO   Light cycle oil

LSC   Liquid Scintillation Counting

LVGO   Light vacuum gas oil

MCR   Micro Carbon Residue

MSW   Municipal solid waste

NREL   National Renewable Energy Laboratory

PEM   proton exchange membrane

PtL   Power to liquid

RSD   Relative standard deviation

RTD   Raw tall diesel

SAF   Sustainable aviation fuels

SGAB   Subgroup on advanced biofuels

SMR   Steam reforming

SOEC   solid oxide electrolyser cells

SRGO   Straight run gas oil

TAN   Total acid number

TRL   Technology readiness level

UCO   Used cooking oil

VGO   Vacuum gas oil

W2F   Waste to fuel

1. Introduction

Global climate targets and the race to net-zero by 2050 has created an urgency in decarbonising human activities. Transportation contributes significantly to GHG emissions and is a critical target for emission reductions. According to the IEA, transportation is responsible for 24% of direct CO_2 emissions from fuel combustion (https://www.iea.org/topics/transport). Road vehicles account for nearly three-quarters of transport CO_2 emissions, but emissions from sectors such as aviation and shipping continue to rise, and these sectors will be more difficult to decarbonise (https://www.iea.org/topics/transport). Thus, these sectors will need drop-in biofuels or lower-carbon-intensity (CI) liquid fuels as electrification and other lower CI options are problematic.

According to the IEA, global transport emissions increased by less than 0.5% in 2019 (compared with 1.9% annually since 2000) owing to efficiency improvements, electrification and greater use of biofuels. (https://www.iea.org/topics/transport).

Although biofuels have played a role in reducing transportation emissions, they still only contribute about 4% to overall liquid transportation fuels demand. The main biofuels used are ethanol and biodiesel, which are mainly used in road transportation as gasoline and diesel substitutes. The current global production of ethanol and biodiesel is about 150 billion litres per year. However, due to ethanol and biodiesel's chemical and "operational" characteristics, only limited blends have been possible using current vehicles without modifications. These biofuels cannot be used in sectors such as aviation, and drop-in biofuels such as biojet or sustainable aviation fuels (SAF) are needed.

Drop-in fuels that are functionally equivalent to fossil-based liquid transportation fuels and compatible with existing infrastructure can allow high blends and even be used as a 100% substitute for petroleum fuels. These fuels can be used by the long-distance transport sector such as aviation, marines, rail and long-distance trucking. However, drop-in biofuels have been slow to commercialise, and only renewable diesel (hydrotreated vegetable oils (HVO)) is available in significant quantities. Smaller quantities of biojet/sustainable aviation fuels (SAF), such as HEFA synthetic paraffinic kerosene (SPK) (sometimes called hydrotreated renewable jet), are also produced and used. Although global HVO production in 2021 was about 6 billion litres, this volume is insignificant compared to the volumes of ethanol and

biodiesel produced and used. While electric vehicles are expected to replace most internal combustion engines in urban environments eventually, electrification is anticipated to have only a limited impact on aviation, marine and other difficult-to-decarbonise sectors.

The recent spate of announcements for new HVO/HEFA production facilities, based on new construction and repurposing, is expected to result in a dramatic increase in drop-in biofuels availability in the coming years. The aviation sector's interest in biojet/SAF has also encouraged investment by companies and governments, with several processes such as alcohol-to-jet, gasification/FT, etc., all being scaled up to demonstration-and-commercial levels. For example, Fulcrum Bioenergy (gasification/FT) recently completed construction of their facility, while the Red Rock Biofuels facility (gasification/FT) is reported to be near completion. Other companies such as Gevo and Lanzajet, who are commercialising the alcohol-to-jet approach, have announced the construction of multiple facilities.

In parallel, many oil companies have been investing in lower carbon-intensive transportation fuels by "repurposing" refineries. These repurposed facilities hydrotreat lipid feedstocks (e.g. fats, oils, and greases (FOG's)) to produce products such as renewable diesel. Prominent examples include World Energy (Paramount, California), Total (La Mede, France) and ENI (Gela, and Porto Marghera, Italy). An alternative strategy has been followed by companies such as BP and Parkland, who are commercially co-processing biogenic feedstocks in their existing refinery infrastructure to reduce the carbon intensity of the final fuels. In this way, they gain access to an increasingly lucrative low carbon intensity (CI) fuel market, particularly in jurisdictions such as California and British Columbia, which have low carbon fuel standards (LCFS). The Swedish company Preem has been coprocessing raw tall diesel (RTD) (30% blends) at their Gothenburg refinery for many years and plans to co-process pyrolysis bio-oils, produced by Pyrocell[1], at their Lysekil refinery in 2022. The first successful trials at the Lysekil refinery was carried out by Honeywell and

---

[1] https://news.cision.com/preem-ab/r/pyrocell-commences-production,c3418069

Preem in September 2021[2]. The first SAF produced via coprocessing of lipids was produced by BP in 2021 at their Castellon refinery in Spain. Currently, ASTM D1655 only permits co-processing of 5% lipids or Fischer-Tropsch liquids. However, this is likely to be reviewed in the near future to boost SAF production.

It has been suggested that there are four dominant ways in which refineries can produce low-carbon intensity fuels. These include the development of stand-alone facilities, as exemplified by World Energy, refinery-integrated facilities (shared logistics and utilities between bio- and oil refinery), refinery co-processing (low-carbon feed processed with fossil feed), and the conversion of an existing refinery processing unit, e.g. a hydrotreater, to process 100% low-carbon feed (CONCAWE, 2020).

This IEA Bioenergy Task 39 report provides an update of previous work (Van Dyk, Su, Mcmillan and Saddler, 2019) and describes progress in the commercialisation of stand-alone refineries and the increased adoption of co-processing by refineries. The past Task 39 reports described the broad concepts of drop-in biofuels and the potential to co-process lipids and biocrudes in the hydrotreater or fluid catalytic cracker. The most recent report highlighted some of the challenges that were anticipated when inserting biogenic feedstock in existing refineries. In work described here, with more operational information now available, the problems and the various solutions that have been developed are described, particularly how the biogenic content co-processed fuels might be determined and the challenge in following the "green molecules" in a refinery.

With the recent release of the IPCC 6th Assessment report, the urgency to tackle climate change has seen commitments from many corporations and countries beyond the Paris agreement. Many have set targets to achieve net-zero by 2050, and several oil refineries have announced the need for a significant transformation to stay relevant. It is recognised that the substitution of fossil crudes with biobased feedstocks can result in significant reductions in the carbon intensity of fuels

---

[2] https://uop.honeywell.com/en/news-events/2021/september/honeywell-and-preem-conduct-commercial-co-processing-trial-to-produce-renewable-fuel

(depending on the blend ratio). Due to the ever-increasing economic impact of climate change, it is highly likely we will see oil companies, particularly their refinery operations, transitioning to lower carbon-intensive ways of operating, with increased "repurposing" of oil refineries to stand-alone biorefineries and the increased use of co-processing to make use of existing facilities while producing lower carbon-intensive transportation fuels.

2. Stand-alone refineries for the production of drop-in biofuels

Production of drop-in biofuels is a complex process that requires multiple steps and similar processing units to petroleum refineries. Key steps in the production of any drop-in biofuel include processes such as hydrotreatment and distillation, which are found in almost every refinery. Due to their greater complexity and the requirement for multiple process steps, the capital investment required to construct a typical drop-in biofuel refinery is high compared to building a bioethanol and biodiesel facility (Figure 1).
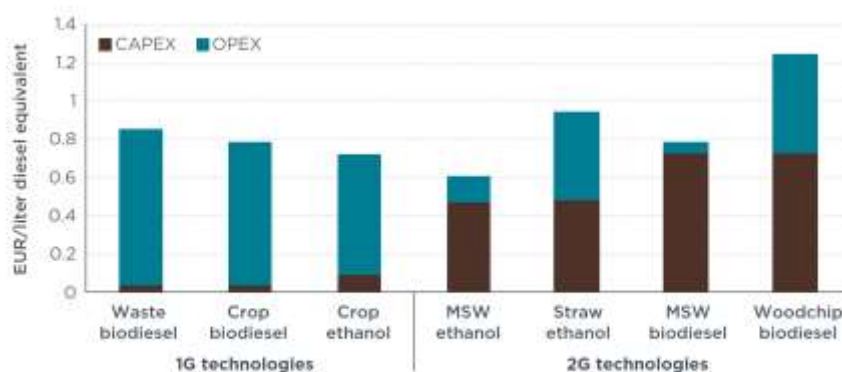
Figure 1 Comparison of the capital and operating expenses for various biofuel technologies showing the higher capital costs needed to develop advanced biofuel technologies. MSW Biodiesel and Woodchip biodiesel are drop-in biofuel technologies (Figure from (Bitnere and Searle, 2017).

In order to reduce the capital investment, several companies have "repurposed" or converted underutilised petroleum refineries to so-called brownfield rather than greenfield developments. Examples of repurposing include World Energy in California, formerly an asphalt plant, Total's La Mede refinery in France, and ENI's facility in Gela, Italy. These facilities were converted to produce renewable diesel/hydrotreated vegetable oils (HVO) using lipid feedstocks such as FOGs. Companies such as Phillips66 and Marathon have also announced the repurposing of some of their refineries.

In parallel, several companies have announced the use of corn-derived-ethanol as the feedstock for alcohol-to-jet, while Gevo's isobutanol production facility is a conversion of an ethanol facility. Recently, Gevo and ADM signed an MoU

16

that describes the intent to convert several ADM ethanol facilities to produce iso-butanol based on Gevo's fermentation process [3].

Other possible pathways to make drop-in biofuels include gasification and Fischer-Tropsch, pyrolysis and hydrothermal liquefaction. These technologies are at various stages of commercialisation, with many based on de novo construction as the infrastructure required is quite distinct from refinery processes. However, the possible upgrading of biogenic intermediates from these technologies via hydrotreatment, hydrocracking, and catalytic cracking is very similar to several existing refinery processing steps. The possible upgrading of these biogenic intermediates by refineries, as possible co-processing feedstocks, could overcome the high investment costs that would be encountered if constructing de novo hydroprocessing and cracking processing units.

2.1 RENEWABLE DIESEL FACILITIES – STAND-ALONE AND CONVERSIONS/REPURPOSING

About 6 billion litres of renewable diesel are currently produced worldwide, and a significant expansion is currently underway with multiple facilities under construction. These facilities and their capacities are summarised in Table 1 below.

---

[3] https://www.globenewswire.com/news-release/2021/10/25/2319898/23976/en/ADM-Gevo-Sign-MoU-to-Produce-up-to-500M-Gallons-of-Sustainable-Aviation-Fuel.html

Table 1: Current world annual production capacity of HEFA drop-in biofuels, stand-alone construction and repurposed facilities

(https://demoplants.best-research.eu/)

Company	Location	Feedstock	Capacity	
Neste	Rotterdam	Vegetable oil, UCO and animal fat	800,000 t/y (1.26 bn L/y)	
Neste	Singapore	Vegetable oil, UCO and animal fat	800,000 t/y (1.26 bn L/y)	
Neste	Singapore expansion	Vegetable oil, UCO and animal fat	1,400,000 t/y)	
Neste	Porvoo 1, Finland	Vegetable oil, UCO and animal fat	190,000 t/y (240 m L/y)	
Neste	Porvoo 2, Finland	Vegetable oil, UCO and animal fat	190,000 t/y (240 m L/y)	
ENI	Venice, Italy	Vegetable oils	360,000 t/y (450 m L/y)	
ENI	Gela, Italy		750,000 t/y	
Diamond Green Diesel	Norco, Louisiana	Vegetable oils, animal fats and UCO	411,000 t/y (500 m L/y)	
UPM	Lappeenranta, Finland	Crude tall oil	130,000 t/y (120 m L/y)	
World Energy	Paramount, California	Non-edible oils and waste	130,000 t/y - 150 m L/y	
World Energy	Paramount expansion		1,000,000 t/y	2022
Renewable Energy Group	Geismar, Louisiana	High and low free fatty acid feedstocks	225,000 t/y (315 m L/y)	
Emerald Biofuels	Port Arthur, Texas	Vegetable oils	417,000 t/y (330 m L/y)	
TOTAL	La Mede, France	Vegetable oils and waste	500,000 t/y	
TOTAL	Grandpuits, France	Vegetable oils	~350,000 t/y	2024
Preem	Gothenburg, Sweden	Tall oil	800,000 t/y	
Tidewater	Prince George, Canada	Vegetable oils	150,000 t/y	2023
Sunpine	Pitea, Sweden	Tall oil	77,000 t/y	
St1	Gothenburg, Sweden	Oils and fats	200,000 t/y	
Repsol	Cartagena, Spain	Oils and fats	250,000 t/y	2023
Phillips 66 **(Rodeo renewed)**	San Francisco, USA	Oils and fats	2,000,000 t/y	2024
Imperial Oil (Strathcona project)	Edmonton, Canada	Oils and fats	1,000,000 t/y	2024
Marathon	Dickinson, North Dakota	Oils and fats	184 million gallons per year	
Marathon	Martinez, California	Oils and fats	730 million gallons per year	2022/2023
Covenant Energy	Saskatchewan, Canada	Oils and fats	300-325 MLPY	2023/2024
Come by Chance	Newfoundland, Canada	Oils and fats	14,000 bpd	2022
Heartwell Renewables (Cargill JV)	Hastings, Nebraska	Oils and fats	80 MGPY	2023

| Shell | Rotterdam, Netherlands | Oils and fats | 820,000 t/y | 2024 |
| Go Sunshine | New Orleans | Oils and fats | 29 (110) | 2023 |

However, as mentioned earlier, many companies have instead "repurposed"/modified existing facilities to use existing supply chains and infrastructure. As summarised in Figure 2, there are significant advantages in converting/repurposing with regard to the CAPEX compared to building a new stand-alone biorefinery (CONCAWE, 2020).
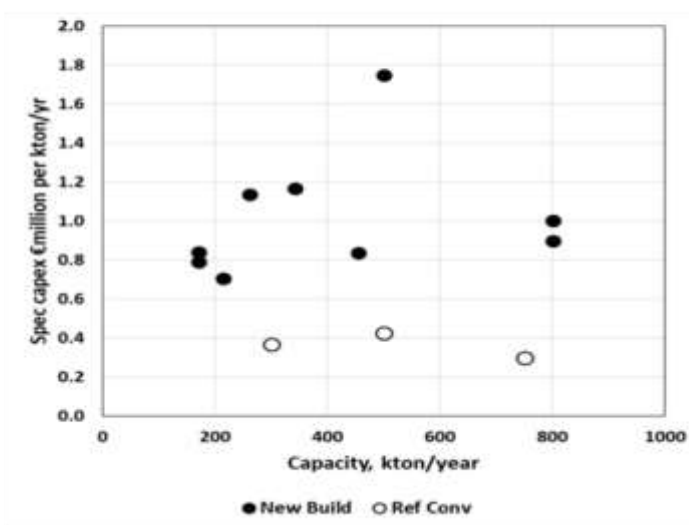
Figure 2. Capital intensity of lipid hydrotreatment plants – new builds and refinery conversion. (Source: Neste, ENI, Total and Darling press releases; Concawe members) (Figure taken from CONCAWE, 2020)

While repurposing an existing refinery to produce drop-in biofuels has a significant cost-saving, additional infrastructure and infrastructure modifications are typically required due to various reasons such as differences in feedstock chemistry. For example, conversion of a hydrotreater to process lipids would require a storage facility for the lipids and modification of the hydrotreater and other ancillary processes will likely be needed. Lipid processing also requires pretreatment, large H_2 consumption, management of heat production and increased effluent treatment volumes with higher biochemical oxygen demand.

For example, the cost for Eni to repurpose one of its refineries was estimated to be about one-fifth of the cost of establishing a new, greenfield facility using the same technology and capacity. Existing hydrotreaters and the naphtha reformer

remained the backbone of the biorefinery, but a pretreatment facility was built to remove any contaminants in feedstocks and reduce the acidity from free fatty acids and prolong the life of the catalysts. A steam reformer was built to produce hydrogen as the capacity was limited by the amount of hydrogen available. Other changes included modified catalysts, added heat exchangers, changing the acid gas treatment (to deal with CO_2 instead of H_2S from petroleum hydrodesulfurization), adding product recycling for quench purposes, connecting the two reactors, as well as other modifications.

The initial repurposing of the Paramount, California facility by Altair involved modifying the existing hydrotreating and isomerization units and some auxiliary vessels, reactors and stripping units. In terms of the supply chain, an unloading rack was modified, and changes were made to the off-loading manifold, pump and piping so that 25 rail cars of tallow and vegetable oil per day could be processed. The fractionation tower was repurposed from the naphtha hydrotreater as the naphtha stabilizer separates the light gas (burnt as fuel gas) component so the naphtha stream can be blended into renewable gasoline. The hydrogen supply was trucked in and stored in three 18,000-gallon capacity storage tanks. Similarly, a new amine solution was developed to remove both CO_2 and H_2s, which was subsequently transferred to an incinerator where hydrogen sulfide was converted into sulfur dioxide. It was subsequently "scrubbed" with a caustic solution. Storage tanks were also modified in order to store renewable feed and products. Construction took place between 2014-2015, and the facility has been operating since 2016 (capacity of 3,500 bbl/d).

In the second phase of its facility expansion, World Energy is investing US$350 million to expand capacity from 45 million gallons to over 306 million gallons per year. The proposed expansion will include a pretreatment unit and an on-site hydrogen facility.

2.2 OTHER DROP-IN BIOFUEL TECHNOLOGIES AND FACILITIES

Standalone facilities for various other technology pathways, including gasification/Fischer Tropsch, catalytic hydrothermolysis and alcohol-to-jet are currently under construction and projected to come online over the next few years.

Although Table 2 lists a number of facilities, it may not be complete due to the rapid pace of announcements.

Table 2. Facilities based on drop-in biofuel technologies under construction or announced.

Company	Technology pathway	Vol MGPY (MLY)	Status - Start-up date
Gevo (Silsbee)	Isobutanol-to-jet	Demo	2020
Gevo (Luverne)	Isobutanol-to-jet	19 (72)	2023
Fulcrum Bioenergy (Sierra)	Gasification/FT	7 (26)	2021
Red Rock Biofuels (Lakeview)	Gasification/FT	6 (23)	2021
Fulcrum #2 (Indiana)	Gasification/FT	21 (80)	2023
Velocys (Altalto, UK)	Gasification/FT	16 (60)	2025
Velocys (Bayou Fuels)	Gasification/FT	35 (132)	
Lanzajet (Freedom Pines)	Ethanol-to-jet	10 (38)	2022
Lanzajet	Ethanol-to-jet	90 (340)	2024
Readifuels	Catalytic hydrothermolysis	24 (91)	2023

2.3 BIO-OIL/BIOCRUDE PRODUCTION VIA PYROLYSIS, HYDROTHERMAL LIQUEFACTION AND OTHER DIRECT THERMOCHEMICAL LIQUEFACTION TECHNOLOGIES

Direct thermochemical liquefaction of biomass produces liquid intermediates, generally termed bio-oils or biocrudes, which need further upgrading to convert them into drop-in fuels. The technology pathways include pyrolysis, catalytic pyrolysis, hydrothermal liquefaction, hydropyrolysis and similar thermochemical processes. Although the production of bio-oils/biocrudes is already at the demonstration/commercial stage, upgrading the bio-oils/biocrudes to drop-in transportation fuels is at a much lower technology readiness level (TRL).

As mentioned earlier, biocrudes can provide a suitable biogenic liquid intermediate feedstock that can be co-processed at existing refineries after some upgrading. Multiple bio-feedstocks can be used to produce biocrudes, including forest biomass, agricultural residues, municipal solid waste, algae, sludge, etc.

The technology for producing biocrudes through fast pyrolysis has been demonstrated in Finland, the Netherlands, Canada and the USA. A list of some of the key companies is summarised in Table 3. The current primary use of biocrudes is as heating oil, although it has also been used to produce power and for co-generation of

heat and power (CHP). Forest/woody biomass (e.g. sawdust) has been the predominant feedstock due to its greater quality consistency and availability compared to agricultural residues and municipal solid wastes (MSW). While the co-processing and upgrading of bio-oils/biocrudes have been assessed at the pilot scale, the limited supply and the low quality of biocrudes have restricted the number of co-processing and upgrading trials reported. For example, the total global production capacity of biocrude facilities is estimated to be about 300,000 tonnes per year (Table 3).

Table 3. Existing commercial and pre-commercial operating biocrude facilities in the world (Van De Beld, Leijenhorst, Heeres, Oasmaa and Ohra-Aho, 2021; Van Dyk and et al., 2019) (https://demoplants.best-research.eu/)

Company	Location	Status (date)	Capacity (tons/year)	Technology & Application	Feedstock
Ensyn	Ontario, Canada	Pre-commercial	70	Heat	Sawmill residues
Ensyn	Cote du Nord, Quebec, Canada	Commercial	36,000	Gasoline-type products	Sawmill residues
Twence/ Empyro	Hengelo, the Netherlands	Commercial	20,000	BTG-BTL technology CHP fuel	Broken and dust wood pellets
Green Fuel Nordic	Lieksa, Finland	Commercial (2020)	~20,000	BTG-BTL technology Heating oil	Sawdust
Pyrocell (Setra/Preem)	Gavle, Sweden	Commercial (2021)	~20,000	BTG-BTL technology coprocessing	Sawdust
Altaca Energy	Gonen, Turkey	Demonstration	20,000	HTL (CatLiq®, SCF Technologies)	Biomass/coal
Licella	Somersby, Australia	Demonstration	350	Cat -HTR Biocrude	biomass
Arbios	Prince George, Canada	announced	50,000 barrels per year	Cat -HTR Biocrude	Sawdust, bark
Silva Green Fuel (JV – Statkraft, Sodra)	Tofte, Norway	Demonstration (2021)	1400	Steeper Technology Biocrude	Forest residues

3. Co-processing of biobased feedstocks in existing petroleum refineries

As described earlier, co-processing involves the insertion of biogenic feedstocks, such as lipids or bio-oils/biocrudes, into existing petroleum refinery processing units to simultaneously process them with fossil feeds to create lower carbon intensity fuels.

3.1 BIOBASED FEEDSTOCKS FOR CO-PROCESSING

The two main categories of biogenic feedstocks that are and will be used for co-processing are lipids (fats, oils, and greases – FOGs) and bio-oils/biocrudes. As mentioned earlier, these latter feedstocks are produced through technologies such as fast pyrolysis, catalytic pyrolysis and hydrothermal liquefaction of biomass. Although Fischer-Tropsch liquids, produced via gasification or through power-to-liquids technologies, can also be used for coprocessing, they typically still require further upgrading into finished fuels. To date, the co-processing of FT liquids has received limited attention, although co-processing 5% FT liquids have been approved under ASTM D1655 for the production of Jet A/A1 fuel.

Vegetable oils, used cooking oil (UCO), tallow and other lipids such as forest derived Tall Oil are feedstocks that can be used by the oleochemical pathway. Vegetable oils are available globally in significant volumes, are traded extensively, are cost-effectively transported over great distances and are chemically homogenous compared to biocrudes. They require limited pretreatment before co-processing and are already co-processed at a commercial scale in several refineries around the world. However, jurisdictions such as the EU plan to limit the use of crop-based feedstocks due to sustainability concerns. For example, when indirect land use and other factors are considered during life cycle assessment (LCA), it has been suggested that these crops do not always offer substantial carbon intensity reductions. As emission reduction targets become more ambitious, with biofuel sustainability of primary concern, waste-based feedstocks such as used cooking oil have increased in value (although limited volumes are available), as it offers very significant emission reductions and have no sustainability issues. Various reports provide different estimates for global availability of waste lipid feedstocks, with the

ICF report, prepared as part of the ATAG Waypoint 2050 report, estimating a maximum potential of 27 million tonnes of drop-in SAF per year, or 6% of projected demand for SAF by 2050 (ICF, 2021). The recent IRENA biojet report estimated UCO volumes at about 27 billion litres per year (IRENA, 2021). The use of low-quality feedstocks such as UCO presents some additional technical challenges as more extensive pretreatment has to be carried out to remove contaminants, requiring additional infrastructure. However, the challenges are mostly around the cost and availability of feedstocks. For example, UCO has become an expensive commodity, and in October 2021 cost >$1,000 per tonne (Argusmedia, 2021) (greenea EUR1460 for UCOME per tonne in August 2021[4]).

The International Sustainability and Carbon Certification (ISCC) reported that they had certified more than 70 million metric tons of crops in 2020 (includes oil crops, corn, wheat and sugarcane), in addition to more than 15 million metric tons of waste and residues (Norbert Schmitz, presentation at ISCC SAF Stakeholder meeting on 18 November 2021)[5].

With the rapid expansion of renewable diesel facilities, continued biodiesel production and expansion of co-processing activities will increase competition for lipid feedstocks. This will likely lead to higher prices and increasing limited availability. Consequently, it is likely that low-carbon intensity liquid feeds produced from more abundant feedstocks such as forest residues will play a more significant role in the future.

Bio-oils/biocrudes are liquids with very complex chemistry and show significant variability depending on the original feedstock and production method. As mentioned earlier, there are significant challenges in upgrading biocrudes to finished fuels, and biocrude coprocessing is still at a very early stage of development. The availability of biocrudes is also very limited (as shown in Section 2.3), and a significant scale-up of biocrude production is needed. Due to the large scale of

---

[4] http://www.greenea.com/en/market-analysis/

[5] https://www.iscc-system.org/wp-content/uploads/2021/11/1.-Norbert-Schmitz_Sustainability-Certification-of-SAF.pdf

petroleum refineries, even a small blend percentage of renewable feed will require large feedstock volumes. For example, Talmadge and colleagues estimated that a 2000 ton per day pyrolysis facility could supply sufficient bio-oil for co-processing at 10% volumes in a petroleum refinery with 100,000 bpd FCC capacity (Talmadge et al., 2021).

3.2 PRETREATMENT OF BIOBASED FEEDSTOCKS PRIOR TO REFINERY INSERTION

Biocrudes display significant differences from fossil feeds such as crude oil. The most prominent challenge encountered when processing most biogenic feedstocks is the presence of oxygen, sometimes in very high concentrations. In addition to containing water and oxygen, biocrudes may also contain alkali metals such as Mg, Na, K, Ca, and contaminants such as chlorides and phosphorous (Marker, 2005). As contaminants such as metals can potentially cause permanent deactivation of catalysts, they must be removed prior to co-processing (Marker, 2005). (The impacts of co-processing on catalysts are further discussed in Section 4.5). The presence of oxygen and its associated chemical reactions within the refinery can have multiple impacts on refinery operations, which is discussed in detail throughout the report.

Several different pretreatment steps can be used to remove potential contaminants from feedstocks before insertion into a refiner. These include hydrocyclonic removal of particles, desalting, acid washing and ion exchange or fixed guard beds for contaminant removal prior to feeds entering a reactor (Marker, 2005). Guard beds containing demetallization catalysts can also be used prior to hydrodesulfurization reactors or may even be included in the front end of the catalyst bed. Water or acid washing is also used to remove phospholipids from oils and fats. Char particles, produced during biocrude production, have been shown to lead to instability of biocrudes and enhance ageing reactions. Char particles and other solids which can block piping can be removed via filtration (microfiltration or hot vapour filtration). Filtration has also been shown to remove significant levels of alkali metals (Meier et al., 2013; Zacher, Olarte, Santosa, Elliott and Jones, 2014).

Many biogenic feedstocks, including oils, fats and biocrudes, have high acid levels, which can cause corrosion, and refineries sometimes use carbon steel which is not very resistant to acid corrosion. The insertion of high acid biobased feedstocks may necessitate upgrading metallurgy to higher grade stainless steel. Alternatively, the prior reduction of acid levels could be a target for pretreatment. One method for acid reduction is via esterification with alcohol (similar to the production of biodiesel) (Zacher et al., 2014). This method is used by Sunpine to reduce the acid content of the tall oil feedstock into tall diesel, which is used at 30% blend levels in co-processing by Preem (Egeberg, Michaelsen and Skyum, 2010). While esterification of lipids is carried out routinely, esterification of biocrudes could potentially also be carried out to neutralize any acid components (Zacher et al., 2014).

3.3 POTENTIAL REFINERY INSERTION POINTS

Oil refineries have different configurations and target different product streams. Thus, the potential to co-process biogenic intermediates will depend on the availability of processing units as suitable insertion points, the characteristics of the intermediate and the desired products. As every biobased feedstock will have different characteristics, this will impact the choice of the insertion point. For example, higher molecular weight compounds will need to be cracked, oxygen will have to be removed, while linear paraffins require isomerization, etc. However, cracking could be carried out in one or more of the three processing units, the fluid catalytic cracker, the hydrocracker or the delayed coker (thermal cracking). Typically, hetero-atoms such as oxygen are removed through hydrotreating, while isomerization, catalytic reforming and alkylation are used to make high octane gasoline blending components.

When earlier workers assessed which facilities were "well-suited for biorefinery integration", based on their configuration (Freeman, Jones and Padmaperuma, 2013), they identified two key characteristics. Namely, whether they could convert large molecules into smaller molecules (cracking, with or without hydrogen) and whether they contained processes that could remove oxygen, such as hydrotreating. These authors also suggested that refineries with no hydrotreating facilities were not suited for upgrading bio-feedstocks unless oxygen removal was

26

carried out prior to insertion (Freeman et al., 2013). Some of the key upgrading needs for different feedstocks and technologies are summarised in Table 4 (van Dyk, Su, Mcmillan and Saddler, 2019).

Table 4 Characteristics of different bio-intermediates and main refinery requirements. (Biller and Roth, 2017; Griffin et al., 2018; Huber, Iborra and Corma, 2006; Kamara and Coetzee, 2009; Karatzos, McMillan and Saddler, 2014; Lamprecht, Dancuart and Harrilall, 2007)

	Characteristics	Refinery needs
Oleochemicals	Triglycerides and free fatty acids	Removal of oxygen
	Some heterogeneity with respect to chain length of fatty acids, but chemically quite homogenous	Some cracking may be required for specific products such as jet fuel as lipids in diesel range
	Lipids in diesel range	
	11% oxygen, 1.8 H/effC ratio	Isomerization/branching to improve cold-flow properties (biojet)
	Waste oils have higher free fatty acids which affects the acidity.	Needs the least upgrading
	Waste oils also have other contaminants	Fractionation may be required after cracking
	Metals/inorganic compounds	
Pyrolysis bio-oils	Up to 400 different components	Removal of oxygen
	High oxygen levels over 40%	Thermal or catalytic cracking of large molecules into smaller molecules
	Variable aromatic content from degradation of lignin	Potential hydrocracking of aromatics
	Water content	Fractionation into different products after upgrading
	Catalytic pyrolysis oils or partially hydrotreated pyrolysis bio-oils have lower oxygen levels than bio-oil (for catalytic pyrolysis oil, the oxygen content is generally between 18-24 wt%)	
HTL biocrudes	Lower oxygen content (range: 6-18%)	Oxygen removal
	Lower water content	Cracking of larger molecules
		Hydrocracking of aromatics
FT liquids	High temp FT creates smaller molecules suitable for gasoline	Fractionation required
	Low temp FT creates longer molecules in the diesel range	May require cracking & Isomerization

As mentioned earlier, the most likely insertion points in a refinery where co-processing could take place are at the FCC, hydrotreater or hydrocracker. The fluid catalytic cracking (FCC) unit is typically used for size reduction of heavy molecules (the usual feed is heavy gas oil, vacuum gas oil or residues) and is typically the main process used to produce gasoline (50%) and propylene (Vogt and Weckhuysen, 2015). The FCC insertion point is attractive as no external hydrogen is required, and FCC catalysts are more tolerant to higher oxygen levels in the biofeeds than hydroprocessing catalysts (Agblevor, Mante, McClung and Oyama, 2012). Another

27

benefit is that FCC catalysts are continuously regenerated on-site by burning off coke deposits in a regenerator attached to the FCC unit before recirculating the catalyst. This contrasts with other processes such as hydrotreaters, where operations are sometimes interrupted while catalysts are cleaned offsite. Thus, the FCC as an insertion point presents a much lower risk to the refinery. However, it should be noted that aromatics do not undergo any cracking within an FCC and that any potential insertion of pyrolysis bio-oils into the FCC will likely result in a greater aromatic content in the products (Pinho, De Almeida, Mendes, Ximenes and Casavechia, 2015).

As fluid catalytic cracking capacity is closely linked with the demand for gasoline, it is more common in North American refineries where there is a higher demand for gasoline. In contrast, refineries in Europe have a higher demand for diesel which is typically produced via hydrotreating/hydrocracking (Cooper, 2017; OPEC, 2017). It has been suggested that, as vehicle electrification expands, a reduction in demand for gasoline will likely take place, and the FCC may become less attractive as a co-processing unit.

Hydrotreating is primarily used in petroleum refineries to remove heteroatoms (nitrogen, sulfur) from petroleum product streams. The process involves higher temperatures and pressures as well as specialized catalysts. Hydrotreating reactors are mostly fixed catalyst beds, with cobalt and molybdenum sulfide on alumina catalysts often used. Typically, catalysts are regenerated at an off-site facility after months or years (12 to 60 months) of operation as replacement of catalyst is costly (Robinson, 2006). In the absence of in situ regeneration, as occurs with the FCC catalysts, the hydrotreater is less tolerant to contaminants. Thus, deactivation and the risks associated with the insertion of unknown feeds are much greater. Removal of oxygen and formation of CO_2 and CO can cause inhibition of catalysts and, since regeneration does not take place in situ, can cause significant operational and economic problems for the refinery.

Hydrocracking is more severe and requires specialised bifunctional catalysts (Jones and Pujadó, 2006; Uner, 2017). Hydrocracking involves the reduction of large molecular weight compounds into lower molecular weight products while adding hydrogen and carrying out similar reactions to those described previously for hydrotreating. However, this is typically carried out at much higher hydrogen

28

pressures. Although hydrocracking is costly, the resulting products require less downstream processing. Hydrocracking reactors are not suitable for feedstocks containing oxygen or other impurities unless the feeds have first been hydrotreated. As the high cost of catalyst and off-site generation makes this process very sensitive to any contamination, hydrocracking will likely be used as a secondary step in upgrading biobased feedstocks where size reduction is still required.

Distillation typically separates a complex mixture based on boiling points in order to produce different fractions that can be further upgraded into finished fuels. Atmospheric and vacuum distillation processing units are used at the beginning of the refining process before further upgrading is carried out. Due to the high risk of contamination, refineries will likely be resistant to the insertion of biogenic feeds at the distillation stage as this could result in the contaminants (e.g., oxygen) being distributed throughout the refinery. Any biogenic feedstocks that are inserted at this stage of the refinery will have to be virtually oxygen-free and free of possible contaminating and reactive species such as olefins, carbonyls, alcohols and aldehydes.

An additional problem with the insertion of biocrudes at the distillation stage is the unstable nature of biobased intermediates at increased temperatures. Heating will increase polymerisation as the compounds react with each other, leading to increased viscosity and increased residue formation. Many biocrudes also contain significant amounts of non-volatile compounds such as sugars and oligomeric phenolics that are unsuitable for distillation. Pure biocrudes (from fast pyrolysis) can form 35-50% residues during distillation, and this is a significant problem for co-distillation (Czernik and Bridgwater, 2004). Biocrude insertion at the atmospheric distillation unit is therefore unsuitable and, although vacuum distillation units operate at lower temperatures, the use of biocrudes will likely result in the production of significant residues.

Some authors have indicated that a partially upgraded pyrolysis oil with ~8% oxygen content could potentially be integrated into a distillation column based on previous work (Arbogast, Bellman, Paynter and Wykowski, 2017a). However, when Hoffman and colleagues investigated the potential for insertion of HTL biocrudes (with 5.3% oxygen) at the distillation phase, they concluded that further hydrotreatment is still required to produce a suitable co-processing feed (Hoffmann,

29

Jensen and Rosendahl, 2016). When further upgrading of the HTL biocrude was carried out, the oxygen content was reduced to 0.3%, which was considered suitable as a co-processing feed (Jensen, Hoffmann and Rosendahl, 2015a).

While insertion of biofeeds at the distillation phase of a refinery is likely to be challenging, prior fractionation of biocrudes may be a useful step prior to refinery insertion as it may facilitate more appropriate upgrading steps of heavy and light fractions. As biocrudes are comprised of hundreds of molecules over a wide range of sizes, separation of fractions will allow more suitable upgrading strategies for different components, e.g. cracking of larger molecules. A recent study investigated the initial vacuum distillation of HTL biocrudes as a way of removing the heavy fraction before co-processing at the hydrotreater (Xing, Alvarez-Majmutov, Gieleciak and Chen, 2019). However, distillation resulted in 26.8% below 343°C, 36.6% between 343°C and 520°C, and 36.5% of the biocrude separating out as a heavy fraction with a boiling point above 520°C. The biocrude distillate fraction obtained in the 343-520°C range was further co-processed at the hydrotreatment with vacuum gas oil (Xing et al., 2019).

Molecular distillation offers many advantages when compared to vacuum distillation, including the use of "low temperature, short heating time and high separation efficiency" (Wang, 2013). For example, the carboxylic acids and water components of the pyrolysis bio-oil fractionated preferentially into the light fraction. This improved the quality and stability of the heavy fraction for further upgrading, while the carboxylic acid light fraction could be esterified to produce a stable intermediate (Wang, 2013). Unlike crude oils, where contaminants such as N and S preferentially fractionate to the heavier fractions, biocrudes displays an even distribution of contaminants, such as oxygen, into all the fractions (Jensen, Hoffmann and Rosendahl, 2015b; Xing et al., 2019). Thus, it is likely that all of the biocrude fractions will need upgrading to remove heteroatoms such as N and O.

It should be noted that, as lipid feedstocks are comprised of triglycerides that are similar in size and fall within the diesel range, separation through distillation prior to upgrading is not needed.

3.4 POTENTIAL BENEFITS AND RISKS OF CO-PROCESSING

Co-processing can deliver low carbon intensity fuels at economically competitive prices by utilizing existing refining, transport and storage infrastructure. Expensive refinery processes such as hydrogen production, hydrotreatment and hydrocracking can occur without building separate infrastructure. As production of liquid intermediates based on biomass, such as pyrolysis and HTL, are generally limited in scale due to the low energy density of the feedstock, a co-processing strategy has a further advantage that intermediates can be produced in small facilities while upgrading can take place at a centralised location to achieve economies of scale.

Only limited modifications may be required at the refinery at a relatively low investment cost at low coprocessing blends. A coprocessing strategy increases the availability of fuels with renewable content. It also results in significant benefits to the petroleum refineries who are facing increasing pressure to decarbonise due to policies and environmental activism. It is also likely beneficial for the biofuels sector to cooperate with petroleum refineries, such as simplifying market penetration (Jensen et al., 2015b). For example, coprocessing can provide a market for biocrude producers without the expense of upgrading and the associated infrastructure costs. Refinery integration should also provide instant access to markets and downstream supply chains.

However, as discussed previously, biogenic feedstocks can contain high levels of oxygen and alkali metals that can inhibit/deactivate catalysts, corrode metallurgy, etc., all of which can impact operations and product specification. These impacts can be very costly to a refinery, and risk mitigation might be expensive. This is discussed in detail in the following section.

4. Potential impacts of co-processing on an oil refinery

As described previously, biogenic feedstocks are chemically distinct from the crude oils that are typically processed in petroleum refineries. Thus, when moving to a co-processing approach, it is likely that several challenges will be encountered that impact normal refinery operations and will impact components such as catalysts and metallurgy. Processing biobased feedstocks also generates CO_2, CO and H_2O that the refinery has to manage. Many companies, such as Haldor Topsoe, Albermarle, Shell, and Axens, have designed technologies or processing modifications to mitigate these risks and allow co-processing of biobased feedstocks at high blend ratios while delivering fuels that meet specifications. Only limited impacts have been observed when low blend (5%) insertions are used. This has allowed refineries to implement co-processing with minor investment into new and modified infrastructure. At higher blends, it is likely that the impacts will be more significant and that a much higher investment will be needed.

4.1 IMPACT OF BIOBASED FEEDSTOCK DEOXYGENATION ON A REFINERY

While crude oils typically have less than 2% oxygen, biogenic feedstocks can contain up to 45% oxygen. The oxygen is present in the form of various chemical functional groups such as carboxylic acids, alcohols, aldehydes, esters, sugars, furans, ethers and hydroxyl groups, etc., depending on the source of the biobased feedstock. As mentioned previously, oxygen is highly undesirable and has to be completely removed via processing steps such as hydrotreatment.

Oxygen-containing functional groups in biobased feedstocks are hydrophilic, and the presence of water can cause significant problems, including corrosion of metallurgy in refinery processing units and piping. Oxygen-containing groups are also very reactive and can cause polymerisation between molecules, forming gums, acids and other impurities during storage (Pearlson, 2011; Bridgwater, 2012). Biogenic feedstocks such as biocrudes may also contain significant amounts of water. Although co-processing studies have been successful without removing the water from the biocrudes (Pinho et al., 2015), this is unlikely to be done in a commercial refinery.

Oxygen in biofuels also reduces the energy density of fuels and, as indicated in Figure 3, the energy density of biofuels and biocrudes decreases linearly with increasing oxygen content (expressed as the molar ratio of oxygen to carbon (O/C) in the fuel molecule). The energy density, in turn, determines the size of a vehicle's fuel tank, which consequently determines the travel range for all modes of transportation.
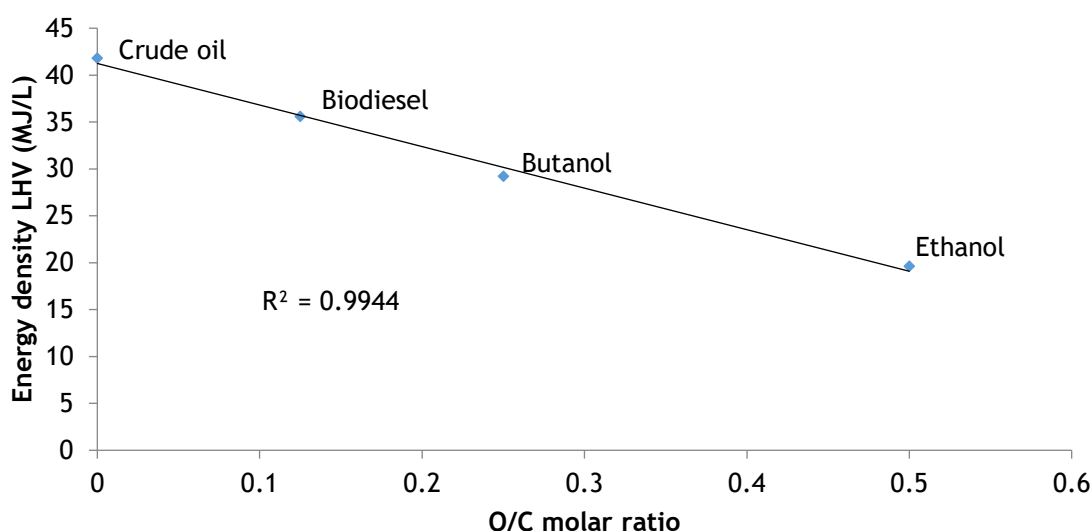
Figure 3 The influence of oxygen content on the energy density of liquid fuels (Data from ORNL, 2013)

The deoxygenation of biomass intermediates is achieved through three main chemical reduction processes: (1) hydrodeoxygenation (HDO) (producing H_2O), (2) decarboxylation (producing CO_2) and (3) decarbonylation (producing CO & H_2O) (Huber, O'Connor and Corma, 2007). Decarboxylation and decarbonylation are grouped together and collectively referred to as DCO. Although these reactions are illustrated below using the deoxygenation of fatty acids as an example (Figure 4), they are generally applicable to the deoxygenation of any oxygen-containing feedstock. All three reactions take place to some extent during oxygen removal, whether hydrogen is used or not. It should be noted that the ratio of these reactions

has implications for a refinery. Thus, controlling these reactions is discussed in more detail in the next section.

Deoxygenation reaction
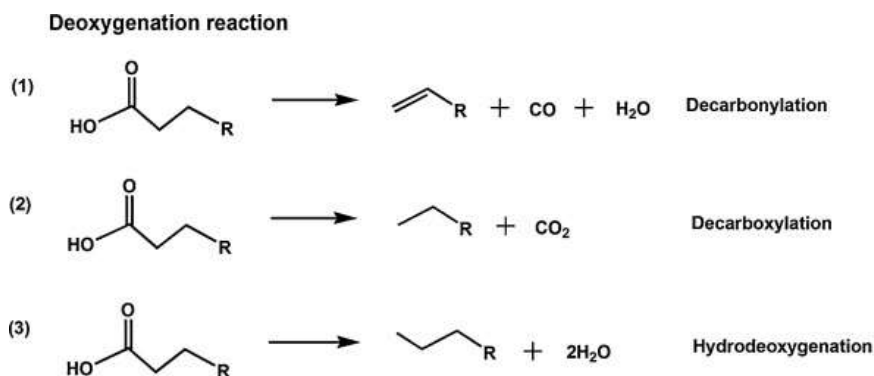
Figure 4 Deoxygenation reactions

During hydrodeoxygenation, the hydrogen present in the biomass intermediates (or supplied externally) is oxidized, with the oxygen subsequently removed as water (H_2O). During decarboxylation, the carboxyl group carbon is oxidized and the oxygen is removed as carbon dioxide. In decarbonylation, the oxygen is removed as carbon monoxide, and a water molecule is formed. When DCO takes place, the carbon in the feedstock is lost by oxidation, and, as a result, the yield of hydrocarbons is reduced (Dimitriadis et al., 2021). For example, in the case of lipids, the decarboxylation reactions of C18 fatty acids will yield C17 paraffins, etc. When hydrogen inputs are used to remove oxygen through HDO, the yields of hydrocarbons are higher as the carbon is retained. However, hydrogen consumption and associated costs increase.

Although CO, CO2, and H2O production are relatively uncommon during crude oil upgrading, its impacts can be managed by modifying some of the processes. For example, any CO and CO_2 gases formed need to be purged from reactors as it can impact operations such as altering the hydrogen partial pressure in the reactor, inhibiting catalyst activity (mainly CO), and forming carbonic acid in the effluent (from CO_2 combining with H_2O) which can result in corrosion (Egeberg et al., 2010). Water may also damage catalysts. It has also been observed that deoxygenation reduces catalyst performance and sulfur removal. Workers have demonstrated that

CO, not CO_2, is the main cause of catalyst inactivation, although this is a reversible reaction (Bezergianni, Dagonikou and Sklari, 2016). While CO_2 is easily removed from a reactor via an amine scrubber, CO removal is more difficult. However, one strategy to deal with this problem is deliberate methanation of the CO into CH_4 as a removal/treatment method (Egeberg et al., 2010).

In addition to the reactions summarised in Figure 4, further side reactions typically take place during upgrading. These include the water-gas shift and the methanation reactions summarised below (Donnis, Egeberg, Blom and Knudsen, 2009; Egeberg et al., 2010).

$CO + H_2O = CO_2 + H_2$ (water gas shift reaction)

$CO + 3H_2 = CH_4 + H_2O$ (methanation reaction)
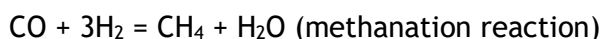
During hydrogenation, the water-gas shift and reverse reactions establish an equilibrium between the formation of CO and CO_2 (Bezergianni, Dimitriadis, Kikhtyanin and Kubička, 2018). The formation of CO_2 and CO is linked, and it is not entirely clear if the formation of CO is a separate reaction or the result of just the water gas shift reaction when they are at equilibrium (Donnis et al., 2009). The methanation reaction is generally undesirable as it significantly increases hydrogen consumption. Hydrogen consumption is exothermic and there is a linear relationship between hydrogen consumption and temperature increase. Methanation reactions can cause local overheating in the reactor, which could damage the catalyst (Jęczmionek and Porzycka-Semczuk, 2014).

> **The impact of methanation reactions on hydrogen consumption**
>
> During the hydrodeoxygenation of rapeseed oil (canola), on a theoretical basis, a maximum of 16 moles of hydrogen per mole of rapeseed oil is required for hydrodeoxygenation (HDO). If the oxygen is removed through a decarboxylation/decarbonylation (DCO) mechanism, only 7 moles of hydrogen per mole of rapeseed oil is required. This seems to indicate that decarboxylation is a "better" route due to its lower hydrogen consumption. However, decarboxylation in combination with the water gas shift reaction and the methanation reaction results in formation of CH_4 from CO. If full methanation takes place, the theoretical hydrogen consumption for the DCO pathway will therefore be 19 moles of hydrogen per mole of triglyceride. On a theoretical basis, it is therefore possible that the DCO route could require more hydrogen than the HDO route.
>
> In practice the chemistry is complex as operating conditions such as temperature and pressure will impact the favourability of methanation taking place. A higher temperature and pressure will push the conversion of CO to methane (Vonortas et al. 2016). As hydrodesulfurization is simultaneously taking place within a hydrotreater, optimal reaction temperatures and pressures that allow complete desulfurization while suppressing methane formation would therefore be the "sweet spot" of operating conditions. An example of the impact of methanation reactions on hydrogen consumption is provided by Donnis et al., 2009.

While all three reactions summarised in Figure 4 take place during deoxygenation, the reaction conditions can be adjusted to favour either hydrodeoxygenation (HDO) or decarboxylation/decarbonylation (DCO). This has considerable significance for a refinery from an economic and operational point of view as it influences hydrogen consumption, product yields, catalyst inhibition, off-gas composition and the heat balance (Egeberg et al., 2010). However, the optimum route is not self-evident and will depend on "operating conditions, the flowsheet and the catalyst" in the hydrotreater, as well as "local prices of hydrogen and diesel" (Egeberg et al., 2010).

It should also be noted that achieving hydrodeoxygenation through the addition of hydrogen may not be desired when a refinery does not have excess hydrogen available. In addition, the cost of hydrogen and the impact of HDO versus DCO on the carbon intensity of the final fuels through life cycle assessment and the

source of imported hydrogen must also be considered. Although the addition of hydrogen in the hydrotreater automatically appears to favour hydrodeoxygenation, this is not the case under all circumstances. For example, the choice of catalyst could impact the selectivity of HDO versus DCO, as well as the temperature, pressure and space velocity within the hydrotreater (Al-Sabawi and Chen, 2012; Donnis et al., 2009; De Paz Carmona, de la Torre Alfaro, Brito Alayón, Romero Vázquez and Macías Hernández, 2019).

In earlier work, Donnis et al. (2009) reported a 66/34 ratio of DCO to HDO when co-hydrotreating 25% rapeseed oil (at 350°C, 4.5 MPa, Topsoe NiMo/γ-alumina catalyst). This indicated that, even in the presence of hydrogen, a significant proportion of DCO reactions take place (Donnis et al., 2009). More recently, De Paz Carmona et al. (2019) showed a similar DCO/HDO ratio when co-processing 20% used cooking oil, animal fat or refined palm oil with straight-run gas oil at 350°C, 5.5 MPa, NiMo/Al$_2$O$_3$ catalyst (De Paz Carmona et al., 2019). Zeuthen et al. (2016) demonstrated that triglyceride deoxygenation could be manipulated to proceed mainly through the HDO; HDO and DCO, or the DCO pathways by varying the type of catalysts while maintaining identical reaction conditions (Zeuthen and Rasmussen, 2016).

Other workers showed that NiMo catalysts favour the DCO pathway (although by a small margin), while a bimetallic NiCu catalyst favoured the HDO pathway (Vonortas and Papayannakos, 2014). The impact of changes in pressure and temperature is more complex as multiple reactions take place that respond differently to changing conditions. When the temperature decreases, exothermic reactions, e.g. HDO, are favoured while endothermic reactions, e.g. DCO, are inhibited. Alternatively, increasing the pressure inhibits the DCO pathway while favouring the HDO pathway (Jęczmionek and Porzycka-Semczuk, 2014). Dimitriadis and co-workers indicated that CO$_2$ formation was favored by lower H$_2$/bio-oil ratios, while CO formation was favoured by lower reaction pressures. Similarly, methane formation was enhanced at low temperatures during hydrotreatment (Dimitriadis et al., 2021).

It has also been observed that HDO reactions may take place in the absence of additional hydrogen in the fluid catalytic cracker (as observed by the formation of water). Co-processing studies carried out by Petrobras in Brazil in a fluid catalytic

cracker (where no additional hydrogen was added) showed hydrogen transfer between molecules from the fossil feed to the biofeed. This led to the conclusion that all three deoxygenation reactions were taking place, even without the addition of hydrogen (Pinho et al., 2015, 2017; Pujro, Panero, Bertero, Sedran and Falco, 2019).

Biogenic feedstocks can contain a range of oxygen levels. For example, 11% for oleochemical feedstocks, 7-25% for catalytic pyrolysis and HTL biocrudes, and up to 45% for fast pyrolysis biocrude. As discussed previously, oxygenated species and the need for deoxygenation can significantly impact refineries. Therefore, there is a need to determine the "manageable" oxygen levels in the possible biogenic feedstocks or intermediates used for co-processing as refineries may differ in their willingness and ability to manage the impacts and risks.

Those refineries that currently co-process feedstocks such as lipids (11% oxygen) on a routine basis typically use low blending levels (5%) and have not encountered any significant issues. However, at higher blends, such as 30%, it is likely that more extensive refinery modifications will be required. This will be needed to accommodate the impact of CO, CO_2 and H_2O production and the increased temperatures in the hydrotreater as a result of hydroprocessing (Egeberg et al., 2010).

Oxygen in lipids is uniformly present in the form of carboxylic acid groups, simplifying deoxygenation processes. However, in biocrude feedstocks, multiple types of oxygen species are present, e.g. alcohol groups (OH), carboxylic acids (-COOH), aldehydes, ethers, phenols, etc. (Yildiz, Ronsse, Duren and Prins, 2016). Oxygen species are reactive, and combinations such as carboxylic acids and alcohols can cause polymerization reactions and increase coking. This is exacerbated at higher temperatures. These types of chemical species can be deoxygenated through an initial mild hydrotreatment step to stabilise biocrudes before a second hydroprocessing step is carried out at a higher temperature. Different oxygen species need more severe conditions (temperature and pressure) for deoxygenation. Figure 5 summarises the reactivity scale of oxygenated compounds under hydrotreatment conditions and the reaction temperatures required to remove different oxygen species.
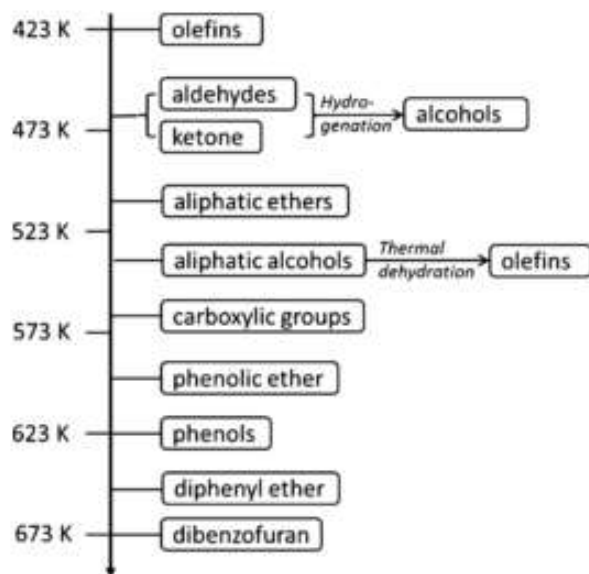
Figure 5: Reactivity scale of oxygenated compounds under hydrotreatment conditions.

Source: copied from Wang et al., 2013, based on work from Delmon and co-workers (Centeno, Laurent and Delmon, 1995; Ferrari, Bosmans, Maggi, Delmon and Grange, 2001) as adapted and plotted by Elliott, 2007.

It has been demonstrated that raw fast pyrolysis biocrudes with a 45% oxygen content can be successfully co-processed in an FCC, provided the reactor is modified (Pinho et al., 2015). The biocrude was inserted into the FCC through a separate injection nozzle. This allowed the biocrude to be kept below a temperature of 50°C to avoid temperature-related polymerization during feeding. This is likely the most feasible method by which raw fast pyrolysis biocrudes with high oxygen content can be co-processed in an FCC.

However, the decision to co-process biocrudes with high oxygen levels will also depend on other factors, such as the resulting low yields. For example, earlier work showed that only 2-3% biogenic carbon was present in the liquid products when using a 10% initial blend for FCC co-processing. Although, higher levels of biogenic carbon in the final products could be obtained when co-processing biocrudes containing a lower oxygen content (Wang, Venderbosch and Fang, 2018). These workers found that co-processing a hydrotreated pyrolysis oil resulted in a 5.6% (39% oxygen in starting biocrude) and 6.4% (27% oxygen in biocrude) biogenic content compared with 2% (50% oxygen in biocrude) for untreated pyrolysis oil (Wang et al., 2018).

39

In order to avoid most potential risks, refineries could require that any potential biogenic feedstock be supplied with zero oxygen (T Marker, 2015). While this risk-averse approach is understandable, it likely puts biocrude producers into an untenable business model where they have to carry out overly expensive upgrading (Arbogast *et al.*, 2017a). For example, when a biocrude producer was required to supply completely deoxygenated biocrude to a refiner, it was unviable for the company (Arbogast *et al.*, 2017a). This work highlighted the challenges in removing residual oxygen from biocrudes, resulting in yield losses and exponential increases in hydrogen consumption (Arbogast *et al.*, 2017a). For example, yield losses of 12-20% can be incurred when trying to drive out the last oxygen from pyrolysis biocrudes (Arbogast *et al.*, 2017a).

Therefore, a balance is needed between risk management at the refinery and the overall efficiency and economics of the entire supply chain. This will require more data on the impact of biocrudes with different oxygen levels on the refinery and an estimation of the cost impacts of providing low oxygen biocrudes. A rough analysis based on certain assumptions has led some researchers to conclude that value chain savings of 20%–25% are potentially available if refineries accept a 5% oxygen concentration in the biocrude rather than zero oxygen (Arbogast *et al.*, 2017a).

4.2 IMPACT OF DEOXYGENATION ON DESULFURIZATION OF FUELS

With increasingly stricter limits on sulfur in fuels (most recently in the international shipping industry), increasing the efficacy of hydrodesulfurization (HDS) will be needed to ensure high product quality. Hydrodesulfurization takes place in the hydrotreater and removes sulfur in the presence of hydrogen. As this is the same processing unit where biobased feedstocks are deoxygenated, many researchers have investigated whether the addition of biogenic feedstock into the diesel hydrotreater will have an impact on hydrodesulfurization. Under certain circumstances, hydrodeoxygenation of biofeeds affected hydrodesulfurization, and hydrodesulfurization also impacted oxygen removal during hydrodeoxygenation (HDO).

Several studies have concluded that hydrodeoxygenation interferes with hydrodesulfurization (De Miguel Mercader et al., 2011; De Paz Carmona et al., 2019; Pinheiro, Dupassieux, Hudebine and Geantet, 2011; Templis, Vonortas, Sebos and Papayannakos, 2012). However, other studies have contradicted these observations (Rana et al., 2013), while later work showed that the use of CoMo catalysts, employed in the studies of Pinheiro and Templis, impacted the influence of hydrodeoxygenation (HDO) on hydrodesulfurization (HDS). In related studies, Vonortas saw no impact of HDO on HDS when using NiMo catalysts when co-hydrotreating up to 30% lipids (Vonortas, Kubicka and Papayannakos, 2014), unlike the effect when using a CoMo catalyst (Vonortas and Papayannakos, 2014). Other researchers have suggested that the production of CO during oxygen removal resulted in the inhibition of the hydrotreating catalyst, reducing hydrodesulfurization (HDS) (Egeberg et al., 2010; Pelardy et al., 2016). This inhibition did not occur when using a NiMo catalyst, but was severe when using a CoMo catalyst (Egeberg et al., 2010). Thus, it is likely that NiMo catalysts will be preferred to CoMo catalysts in co-processing.

Xing et al. recently found that sulfur removal was reduced in the presence of HTL biocrude during co-hydrotreating with vacuum gas oil (Xing et al., 2019). When the impact of blend levels and temperature was assessed, the authors determined that at blend levels of 5% and 10% with temperatures above 370°C, normal levels of sulfur removal were obtained. However, when using 15% blends, further temperature increases did not restore sulfur removal to normal levels (Xing et al., 2019). Standard conditions for hydrodesulfurization (HDS) usually use a temperature between 310-350°C and a pressure of 33bar. This indicated that increased severity might be required when HDO and HDS are carried out simultaneously (Vonortas and Papayannakos, 2014). The formation of H_2S also inhibited HDO reactions, and this occurred in the presence of both NiMo and CoMo catalysts (Al-Sabawi and Chen, 2012).

4.3 PROBLEMS WITH THE MISCIBILITY OF CRUDE OIL FEEDS AND BIOGENIC FEEDSTOCKS

In general, co-processing involves the insertion of a mixture of fossil and biogenic feeds into a refinery processing unit to produce fuels with lower carbon-intensive content. The miscibility of any blend is an important factor for co-processing and is a function of the characteristics of both the fossil and biogenic feeds. Various factors can affect the miscibility between two feeds, such as the density, viscosity, surface tension, heteroatom distribution and refractive index of the two feeds (Manara, Bezergianni and Pfisterer, 2018). In addition, the compatibility between a fossil and biogenic feed might also be influenced by the boiling point range of both feeds (Jechura, 2016).

Lipids are readily blendable with fossil feeds as they are surfactant molecules (polar head and hydrophobic tail) which allow them to form stable emulsions. However, for feedstocks such as biocrudes, the occurrence of multiple types of oxygen-containing molecules results in a variety of compounds. These compounds have various polarities and chemistries that do not readily form emulsions and are more likely to phase-separate when blended with fossil feeds. This makes co-processing very difficult as a homogenous blend/emulsion is required for feeding into processing units. However, miscibility can be achieved by the addition of surfactants or by mechanical mixing.

Two immiscible liquids can be mixed by the formation of droplets, with one liquid evenly distributed within the other liquid, typically requiring the addition of surfactants (Leng, Han, Yuan, Li and Zhou, 2018; Marker, 2005). The size of the droplets determines whether it is an emulsion (1-10 μm) or a microemulsion (1-100 nm). Emulsions require lower levels of surfactant but need extra energy input for mixing via mechanical agitation (stirring, shaking, blending), ultrasonic waves, homogenisation, vortex blending, etc. (Leng et al., 2018). A stable emulsion is typically formed when an even distribution of small droplets (as examined under a microscope) are observed for at least 10 minutes at room temperature and at 75°C (Lindfors, Kuoppala, Oasmaa, Solantausta and Arpiainen, 2014). Phase separation, a clear characteristic of immiscibility, can also be determined by visual observation. However, in the case of dark biocrudes, this may not be effective (Manara et al., 2018).

Miscibility, the ability to form stable blends, also depends on the properties of the fossil feed and their characteristics (Bezergianni et al., 2018; Manara et al., 2018). Common feedstocks that can be co-processed in the hydrotreater include straight run gas oil (SRGO), light atmospheric gas oil (LAGO), heavy atmospheric gas oil (HAGO) and heavy vacuum gas oil (HVGO) (Bezergianni et al., 2018). Feedstocks suitable for FCC co-processing include distillate fractions such as vacuum and heavy vacuum gas oils, FCC cycle oils and atmospheric distillation residues (short or long residues) (Bezergianni et al., 2018). While the SRGO is suitable for co-hydroprocessing, Light Cycle Oil (LCO) on its own is not considered suitable as a co-processing feedstock with lipid feeds. However, it is claimed that blends of fossil feeds such as SRGO and LCO can be co-processed with lipids (Bezergianni et al., 2018). When Manara et al. (2018) investigated mixing binary blends with 30% hydrotreated biocrudes (Manara et al., 2018)(See Table 5), they found that the SRGO and gasoil were not suitable fossil feeds for co-hydroprocessing with bio-oils.

Table 5. Assessment of compatibility of hydrotreated bio-oil with different fossil feeds (Manara et al. 2018) (LVGO-light vacuum gas oil; HCO-heavy cycle oil)

Fossil feed	Process unit	Miscibility
FCC LCO	Hydroprocessing	Good miscibility
LVGO	Hydroprocessing	Quite good miscibility
FCC HCO	Hydroprocessing	Quite good miscibility. Some agglomerates are formed
SRGO	Hydroprocessing	Quite bad miscibility. Different phases are formed
Gasoil	Hydroprocessing	Rather bad miscibility. Different phases and agglomerates are formed

They showed that miscibility depends on the degree of oxygen removal and that improved miscibility could be achieved through the addition of solvents, including methanol, isopropanol, etc. However, this is not practical at a large, commercial scale due to the costs involved (Linck, 2016). Alternatively, miscibility could be achieved if the temperature was increased, in this case, when a biocrude blend was heated to 75°C (Ramirez, Brown and Rainey, 2017).

As the immiscibility of biofeeds is primarily due to the polarity of the compounds and the presence of water, it has been suggested that reducing the

oxygen content of fast pyrolysis biocrudes might improve miscibility (Manara et al., 2018). However, it is still not clear at what oxygen content miscibility will be enhanced. When researchers reduced the oxygen levels in a fast pyrolysis biocrude through hydrotreatment, they found that miscibility was still poor even at a 27% oxygen level (Wang et al., 2018). Mercader reported that blends with biocrude at oxygen concentration between 16-28% were miscible at 75°C, but 2% isopropanol was added to the biocrude to ensure homogeneity, which would have contributed to the miscibility (de Miguel Mercader et al., 2010). Other workers found that hydrotreated pyrolysis biocrude was able to form a "homogenous mixture" with Vacuum Gas Oil (VGO) (that could be handled by an HPLC pump) when the oxygen content was below 20% (Fogassy et al., 2010). Others have claimed miscibility with biocrudes at 22% oxygen (Agblevor et al., 2012). Other work has indicated that the solubility threshold of pyrolysis biocrude in petroleum "appears to be somewhere above 7%". However, it remains unclear at which oxygen concentration biocrudes become miscible (Arbogast, Bellman, Paynter and Wykowski, 2017b).

Due to the immiscibility of pyrolysis biocrudes (even when partially hydrotreated), FCC co-processing can be facilitated by using separate injection ports at axial positions at the bottom of the riser of the FCC reactor (Pinho et al., 2015, 2017; Wang et al., 2018). Although the addition of surfactants or solvents to achieve miscibility can be used, the use of surfactants has a significant, negative impact on the carbon intensity of the final fuels as the surfactants are generally fossil-derived, thus contributing to the emission profile of fuel production (Van Dyk et al. 2019). The use of solvents is likely to have a similar effect.

4.4 POTENTIAL CORROSION IMPACTS OF CO-PROCESSING HIGH TAN FEEDSTOCKS

Refineries routinely measure the total acid number (TAN) of crude oils before processing. The TAN measures acidity determined by the amount of potassium hydroxide required to neutralize the acids in one gram of oil (as described in ASTM D664). Biofeeds such as lipids and biocrudes often have very high TAN levels (from 2-200 mg KOH/g), which indicates that they are quite corrosive. Crude oils, by comparison, have a very low TAN level, with a high TAN crude having an acid number >1.0 mg KOH/g (Bezergianni et al., 2018). Refineries deal with high TAN crudes by

44

using strategies such as blending with low TAN crudes, upgrading construction materials and using corrosion inhibitors. Thus, it is likely that similar methods will be used for high TAN biobased feeds (Bezergianni et al., 2018). However, the TAN level is a major consideration from an engineering perspective as more expensive metallurgy will likely be required as TAN levels of 0.5 and 0.6 mg KOH/g are the industrially accepted limit before considering upgrades to metallurgy (Marker, 2005). However, other work has suggested that a feedstock with a TAN number of 0.4-0.5 will require significant design changes (Terry Marker, 2015). While some studies report the corrosion impacts of high TAN biobased feedstocks, these results may not always be comparable. For example, some are carried out at specific reactor conditions (e.g. high temperatures and in blends with fossil feeds), while other studies merely look at TAN in the context of the storage stability of the pure biobased feedstock at ambient temperatures.

Other workers have highlighted some of the shortcomings of using TAN to assess biogenic feedstocks and have shown that biofeedstock with one TAN level may not be the same as crude oil with the same TAN level and that a modified TAN method may be needed (Arbogast et al., 2017b). It should also be noted that the ASTM standard is only accurate within a limited range of 0.1 mg/g KOH to 150 mg/g KOH (ASTM 2018). While TAN measures the total acid content, the modified method differentiates between carboxylic acids (CAN) and other weak acids such as phenolics (Christensen et al., 2016; Ferrell, Olarte and Padmaperuma, 2015). The inadequacy of the ASTM D664 "TAN method" has also been highlighted by the fact that many biocrudes are immiscible in the non-polar solvent required by the standard method (Keiser, Brady, Thomson, Connatser and Lewis, 2014). These researchers have proposed a different modified TAN method that uses aqueous extraction. It should be noted that high free fatty acid lipid feedstocks, such as used cooking oil, tall oil, animal fats and palm oil, will have higher TAN levels than lipids in the form of triglycerides (Juan A Melero et al., 2010). For biocrudes, high TAN levels are likely to correlate with oxygen levels, with high oxygen-containing biocrudes such as fast pyrolysis biocrudes showing the greatest TAN levels.

Earlier work has shown that the metallurgy of a hydroprocessing unit will have to be upgraded if any significant quantity of biofeeds is going to be co-processed (Marker, 2005). The cost of upgrading a hydroprocessing unit's metallurgy to 317L

45

stainless steel to process brown grease (5.8%) was estimated in 2005 to be about $USD7-8 million. This excluded the cost of storage tanks and pretreatment equipment (Marker, 2005). In related work that looked at the storage stability of different oleochemical feedstock and petroleum feedstocks, the different mixtures could be considered stable at 77ºC for at least 180 days, according to the UOP 174-84 method (Juan A Melero et al., 2010).

When PNNL co-processed various biobased feeds in a Davis Circulating Riser and investigated the impact of the biofeeds on the possible corrosion of different grades of metallurgy (Zacher, 2015) (Table 6), the more stabilized feeds (partially upgraded) displayed lower corrosion rates.

Table 6. Calculated corrosion rates in mm/yr based on ex situ tests (from Zacher, 2015)

Oil/stab	Exposure	C steel	2 ¼Cr-1Mo	409 SS	304L SS	316L SS
Pine bio-oil	Vapor	0.20	0.30	<0.01	<0.01	<0.01
	Liquid	2.29	2.71	0.44	<0.01	<0.01
Straw bio-oil	Vapor	0.40	0.36	<0.01	<0.01	<0.01
	Liquid	0.94	2.93	0.33	<0.01	<0.01
Pre-stabilized	Vapor	1.68	1.43	0.04	<0.01	<0.01
	Liquid	1.18	2.07	0.10	<0.01	<0.01
Mild, organic	Vapor	0.59	0.50	<0.01	<0.01	<0.01
	Liquid	0.12	0.70	0.15	<0.01	<0.01
Mild, aqueous	Vapor	1.57	1.89	0.06	<0.01	<0.01
	Liquid	0.35	1.72	0.48	<0.01	<0.01

When other workers (Arbogast et al., 2017b) reviewed the available information on corrosion problems of partially upgraded pyrolysis biocrudes, they indicated that more information was needed. The limited work that had been done showed that partially upgraded pyrolysis biocrude at 3.3% oxygen had negligible corrosion effects at 50ºC. In comparison, a partially upgraded pyrolysis biocrude at 0.5% oxygen had a negligible effect on carbon steel at temperatures up to 350ºC. It appeared that acidity might be concentrated in the lower boiling point fractions of the biocrude, which could have an impact if the biocrude fractions were upgraded separately. From a refinery perspective, corrosion impacts at high temperatures will have to be assessed to evaluate risk under realistic circumstances.

When the possible corrosive impact that biocrudes might have on various alloys within a FCC pilot-scale reactor were assessed (Brady et al., 2017), greater corrosion was observed with higher oxygen-containing biocrudes (~28% oxygen) while

lower oxygen biocrudes (~11% and ~2% oxygen) displayed lesser, but comparable corrosion effects (i.e. 2% and 11% similar) (Brady et al., 2017). When stainless steel alloys (409, 410, 304L, 316L, 317L and 201) were assessed, surprisingly, the cheaper 201 alloy exhibited the greatest resistance to corrosion due to its low Ni and high Mn content compared to the more expensive stainless steels. The authors claimed that the combination of sulfur in the VGO and the high oxygen content in the biocrude had a synergistic effect, resulting in increased corrosion under the conditions tested (Brady et al., 2017).

A modified TAN method has been used to measure total acid, and specifically the formic and acetic acid content of biocrudes, while also comparing the acids and corrosivity of biocrudes based on different feedstocks, hardwood, softwood and cellulose powder biocrude (Keiser et al., 2016). Hardwood biocrudes were found to have the highest modified TAN levels, with the hydrotreated hardwood biocrude having an increased TAN compared to the untreated biocrude. The lowest modified TAN levels were found in the softwood biocrudes followed by the cellulose powder biocrude (Keiser et al., 2016). However, it is apparent that more data is required to accurately inform refineries of the corrosion risk associated with different biobased feedstocks. For example, when Valero performed a risk analysis for a hydropyrolysis project led by GTI, they found that the introduction of any oxygen-containing feeds in their refinery equipment was problematic (Terry Marker, 2015). The high acid and low sulfur levels encountered in the biogenic feedstocks further complicate possible corrosion issues (Terry Marker, 2015).

4.5 IMPACT OF COPROCESSING ON CATALYSTS

Catalyst inhibition and deactivation is a major concern for refiners as it can impact product quality and specifications, reduce the lifespan of the catalyst before regeneration and result in unforeseen interruptions in production. These issues can all have serious economic impacts on the refinery. Of the different potential biogenic insertion points, the FCC presents the lowest risk with respect to potential catalyst impact as catalyst regeneration takes place on-site on an ongoing basis. However, for other catalysts present in locations such as the hydrotreater, the six possible mechanisms of catalyst deactivation such as poisoning, fouling, thermal degradation,

47

vapor compound formation and/or leaching, vapor-solid and/or solid-solid reactions and attrition/crushing can all have an impact (Argyle and Bartholomew, 2015). However, the three main challenges of poisoning, fouling and degradation are discussed here.

Poisoning refers to chemical adsorption and blocking of catalytic sites, resulting in inhibition which may be reversible or irreversible. Catalyst poisons can include electropositive contaminants, such as alkali and alkaline earth metals (e.g. calcium, potassium, magnesium), which target acid sites or electronegative contaminants, which target hydrogenation sites (Lange, 2015). Biofeeds generally contain alkali metals that must be removed through pretreatment processes prior to refining. The typical concentration of contaminants found in different feedstocks is summarised in Table 7.

Table 7. Contaminants present in different lignocellulosic biomass feedstocks (Lange, 2015).

Contaminant (ppm)	Hardwood	Softwood	Grasses
Ca	700-1000	200	1000-3000
K	300-500	100	2000-10000
Mg	100-300	50	50-100
Na	20	10	20-100

The inhibition caused by carbon monoxide, produced during deoxygenation of biogenic feeds, is reversible and its removal from the reactor through gas purging restores catalytic activity. Irreversible inhibition has significant consequences for the refinery, specifically in the hydrotreater or hydrocracker, as refinery operations will be disrupted, and the catalyst will have to be removed for regeneration.

Fouling involves physical deposition onto the catalyst surface or the catalyst pores. This is typically caused by insoluble components in the feed or formed by degradation of the feed or intermediates (Lange, 2015). The formation of coke during processing can cause fouling which, in the case of the FCC, is burned off in the regenerator. However, it presents more serious consequences for other processing units. Biofeeds with reactive chemistry can undergo polymerisation reactions at elevated temperatures, resulting in fouling. For fast pyrolysis biocrudes,

48

a two-step hydrotreatment with the first stage carried out at lower temperatures has been shown to reduce the potential for fouling. This way, it stabilises the more reactive compounds before hydrotreatment at higher temperatures (Elliott, 2013; Lange, 2015).

Refineries have used the Micro Carbon Residue (MCR) test to determine the coking tendency of process feeds, and this test can also be applied to biofeeds (Ibarra, Rodr, Sedran, Arandes and Bilbao, 2016). Biofeeds containing higher molecular weight compounds have been shown to have enhanced fouling tendencies, with the poor miscibility of co-processing feeds exacerbating this problem. As discussed earlier, poor miscibility can result in aggregates forming deposits on the catalyst. Although one solution could be to use a co-solvent for improved miscibility (Lange, 2015), as discussed earlier, associated negative effects, such as the increased carbon intensity of the fuel, may outweigh positive impacts.

Other work has shown that co-processing of biocrude with VGO in an FCC resulted in the formation of less insoluble coke than cracking VGO alone (Ibarra et al., 2016). These authors concluded that co-processing did not impact catalyst deactivation and that the steam (generated from the water in the raw bio-oil) attenuated catalyst deactivation during co-processing (Ibarra et al., 2016). However, high concentrations of phospholipids in lipid feedstocks, specifically trap grease and waste oils, has been shown to result in catalyst deactivation due to coking. This is exacerbated in an acidic environment as a result of the high free fatty acid content of most waste oils (Kubička and Horáček, 2011). This results in alkali phosphates deposits on the catalyst. Catalyst degradation or destruction refers to the loss of catalyst surface or support due to heat generation in the reactor outside design parameters or leaching of the catalyst support due to corrosive mediums. As discussed earlier, unexpected thermal increases can take place during the co-processing of biofeeds. Uncontrolled exothermic reactions during hydrogenation can result in catalyst damage. The formation of water during hydrodeoxygenation and subsequent reaction with carbon dioxide to form carbonic acid can also lead to dealumination (loss of catalyst support). Related work has shown that oxidic catalyst supports such as SiO_2 and Al_2O_3, commonly used in refining, are not suitable in biomass conversion processes. Thus, alternative supports such as ZrO_2, TiO_2 or carbon should be used (Lange, 2015).

4.6 INSERTION OF DIFFERENT RATIOS OF BIOBASED FEEDSTOCKS AND THEIR IMPACT ON THE REFINERY

As mentioned earlier, the blends of biogenic feedstocks that can be co-processed will vary based on multiple factors such as the type of feedstock, the oxygen content of the feedstock, the refinery infrastructure and catalysts available, as well as the limitations placed by ASTM certification for the production of sustainable aviation fuels. Apart from the technical challenges experienced during co-processing, the other main consideration will be the refinery's willingness to assume and mitigate the risks associated with co-processing. The value of the co-processed fuels will also play a role and will be influenced by policy.

Co-processing involves the combined reactor processing of a fossil feed with a biobased feed in a specific ratio, either through mixing the two components before insertion or separate insertion into the same reactor. The percentage of biogenic feedstock used for co-processing will depend on several factors. It is unlikely that a single "ideal" blend will be derived from all feedstocks for insertion at all points in a refinery. Due to the limited supply of both lipids and biocrudes, the cost and availability of these feedstocks will determine the blend ratio that is used. As petroleum refineries operate at a very large scale, even low blend rates of 5% amount to significant volumes based on FCC and hydrotreater capacities.

It goes without saying that an optimal blend rate for each individual case should result in optimal product yield and a reduction in the carbon intensity of the final fuels. In addition, each refinery will want to minimise the risk to current processing units and operations. Depending on each refinery's co-processing objectives, a refinery will want to minimise any infrastructure costs. Similarly, the optimal blend rate will be guided by the specific refinery and its configuration such as the availability of additional hydrogen, etc. The characteristics of the biobased feedstock will also influence the optimal blending rate with biocrudes with low oxygen levels more effectively co-processed at higher blend rates than biocrudes with high oxygen levels. This will be a result of various factors such as hydrogen demand, formation of water, etc. As biogenic feedstocks can have a wide range of oxygen levels, just using a blend ratio will likely not be sufficient. It is likely that the

total oxygen in the co-processing blend will be a more appropriate metric to consider.[6]

While higher co-processing blends might be desirable, a greater investment in infrastructure will be required to manage issues such as heat generation and corrosion. Additional hydrogen demand will also require increased hydrogen capacity, while hydrotreating of higher blends may require modified cooling infrastructure as a result of the exothermic reactions taking place. Hydrotreating of lipids will likely increase the paraffinic content of the diesel product but reduce the cloud point of the fuel. This may require additional processing such as isomerisation and additional processing units if this process is not already part of the refinery configuration.

It should also be noted that regulatory requirements may also limit blending rates for co-processing. For example, current jet fuel specifications (ASTM D1655) provide for jet fuel production through co-processing, but the biobased component is limited to 5% lipid or Fischer-Tropsch liquid feeds for the production of jet fuel.

Ongoing research to determine the "best" blend ratio has assessed several different parameters, making it difficult to draw universal conclusions. For example, blend ratios can positively or negatively impact the product slate, product yields, and product quality. It is also very difficult to draw clear conclusions with respect to the behaviour of feedstocks, particularly for biocrudes where characteristics can differ dramatically. Research-based results may also lead to incorrect conclusions unless the experimental procedures reflect real-life circumstances. For example, for the case of FCC co-processing, numerous studies were carried out in MAT reactors, leading to claims of increased coke and increased gaseous products as a result of co-processing. However, these studies were not representative of the impact of FCC co-processing of biobased feeds, as shown in the Petrobras demonstration unit (Pinho et al., 2015, 2017).

---

[6] Also see section 4.4 discussing other metrics such as carboxylic acid number

With regard to lipid co-processing in the hydrotreater, contrasting opinions about optimal blend levels have been reported. Although this pathway has been commercialised in many locations, as discussed earlier, the blend ratio for co-processing in the US is also limited by "pump labelling issues" where, beyond a certain limit (i.e. 5%), the co-blended nature of the fuel has to be identified at the pump. One consideration with respect to co-processing of lipids in the hydrotreater is the impact on the cloud point of the final fuel product. The higher the blend ratio, the greater the impact on the cloud point. Unless isomerization is carried out, the diesel produced via co-processing might need to be blended with lighter fractions such as kerosene to meet the required cold flow properties. It has been suggested that a lipid content below 10% will produce a summer diesel that meets specifications (Bezergianni et al., 2018).

The most important consideration seems to be heat release (large exotherm) during hydrotreatment. Some workers have suggested that co-processing blend rates in the hydrotreater should be limited to 5% lipid feed unless special precautions are taken to control heat release (Banerjee and Hoehn, 2014). It should be noted that these workers were specifically referring to lipids with a high level of unsaturation (double bonds), such as canola oil. Higher hydrogen levels will be required to hydrotreat these types of lipids into fully saturated hydrocarbons (resulting in a greater number of exothermic reactions and heat release). For more highly saturated oils, such as palm oil, less hydrogen will be consumed and therefore less heat generated. This implies that higher blends than 5% might be safely co-processed. Other workers have suggested that 5% blends are optimal as blends above 5% resulted in reactor plugging, although it was not clear if other factors could have contributed to this result (Chen, Farooqi and Fairbridge, 2013). For example, vegetable oil feedstocks may have high levels of phospholipids that can form gums if not removed during a pretreatment step.

Although some workers have suggested that a 10% waste cooking oil blend ratio for co-hydrotreating is optimal, this study evaluated only one parameter, namely optimal hydrogen consumption (Bezergianni et al., 2018). Preem has been co-processing 30% tall oil in their hydrotreater, indicating that high blend ratios are possible. However, this would not be possible in an existing unit that was not built to handle challenges such as higher temperatures, increased corrosion etc. (Egeberg,

52

Knudsen, Nyström, Grennfelt and Efraimsson, 2011). Other work that looked at hydrotreating canola oil with HVGO (up to 20% canola oil) concluded that a high total liquid product for the 80/20 blend could be achieved. This was done by adjusting the co-processing conditions, such as lowering the reaction temperature used for hydrotreatment due to the higher crackability of the canola oil (Chen et al., 2013).

When VGO was co-processed with rapeseed oil in an FCC, other researchers found that a lipid ratio of between 5-10% had the greatest impact on increased gasoline yields (Doronin, Potapenko, Lipin and Sorokina, 2013). At higher blend ratios, an increase in aromatics was observed (particularly with unsaturated lipids). This may be desirable, up to a certain point, as it increases the octane number of the fuel. Higher blends of lipids will initially lead to higher aromatic levels, but higher blends of biogenic feeds could lead to increased coke (Juan A. Melero et al., 2010). With regard to lipid co-processing in an FCC, as the blend ratio of lipids are increased, the yield of liquid product is reduced, due to the higher crackability of lipids, while the yield of gaseous products increases (Juan A. Melero et al., 2010). However, reducing the operating temperature of the FCC could prevent this, as cracking will be reduced (Doronin et al., 2013).

Very limited information is available on the co-processing of biocrudes in the hydrotreater. The few studies that have been carried out have used model compounds rather than actual biocrudes. When a recent study looked at co-hydrotreating 20% HTL biocrude (with a 12% oxygen content) with SRGO and/or LCO, the mixture could be readily co-processed, resulting in the complete removal of oxygen in the feed after a 50 h run, without a significant increase in coke deposits on the catalyst (Sauvanaud et al., 2018). However, further studies need to be carried out at larger scale and for longer run-times in order to understand the longer-term impact on the catalyst when using such high blend ratios.

A significant number of studies have assessed the potential of co-processing biocrudes in the FCC. However, due to the high variability of biocrude characteristics (depending on the type of technology such as fast pyrolysis, catalytic pyrolysis or hydrothermal liquefaction; oxygen level, the difference in aromatic content, etc.) it is extremely difficult to draw any clear conclusions. In addition, it is recognised that operating conditions such as temperature, catalyst to oil ratio, etc., all have a significant impact on the results. A recent review provides a comprehensive summary

53

of the possible impact of these variables (Bezergianni et al., 2018). As also pointed out previously, the experimental setup has an important impact on the results, with, for example, MAT reactors overestimating coke and gas yields. In many cases, the opposite trend, lower coke yields, were found in co-processing studies when biocrudes were processed in a pilot-scale FCC (Agblevor et al., 2012; Pinho et al., 2015).

Although some studies have indicated that co-processing of untreated fast pyrolysis biocrude of 20% in the FCC is technically possible (Pinho et al., 2015, 2017), increasing the blend ratio from 10% to 20% did not result in a linear increase in the biogenic content of the liquid products. Instead, more coke was formed. Therefore, if maximum biogenic content in the liquid products is a primary objective, a blend ratio of 10% fast pyrolysis biocrude might be optimal. However, as this biocrude had a very high oxygen content, comparative studies using a range of biocrudes with different oxygen content need to be carried out. Other work found that co-processing 10% biocrude with VGO in an FCC was effective as a similar product slate and yield was achieved compared to VGO alone. However, this changed when the biocrude ratio was increased (Ibarra et al., 2016).

4.7 IMPACT OF COPROCESSING ON PRODUCT DISTRIBUTION AND QUALITY

An important consideration for a refinery when undertaking co-processing is the assurance that product yield and quality will not be compromised and that any products will still meet fuel specifications. With respect to total yields, biogenic feedstocks containing various levels of oxygen will result in a reduced yield as oxygen is partially removed through decarboxylation /decarbonylation reactions, and carbon is lost as low-value gases in the process (Arbogast et al., 2017b).

Co-processing of lipid and fossil feed blends in the FCC has been shown, in some cases, to result in a reduction in overall yield. While gasoline production seemed to remain constant, gases and residues may be increased. However, this profile can be impacted by the type of lipids (saturated or unsaturated), blend level and operating conditions (temperature and catalyst/oil ratio) that are used (Al-Sabawi, Chen and Ng, 2012). Lipids seem to be more susceptible to cracking to form

54

higher levels of gases and, as the lipid content in the feed increases, increased formation of gases become more likely. By lowering the cracking temperature (or inserting into a higher point along the riser), this effect can be reduced (Pinho, Silva, Neto and Cabal, 2009). Some studies have suggested that the gasoline produced from the co-processing of lipids in the FCC results in a product with a higher RON and MON due to higher aromatics formation (Al-Sabawi et al., 2012).

When other workers assessed the co-processing of different types of pyrolysis biocrudes (including fast, catalytic and hydrotreated fast pyrolysis biocrudes) in the FCC, they found that similar yields of gasoline were obtained compared to cracking a fossil feed (VGO), with a slight increase in coke formation (D. Castello and Rosendahl, 2018). Although the product distributions based on different biofeeds, blend ratios and oxygen content has been published (See Table 8) (D Castello and Rosendahl, 2018), it is difficult to compare these observations with what would be obtained in an FCC with VGO. Multiple variables make it difficult to draw clear conclusions as, for example, sometimes a small decrease in coke yield is observed, while in other studies this is not the case. Co-processing can also result in fuels with improved characteristics due to synergy between fossil feeds and biofeeds. For example, co-processing lipids in the hydrotreater can result in a diesel fraction with a higher cetane level (Al-Sabawi and Chen, 2012). In addition, co-processing of biocrudes and lipids in the FCC can, under certain circumstances, produce gasoline with a higher octane rating. This is due to the increased formation of aromatics resulting from the hydrogen transfer reactions (Melero, Iglesias, and Garcia 2012; Pinho et al. 2015).

Distribution of biogenic content in the different fuel products after co-processing is an important factor with respect to product characteristics, and it is an essential reason for carrying out co-processing in the first place. Work using a MAT reactor showed that co-processing 20% biocrude in an FCC resulted in a slightly lower biogenic content (compared with the feed) in the gasoline fraction, with a slightly higher biogenic content observed in the coke and gases (Fogassy, Thegarid, Schuurman and Mirodatos, 2012).

As mentioned earlier, work carried out at lab scale with certain experimental set-ups, such as the MAT reactor, generally overestimate coke and gas formation and does not resemble real-life FCC conditions (Bezergianni et al., 2018). Experimental

conditions should therefore be considered in the evaluation of reported results. For example, other workers found that co-processing of raw fast pyrolysis biocrude at 20% blends produced higher coke levels than at 10% blends. However, coke production was lower than anticipated based on the MAT reactor studies (Pinho et al., 2017).

Table 8 Summary of published studies regarding FCC co-processing of biocrudes/bio-oils (D Castello and Rosendahl, 2018) FPO=fast pyrolysis oil; CPO=catalytic pyrolysis oil; HDO=hydrodeoxygenation bio-oil

Feedstock	Ratio	Oxygen content	Co-FCC yields		FCC yields	
			Gasoline	Coke	Gasoline	Coke
FPO	10-20	38	36-42	8-10	40-42	7-8
FPO	5-10	33	37-42	5.6-7.2	40	6.5
FPO	5-20	32	29-35	4.2-5.5	44	5.6
FPO	20	36.5	17	10	16	5
CPO	10	27	~55	4-6	~50	2-4
CPO	15	22	44.4	6.8	44	7.1
CPO	10	19.5	40.7-42	7.5-8.4	40-42	7-8.2
CPO	20	22	19	10	16	5
HDO[a]	3.75	4.9	42-46	4-6	38-46	2-5.5
HDO	20	21	45-47	4-7	42-48	2-4
HDO	10	7-33	30-41	1.2-5.5	25-37	1.2-3.8
HDO	5	10	32.5	4.2	44	5.6
HDO	20	22	18	8	16	5
HDO[b]	15	4.9	20-26	3-6	16-22	2-3
HDO	20	17-23	40.2-43.5	5.2-7.2	44	5.9

All values are expressed as percentages. Oxygen content is on dry basis

[a] A mixture of VGO/LCO/HDO 85/11.25/3.75 was used. FCC yields are referred to VGO/LCO 85/15.

[b] LCO was utilised as fossil streams.

Earlier work has shown that coke yields during co-processing can be estimated based on the results of micro carbon residue (MCR) testing. This is a test that is carried out routinely at refineries (Lindfors et al., 2015). Although these workers found that gasoline yields for the different biocrudes after co-processing were

56

similar, although coke yields differed, other workers found that co-processing of bio-oils/biocrudes lead to increased formation of low-value gases and aromatics (Al-Sabawi et al., 2012). It has also been shown that co-processing of lipids in the hydrotreater increased the cetane level of diesel due to the paraffinic nature of the lipid feedstocks. This, consequently, improved the characteristics of the diesel product. An increased cetane level of 2-3 was observed at lipid blends of 10% during co-processing (Al-Sabawi and Chen, 2012). However, as the blend percentage of lipids in the hydrotreater was increased, the increased paraffinic content also increased the cloud point, melting point, pour point and the cold filter plugging point (Al-Sabawi and Chen, 2012). The increase in cloud point could be partially mitigated by increasing the temperature in the hydrotreating reactor. These researchers showed that co-processing at 360-380°C produced a gas oil with similar CFPP properties to an un-co-processed gas oil (Tóth, Baladincz, Kovács and Hancsók, 2010). Related work has shown that increased temperatures during hydrotreatment of lipids can lead to cracking, resulting in a decreased cloud point. However, this was based on the hydrotreatment of pure lipids (Watkins and Lansdown, 2012). At low lipid blends during co-processing, increased cracking does not seem to have a significant impact on middle distillate production (Al-Sabawi and Chen, 2012). However, if co-processing is carried out in the hydrocracker, lipids are expected to form lighter hydrocarbons.

It has been shown that cracking reactions can be minimised at optimal hydrotreatment temperatures, with vegetable oils preferably co-processed in a hydrotreater at temperatures between 360-390°C. Animal fats are optimally co-processed at temperatures between 320-340°C (Bezergianni et al., 2018) as co-processing animal fats above 340°C increases cracking reactions. However, it should be noted that potential competition between hydrodeoxygenation and hydrodesulphurisation can have an impact on the diesel product not meeting specifications (Bezergianni et al., 2018; D. Castello and Rosendahl, 2018).

4.8 DEALING WITH OPERATIONAL IMPACTS OF CO-PROCESSING

It has been reported that co-processing biofeeds can cause a pressure drop in the hydrotreater due to deposition of solids such as coke or polymerization products

57

(Abhari, Havlik, Tomlinson, Roth and Record, 2013). The pressure drop rises over time and, when the maximum safe operating pressure drop is reached, the reactor has to be shut down and deposits physically removed from the reactor or the catalysts need to be replaced. Another option involves modifying the reactor to have high void fractions in the top layers. In this way it can hold more solids before reaching the pressure drop limit. For example wagon wheels, Raschig rings and other shapes have been used (Abhari et al., 2013). An internal bypass apparatus for fixed bed reactors can also be used, which will allow the hydrotreater feed to bypass the fouled section (Abhari et al., 2013). It should be noted that Haldor Topsoe has reported resolving potential pressure drop issues by using grading of catalysts within the reactor, with large size catalyst particles at the top to trap metals and solids with the bottom layers of catalyst being densest (Haldor Topsoe, 2021).

5. Refinery modifications and additional infrastructure requirements for co-processing

As mentioned earlier, refineries that follow a co-processing strategy will likely need to invest in some additional infrastructure and associated costs to manage operational issues and impacts on metallurgy and catalysts. In addition, facilities such as storage tanks for biobased feedstocks will be required. However, there is limited publicly available information on the cost of co-processing from either a capital investment or operating perspective. It is likely that the costs associated with co-processing will vary considerably depending on the type of feedstock, the insertion point and the blend ratio of the biobased feeds. For example, higher blend ratios of bio-feedstocks will likely require greater investment in infrastructure to manage the specific challenges associated with co-processing.

However, the patent literature can indicate the types of infrastructure associated with co-processing in existing refineries. It also outlines how pioneering refineries are managing certain operational aspects such as miscibility issues, risk of corrosion, deoxygenation, etc., and the impact of heat generation during hydrodeoxygenation. Many biobased intermediates will require heated storage and pumping. For example, high viscosity feedstocks such as tallow and biocrudes produced through HTL or catalytic pyrolysis. As discussed earlier, high TAN feedstocks will also require higher grade metallurgy to prevent corrosion. Some of the additional infrastructure that will likely be required when following a co-processing strategy is summarised below:

- A separate feed injection nozzle into the FCC;

- A separate feed injection port into the hydrotreater;

- Addition of special guard beds, e.g. removal of metals prior to feed entering the reactor;

- Modification of the hydrotreater into stages/phases that operate at different operating conditions and potentially contain different catalysts;

59

– Pretreatment units, e.g. for filtration, degumming, partial and dedicated hydrotreating of high oxygen feeds for stabilization, e.g. bio-oils/biocrudes.

One of the leading companies in this area is the Preem refinery in Sweden, which has reported co-processing 30% tall oil, in the form of tall oil diesel, in their hydrotreater. As tall oil contains high levels of free fatty acids and high TAN levels with potential corrosion challenges, Preem has had to deal with challenges such as increased hydrogen consumption and heat generation as a result of exothermic hydrogenation reactions. The corrosion problem was partially addressed through esterification of the feedstock, by converting the fatty acids in the tall oil into methyl esters, resulting in lower acidity. In addition, the tall oil methyl esters were kept separate from the regular piping and pumping infrastructure. They can be injected through separate pumping and piping into the hydrotreater after the fired heater (Egeberg et al., 2011). In this way, the potentially corrosive feedstock does not come into contact with the heating element in the hydrotreater. At the same time, the unheated tall oil can have a quenching effect upon insertion in the hydrotreater. This limits overheating due to the exothermic oxygen removal reactions. Overheating is also managed through a second injection port for the tall oil feed before the second catalyst bed in the hydrotreater unit. The modified hydrotreater design is summarised in Figure 6 (Egeberg et al., 2011).
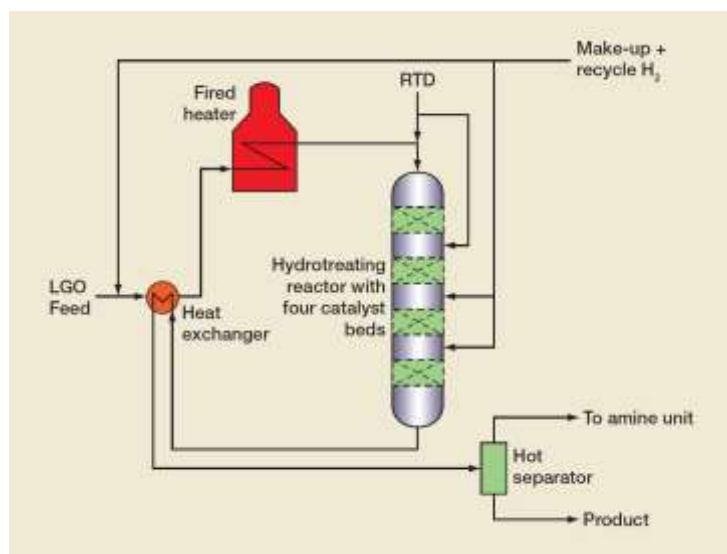
Figure 6. Modified hydrotreater at the Preem facility for coprocessing of 30% tall oil (Egeberg et al 2011).

With regard to co-processing pyrolysis derived biocrude in the FCC, the three major challenges are the immiscibility of the two feeds, the instability of the biocrude at the FCC injection temperatures (~500°C) to form large quantities of coke, and the high TAN of the pyrolysis biocrude. Pyrolysis biocrudes are stable below 50°C and do not form solids due to polymerisation at these temperatures. The company Ensyn developed a patented solution to overcome these specific challenges (Freel and Robert, 2015). This patented design was implemented during the co-processing of fast pyrolysis biocrude carried out by Petrobras. In this study, the modified FCC had a separate injection nozzle at the bottom of the riser which allowed for injection of the biocrude into the reactor below the FCC feed. As described in various publications, this method was very effective and allowed the co-processing of raw pyrolysis biocrude with very high oxygen levels (Pinho, De Almeida, Mendes and Ximenes, 2014; Pinho et al., 2015, 2017). The authors were able to show that coke formation was much lower than expected and that the biogenic content was distributed in all of the liquid fractions.

As discussed earlier, there is some concern about potential interactions between hydrodeoxygenation and hydrodesulfurisation during co-hydrotreating, resulting in potential product quality issues. This interference is impacted by factors such as operating temperatures, blend levels, etc. The release of CO during

61

hydrodeoxygenation results in catalyst inhibition which can impact HDS. In addition, the formation of H_2S during HDS can decrease the efficiency of HDO. Several patents have been registered to address this challenge where the hydrotreater was modified and divided into two sections to provide different optimal conditions for both HDS and HDO (Bertoncini and Marchand, 2011; Gudde and Shabaker, 2014). Although some minor variations are listed in different patents, the basic concept is essentially the same (Cole, Hanks and Lewis, 2011; Debuisschert, Cosyns, Chapus and Hudebine, 2014; Gomes, Zotin, Pacheco and Da Silva, 2013; Gudde and Shabaker, 2014).

Although both HDO and HDS take place in the first section of the reactor, the potential inhibition of CO on HDS may impact sulfur removal. Consequently, the fuel might not meet (diesel) specifications. The principal solution, as described in various patents, involves purging gases (including CO, CO_2, H_2O) from the reactor to prevent inhibition of the HDS in the second stage, while serving as a polishing step to reduce the sulfur levels to specifications. The two processes can also be reversed with HDS carried out on only the fossil feed in the first stage of the reactor. The resulting feed is then blended with the biofeed and further subjected to hydrotreatment to remove the oxygen from the feed in the second phase (Bertoncini and Marchand, 2011; Lewis, Mizan and Hou, 2013). The two-stage setup can also be used to reduce hydrogen consumption (due to undesired methane formation) as the two stages can be operated at different conditions. This reduces unwanted methane reactions.

During co-processing, CO_2 and CO is produced due to deoxygenation. Although CO_2 is easily treated through an amine scrubber, this does not remove the CO. An example of a patented technology dealing with the challenge of removal of CO is the addition of a separate methanation reactor that is used to convert CO to methane as one way of removing the CO while also generating a useful product (Egeberg et al., 2011). Another patented way to reduce CO production is to lower the hydrotreatment temperature and hydrogen pressure. As a result of the water gas shift reaction taking place, CO_2 is preferentially formed (Cole et al., 2011), which also results in lower hydrogen consumption.

As discussed earlier, co-processing of lipids in a hydrotreater results in a higher paraffinic content product and, therefore, an increase in the cetane of the diesel. However, this also impacts the cold flow properties of the diesel as, at high blend levels of lipids, the impact on the cold flow properties becomes problematic.

62

Depending on product specifications and the desired blend level, this may require additional isomerisation to be carried out to improve cold flow properties. This can be achieved through additional or modified infrastructure, e.g. an isomerisation reactor, or modification of the catalyst bed to include isomerisation catalysts.

Other patents that relate to co-processing include:

- methods for improving miscibility of a fossil and biofeed by creating an emulsion using surfactants (Ray and Banerjee, 2016), alcohols, etc., as well as mixing with another biofeed such as tall oil pitch to improve miscibility (Paasikallio, Toukoniitty and Pasanen, 2019), and blending bio-oil with biodiesel (fatty acid methyl esters) (Ramirez Corredores and Iglesias, 2016);
- Various patents for pretreatment steps include removal of impurities from lipids (phosphorous, iron) (Guay et al., 2016; Havlik, Abhari, Roth and Tomlinson, 2013), using ion-exchange resin to remove metals from pyrolysis oils (Zhou, Roby and Kuehler, 2015), or tallow (Mezza, Bhattacharya and Lupton, 2014), and using the formation of amides to remove metals from high free fatty acid biofeeds with metals transferred to the aqueous phase (Kothandaraman, Uppili and Yao, 2011);
- Conversion of a petroleum refinery into a biorefinery (Rispoli, Bellusi, Calemma and De Angelis, 2015)
- Injection of an unheated biofeed into a hydrotreater to provide a quenching effect (Banerjee and Hoehn, 2014)
- Other approaches that fell outside the scope of this report included the insertion of a biomass slurry (sometimes from torrefied pellets) into the FCC (Gong, Platon, Cantu and Daugaard, 2014).

With respect to the initial investment costs required to initiate co-processing, very limited information is available in the public domain. As there are multiple options for feedstock type and insertion points, the range of costs will likely be substantial. However, for low blends of biobased feedstocks that have already been

63

pretreated, the investment costs should likely be minimal, e.g. additional storage tanks. A recent techno-economic analysis by Talmadge and co-workers has summarised the infrastructure and cost of bio-oil co-processing in the FCC (Talmadge et al., 2021). The additional infrastructure includes storage tanks, pumps, and piping using materials compatible with bio-oil properties. The other capital requirements that were identified downstream of the FCC, included wastewater treatment that can deal with added phenolics, carbonate formation from CO_2 in the fractionators, and amine and sulfur plant capacity from CO_2 (Talmadge et al., 2021).

The estimated capital cost required for the storage and pumping of bio-oil during FCC co-processing was approximately $1.36 million for a 5% co-processing ratio, $2.24 million for a 10% ratio, and $3.67 million for a 20% bio-oil ratio (Talmadge et al., 2021).

6. Techno-economics of coprocessing

As discussed earlier, several refineries are currently co-processing fats, oils and greases (FOG's) via hydrotreating units at a commercial scale. Co-processing bio-oils/biocrudes is still at the development stage. Due to the disparate characteristics of the two types of feedstocks, co-processing costs will likely differ between these two categories of biogenic feedstocks. In addition, different types of bio-oils/biocrudes and the extent to which they have been upgraded prior to co-processing will likely also affect the cost of these feedstocks.

It is recognised that a thorough techno-economic analysis is important for assessment of co-processing options. For example, Yanez points out that current studies have focused on individual biooils in a specific refinery unit without including key aspects such as the bio-oil production method, cost or distinguish between insertion in the hydrotreater or FCC (Yáñez, Meerman, Ramírez, Castillo and Faaij, 2021). These authors also pointed out that the technology readiness level of bio-oil production and upgrading creates a high degree of uncertainty in techno-economic assessments of co-processing. These assessments should be carried out in a more comparative approach, taking into account aspects such as mass and energy yields under different operating conditions and blending restrictions (Yáñez et al., 2021). The main technical indicator used in the Yanez study is the net change in annual emissions in tCO2/y for different pathways. Yanez and colleagues carried out techno-economic analyses on 13 different co-processing pathways, including vegetable oil, fast pyrolysis oil, hydro-deoxygenated boil, catalytic pyrolysis oil, hydrothermal liquefaction oil and Fischer-Tropsch fuels (Yáñez et al., 2021). The goal of the study was to determine the performance of co-processing pathways with respect to CO_2 emissions avoided. They did not find any single pathway as a clear winner as it depended on the criteria used and the target of the co-processing route. However, these workers found that production costs varied from 17-to-31 EUR/GJ (i.e. $118-213/bbl_{eq}$). Although co-processing vegetable oil resulted in the lowest emissions, this was based on using palm oil as a feedstock with high emissions produced during feedstock production. Overall, the cost of CO_2 emissions reductions for the different pathways varied between EUR99-651 per tCO_2.

With regard to the production of different types of bio-oil, Yanez and co-workers found that the biggest share of CO_2 emissions per energy unit of biofuel,

65

excluding the final use, comes from the bio-oil production at ~85% (Yáñez et al., 2021). Therefore mass and energy yields in the bio-oil production stage has a critical impact on the CO_2 intensity (Yáñez et al., 2021). The emissions associated with the refinery upgrading stage is the second-highest contributor and is mostly associated with hydrogen consumption (Yáñez et al., 2021). In related work, Talmadge and co-workers carried out a techno-economic analysis of co-processing bio-oil at different blend ratios in an FCC (Talmadge et al., 2021). Total installed capital cost for bio-oil feed tanks and feed pumps were determined at $1,358,026 (5wt% bio-oil), $2,223,565 (10wt% bio-oil), and $3,670,537 (20wt% bio-oil).

In addition to these costs, other capital costs may be required when co-processing pyrolysis oils, for example, for increased wastewater treatment due to phenolics in biomass, carbonate formation from CO_2 in fractionators, and amine and sulfur plant capacity from CO_2 for in-plant reuse of gases or environmental releases. As this data was not available, it was not included in the analyses carried out by NREL and Petrobras colleagues (Talmadge et al., 2021). However, these workers assessed the cost of raw, filtered bio-oils as part of their techno-economic analysis. For a 400 t/d facility (near-term commercial) the bio-oil minimum selling price was calculated as $78-to-82/bbl, while costs for a mature commercial plant (2,000 t/d) decreased to $48-to-56/bbl (Talmadge et al., 2021).

A review of biofuel production cost in 2020 by the European Commission Subgroup on Advanced Biofuels (SGAB) indicated that co-processing bio-oils costs between 79-to-139 EUR/MWh and 82-to-127 EUR/MWh[7] for standalone processing (Brown et al., 2020). Although the capital cost for the co-processing option is lower than that for the stand-alone plant, the co-processing blend ratios in the refinery processing units are usually limited to 2-10%, depending on the pre-processing of the pyrolysis oil intermediate. The conversion efficiency for co-processing is reported to

---

[7] 1 EUR/MWh = 0.277 EUR/GJ = 0.265 EUR/MMBTU = 11.63 EUR/toe (Brown et al., 2020)

be lower than a standalone plant with the overall conversion efficiency from the feedstock estimated to be 29% (Brown et al., 2020).

An earlier SGAB report showed cost estimates for pyrolysis bio-oil co-processing production costs as 58-to-104 EUR/MWh, compared with stand-alone production of upgraded pyrolysis bio-oil at 83-to-118 EUR/MWh (Landälv and Waldheim, 2017). However, the share of OPEX from the refinery processing stage was not included due to a "lack of a basis for allocating such a cost". The report also noted the low efficiency of co-processing (below 30%) (Landälv and Waldheim, 2017). For conversion of biomass to pyrolysis oil, a conversion efficiency of 65-70% was reported.

7. Potential for coprocessing based on global refinery processing capacity

The potential amount of low-carbon-intensity fuel that might be produced via co-processing can be assessed based on the global refinery capacity of specific types of refinery processing units and the possible blend ratios used during co-processing. As summarised in Table 9, the potential global capacity for catalytic cracking is 19.3 mb/d, for hydrocracking, 10.4 mb/d, and for middle distillate desulphurization, 30.8 mb/d (OPEC, 2020). Based on a 10% blend ratio for the total capacity of these three operations, a total amount of 6.04 mb/d biogenic intermediate could be inserted into existing refineries to produce low carbon intensity fuels.

Table 9 Assessed global available refinery base capacity in January 2020 (OPEC, 2020) (mb/d)

Distillation	
Crude oil (atmospheric)	102.6
Vacuum	38.0
Upgrading	
Coking	8.9
Catalytic cracking	19.3
Hydrocracking	10.4
Visbreaking	4.1
Solvent deasphalting	1.2
Gasoline	
Reforming	14.3
Isomerization	2.9
Alkylation	2.4
Polymerization	0.1
MTBE/ETBE	0.3
Desulphurization	
Naphtha	17.2
Gasoline	7.5
Middle Distillates	30.8
Heavy oil/Residual fuel	9.7
Sulphur (short tons/day)	147,375
Hydrogen (million scf/d)	30,424

8. Current status of coprocessing

Several refineries are already commercially co-processing biogenic feedstocks. Lipid feeds predominate, although some co-processing trials using pyrolysis and HTL biocrudes are also underway.

BP

BP is reported to co-process up-to10% lipids in their hydrotreater at their Cherry Point refinery in Blaine, Washington, producing a lower carbon intensive (CI) diesel. BP also announced in July 2021 that they produced commercial sustainable aviation fuel via co-processing at the BP refinery in Castellon, Spain. (https://www.bp.com/en/global/air-bp/news-and-views/press-releases/Airbp-announces-netjets-europe-first-to-purchase-iscc-plus-saf.html). The co-processed SAF will be certified by ISCC PLUS and will provide about 80% carbon emission reductions over its lifecycle compared to the use of conventional jet fuel, based on a mass balance approach.

PREEM

Preem has been a pioneer in commercial co-processing. They have co-processed ratios of 30% tall diesel, a tall oil product produced by SunPine, (to produce Evolution Diesel). A recent second revamp of the Preem refinery in Gothenburg, using Haldor Topsoe Hydroflex technology, has achieved an 85% co-processing of renewable feedstocks[8].

Preem has used tallow and raw tall diesel as its main biogenic feedstocks. Preem and Topsoe are also collaborating to revamp the Synsat unit at Preem's Lysekil refinery. This unit will use Topsoe's HydroFlex technology to produce renewable diesel based on various renewable feedstocks, including rapeseed oil. The unit is scheduled to be fully rebuilt by 2024. The revamp will allow Preem to produce

---

[8] https://blog.topsoe.com/haldor-topsoe-and-preem-achieve-85-co-processing-of-renewable-feedstock

69

950,000 standard cubic meters of renewable diesel per year. As part of the revamp, the unit will be modified to process 100% renewable feedstock.

Preem is also a joint owner of Pyrocell. Working with Setra they will build a pyrolysis plant based on BTG Bioliquids technology that will use sawdust from Setra's Kastet sawmill to produce bio-oil[9]. The Pyrocell project will co-process the bio-oils at a 5% ratio in the fluid catalytic cracker (FCC) (Lammens, 2021). The bio-oil will be fed by a separate injection line and nozzle into the FCC. The Pyrocell plant started processing bio-oil in September 2021[10].

Preem, being Sweden's largest fuel producer, provides both gasoline and diesel with varying degrees of renewable content. Preem Evolution Diesel+ contains at least 50 percent renewable content and has the same price as regular diesel.

PARKLAND REFINERY, BURNABY

The Parkland Refinery in Burnaby was the first facility in Canada to use existing infrastructure and equipment to co-process bio-feedstocks such as canola oil, and oil derived from animal fats (tallow) alongside crude oil to produce low carbon fuels. In February 2021, Parkland Corporation announced that approximately 44 million litres of Canadian-sourced canola and tallow bio-feedstocks were co-processed. The company increased this volume to up to 100 million litres in 2021[11]. One of the drivers for Parkland Corporation carrying out co-processing is British Columbia's Low Carbon Fuel Regulations. This requires fuel suppliers to reduce the carbon intensity of fuels supplied to the BC market.

---

[9] https://www.setragroup.com/en/pyrocell/about-pyrocell/

[10] https://news.cision.com/setra-group/r/pyrocell-has-started-production,c3420250

[11] https://www.parkland.ca/en/investors/news-releases/details/2021-02-18-Parkland-sets-new-low-carbon-fuel-production-record-at-its-Burnaby-Refinery-and-targets-125-percent-annual-production-growth-in-2021/609#close

CHEVRON

In March 2020 Chevron announced plans for co-processing of biofeeds in its fluid catalytic cracking unit at its 269,000 b/d El Segundo, California, refinery. Chevron's El Segundo refinery has 73,800 b/d of fluid catalytic cracking capacity and the refinery is a key supplier of gasoline to the Los Angeles area. It has the infrastructure to allow it to use bio-feedstocks and other co-feeds reliably, taking advantage of existing capital investment. However, no firm time frame was given for when the project would start nor were any volumes or type of feeds to be used disclosed at the meeting[12].

Chevron also announced co-processing biofeedstocks via their fluid catalytic crackers (FCC) in 2021[13]. Around the same time, Exxon and Chevron announced they would look at processing bio-based feedstocks such as vegetable oils and partially processed biofuels, with petroleum distillates. In this way they would make to make lower carbon intensity (CI) diesel, more sustainable aviation fuel (SAF) and lower-CI gasoline, without meaningfully increasing capital spending[14].

As the ASTM D1655 specification for Jet A/A1 limits the production of co-processed jet fuel to a maximum of 5% biobased feeds (lipids or Fischer-Tropsch liquids), this presents a significant restriction for refineries targeting high blend ratios of biobased feeds for co-processing. In response, Exxon has initiated a request within international standards and testing organization ASTM International to determine the possibility of increasing the co-processing ratio up to 50% for certain types of biogenic feedstocks.

---

[12] https://www.spglobal.com/platts/en/market-insights/latest-news/oil/030320-refinery-news-chevron-to-co-process-biofeed-at-el-segundos-fcc

[13] https://www.reuters.com/world/middle-east/exclusive-exxon-chevron-look-make-renewable-fuels-without-costly-refinery-2021-08-12/

[14] https://www.reuters.com/world/middle-east/exclusive-exxon-chevron-look-make-renewable-fuels-without-costly-refinery-2021-08-12/

EXXON

Exxon recently announced that it would repurpose its existing refinery units among other strategies to produce more than 40,000 barrels per day of low-emission fuels at a competitive cost by 2025[15]. ExxonMobil Catalysts and Licensing developed a proprietary process technology termed ExxonMobil Renewable Diesel Process, EMRDTM, which includes a second stage dewaxing step with a proprietary catalyst, BIDWdewaxing (https://www.exxonmobilchemical.com/en/catalysts-and-technology-licensing/emrd).

PETROBRAS

Several years ago, the US National Renewable Energy Laboratory (NREL), Petrobras and Ensyn collaborated in extensive biocrude co-processing trials carried out at Petrobras' SIX unit located in the Sao Mateus do Sul refinery in Brazil and using raw fast pyrolysis bio-oil from Ensyn's facilities in Canada. Based on 54 trials the final report concluded that, over a broad range of FCC operating conditions, the substitution of biocrude at 5% and 10% resulted in higher gasoline yields, higher or unchanged diesel yields, and slightly lower coke yields. (http://www.ensyn.com/latest-news/nrelpetrobras-publish-comprehensive-report-on-co-processing-demonstrations)

Petrobras is also engaged in co-processing lipids in its hydrotreater. Petrobras patented a technology in 2006 for the co-processing of vegetable oils using the process called H-BIO. The H-BIO process involves co-processing of a blend of diesel fractions and vegetable oil in a hydrotreating (HDT) reactor. Due to the high price of soy oil, Petrobras suspended the commercialization of H-BIO in 2014[16]. In 2020

---

[15] https://www.reuters.com/world/middle-east/exclusive-exxon-chevron-look-make-renewable-fuels-without-costly-refinery-2021-08-12/.

[16] https://www.greencarcongress.com/2020/08/20200803-petrobras.html

Petrobras successfully concluded co-processing trials at the Presidente Getúlio Vargas Refinery (REPAR), in Araucária, Paraná, for the production of renewable diesel. The trials were at commercial scale and 2 million liters of soybean oil were processed to obtain about 40 million liters of S10 diesel with renewable content. Once regulatory approval has been granted, Petrobras intends to start commercial production using co-processing of vegetable oils. No further reports were available.

EQUINOR

Equinor is a Norwegian company who has carried out co-processing trials using bio-oil feedstocks at their Mongstad and Kalundborg refineries[17]. Co-processing was carried out at both the distillate hydrotreater at Kalundborg and the catalytic cracker at Mongstad. The Equinor has shown that the insertion of even small ratios (5%) of "crop-based feedstock" impacted existing production and unit operations. The oxygen content of the biocrude resulted in corrosion problems within the hydrotreater due to formation of wet CO_2 while in the catalytic cracker, light oxygenates formed and caused challenges in subsequent processing such as the amine unit. They concluded that some form pretreatment must be carried out to remove metals and the acidity of feedstock needs to be controlled. They also recommended that catalysts should be adjusted to mitigate the impact on the cold flow properties of the fuel (Hauge and Allen, 2021).

As well as the co-processing of pyrolysis oil Equinor is also assessing the potential of gasifying the bio-oil to alcohol, followed by an alcohol-to fuels step.

HONEYWELL/UOP COPROCESSING

The Honeywell/UOP co-processing technology is being assessed in four commercial scale trials (Dan Szeezil, 2021) using feedstocks such as lipids, HTL biocrudes and other biomass liquids. This work has indicated some challenges when co-processing at the FCC, including an increase in delta coke, reactor/riser coking,

---

[17] https://www.nmbu.no/en/services/centers/bio4fuels/news/node/40622

elevated chlorides, hydraulics, contaminant metals, fines shift, product quality and elevated oxygenates. A separate injection using the patented Optimix[TM] GF injection distributor was developed by the company to mitigate some of the negative impacts of co-processing. Using this injection technology, successful co-processing trials were carried out at the Preem refinery using pyrolysis bio-oil [18]. Honeywell also has a joint venture with Ensyn (Canada) in 2008, called Envergent, with a focus on the production of fuels via the co-processing of Ensyn's pyrolysis bio-oil.

ENI

ENI has followed two approaches to making renewable fuels which include production in stand-alone renewable fuel units as well as a coprocessing strategy (Fiori, Chiaberge, Pavoni, Bosetti and Landoni, 2021). The ENI Taranto refinery started co-processing activities in October 2021, inserting 0.5% UCO into the existing refinery infrastructure to produce sustainable aviation fuels[19]. Eni also has a proprietary waste-to-fuel technology (W2F) that produces a bio-oil from the organic fraction of municipal solid waste [20]. The bio-oil can be used directly as a marine bunker fuel or further processed in a refinery. Wastewater is treated through anaerobic digestion to produce methane. The yield of bio-oil is up to 16% based on total waste input and contains about 8-12% oxygen and 3-4% nitrogen. Eni operates a W2F plant in Gela, Italy and has been evaluating the possible co-processing of bio-oil at the facility.

Eni is also part of the European HyflexFuel project which hopes to produce sustainable liquid fuels via the co-processing of HTL biocrudes. The HTL biocrude production is carried out by Aalborg University while Eni carries out co-processing

---

[18] https://uop.honeywell.com/en/news-events/2021/september/honeywell-and-preem-conduct-commercial-co-processing-trial-to-produce-renewable-fuel

[19] https://www.biobased-diesel.com/post/eni-begins-coprocessing-saf-at-conventional-oil-refinery-in-taranto-italy

[20] https://www.eni.com/en-IT/operations/waste-to-fuel.html

trials, such as co-distillation. Co-distillation was carried out with partially upgraded biocrude from Aalborg University with a TAN of 2 mgKOH/kg (20% blend ratio). The nitrogen content of the co-distilled blend was much higher than for the crude alone, particularly in the kerosene and diesel fraction. Feedstocks used for evaluation were Spirulina, sewage sludge, miscanthus and pine.

REPSOL

Repsol has produced sustainable aviation fuel via co-processing at their Tarragona refinery in Spain in 2021 [21]. The company has indicated that it intends to carry out co-processing at other refineries in Spain. It also plans to establish stand-alone biofuel production by constructing a new renewable diesel and SAF facility in Cartagena, based on the Axens Vegan Technology.

---

[21] https://www.biobased-diesel.com/post/repsol-coprocesses-sustainable-aviation-fuel-in-tarragona-spain

9. Determining the carbon Intensity of co-processed fuels

One of the primary reasons for co-processing fossil and biogenic feedstocks is to reduce the carbon intensity of the resulting fuels. In a co-processing system, the goal is usually to identify the carbon intensity of the biogenic component so that it can be compared to the fossil components (not the carbon intensity of the co-processed stream compared to a fossil only stream). This both simplifies and complicates the LCA process. For the inventory analysis stage of the LCA process it means that the biogenic component of the finished product must be quantified in order to isolate the system. As will be discussed in more detail, there are a number of methods that can be used to track the biogenic content during co-processing. These include determining the mass balance, carbon balance, C14, and C13 as part of a life cycle assessment.

The LCA process calculations must include process inputs such as power, heat, and hydrogen which must be reported as the difference between the baseline condition, either with or without the biogenic feedstock. However, small differences between two large numbers can be difficult to accurately determine given the precision limitations of the measuring devices. As will be discussed later, an unstable baseline combined with low biogenic inputs can make methods such as mass balance and carbon balance unreliable and imprecise. Similarly, if there are any interactions between the biogenic and fossil system, methods based on the difference with the baseline, such as the mass or carbon balance, can result in inaccurate analysis. Although modelling of the whole refinery can be used to determine the carbon intensity of the products with some biogenic content (such as the fuel from a blend of 95% petroleum and 5% biogenic feed), the biogenic content of the finished fuel must still be determined.

The carbon intensity of co-processed biogenic feedstocks is a function of the feedstock production emissions and the emissions from the processing of the biogenic feed into a drop-in fuel. Although determination of feedstock carbon intensity is well established, emissions from co-processing into finished fuels is an emerging field with very little verified data from real world applications. The feedstock carbon intensity will arguably have the greatest impact on the final carbon intensity of the co-processed fuel.

Although co-processing lipids in a hydrotreater is commercially practised at several locations around the world, undertaking lifecycle analysis has proven to be challenging. In most regulatory systems the LCA needs to be done on an incremental basis so that just the emissions associated with the biogenic fuel are reported. Unfortunately, only one of the inputs (the lipid feedstock) can be directly measured. The other inputs can only be determined through differences in readings between a baseline and the co-processing case. This requires a stable baseline and the absence of chemical reactions occurring between the biogenic and fossil feedstocks.

Thus, a refinery will need to monitor the quality parameters of the fossil feedstock and develop dynamic baselines that would adjust the baseline hydrogen consumption according to changes in factors such as the feedstock sulphur and nitrogen levels. Co-processing also requires the quantity of biogenic carbon to be monitored in the finished fuels. The available data suggests that, for at least an FCC approach, there are chemical reactions between the fossil and biogenic components that make the mass balance approach inadequate. Although the carbon 14 method has been successfully used by companies that are co-processing lipids in a hydrotreater, co-processing biogenic feeds in an FCC will be more challenging. If C14 monitoring is used there are more output streams to measure, plus, the percentage of biogenic carbon in the feed to the FCC is likely to be initially low due to the limited supply of the biogenic feedstock.

9.1 METHODS FOR TRACKING BIOGENIC CONTENT IN CO-PROCESSING

Quantification methods can be categorized into either "administrative calculation methods" in the refining unit, including mass balance and carbon balance methods or, analyses that determine the actual physical composition of the finished fuel after co-processing, such as carbon dating using C14 analysis (Schimmel, Toop, Alberci and Koper, 2018). These different methods are described in more below and are compared based on criteria such as the cost of testing, requirement for new equipment and staff, etc. (Schimmel et al., 2018).

Mass balance
The mass balance approach based on observed yields, also known as a step-change mass balance method, compares the hydrocarbon yields of co-processing to a baseline, measured using only fossil feedstock. There is no direct measurement of

biogenic content. Instead, the amount of biogenic content is based on an observed change in total yield compared to the baseline. The difference in yield is attributed to the biogenic component (Schimmel et al., 2018). Two key conditions are required if the mass balance approach is to be effective. These are, the need for a stable baseline from which to observe the change and an assurance that there are no chemical interactions between the fossil and biogenic components.

The California Air Resources Board (CARB) requires that the baseline is established based on three months minimum average yield data without co-processing (California Air Resources Board, 2017). Also, companies who favour the mass balance method argue that the C14 method is unreliable at low blend rates due to the ±3% absolute error in the C14 method (Jacobs, 2018).

From a cost perspective, the mass balance method is advantageous as it does not require the installation of any new instrumentation or the appointment of new staff. It can also be readily integrated into the refinery and does not require the measurement of any CO, CO_2 or H_2O. Importantly, the monitoring technology is relatively simple and accessible to all refineries. However, the biggest challenge with this method is establishing a stable baseline. Refinery operations vary due to the change in crude feedstock, refinery targets, seasonal variabilities, emergency shutdowns or turnarounds, etc. (Economides, Fuels, Company and Ramon, 2017). These variations can be larger than the impact of co-processing biogenic feedstocks at a low percentage. Measurements using flow meters may also be subject to error, which will make it difficult to establish a baseline and determine changes due to co-processing when low blends are used. Su and co-workers demonstrated the shortcomings of the mass balance method when co-processing low volumes of lipids in an FCC (Su et al., 2021).

Although CARB suggests three months of data to determine a baseline, even this may not be sufficient. In addition, this will limit the refinery's flexibility to adjust reactor operating conditions and use different types of crudes. This method also assumes that no chemical interactions take place between the renewable and fossil components. Thus, the method may not be appropriate for all co-processing configurations. Several researchers have shown that interactions do take place, e.g. hydrogen transfer takes place in the FCC between the fossil and renewable components (Mercader, 2010; Pinho et al., 2015). The determination of carbon

78

intensity in the FCC is discussed later, with recent studies highlighting the inadequacy of the mass balance method at low blends of biobased feedstocks.

From a monitoring perspective, the extensive recordkeeping required may be a disadvantage as, if extensive changes in operating conditions take place, the monitoring may be onerous. However, the advantage of this method is that it is well-known in the refining sector and routinely used to estimate the yields from different crudes.

Carbon mass balance method

The carbon mass balance method measures the amounts of CO and CO_2 produced during co-processing and adjusts the mass of biogenic feedstock to exclude carbon lost as CO and CO_2 (Schimmel et al., 2018). The total mass balance method is a further variation of the carbon balance method and also considers the H_2O losses that occur as a result of co-processing. Any H_2O added as steam is excluded from the total mass balance.

If the fossil baseline shows negligible CO and CO_2 production, all the CO and CO_2 produced during co-processing is assumed to come from the renewable component (Schimmel et al., 2018). This is deducted from the biogenic carbon content and is used to determine the contribution of the renewable component. This method also assumes that the renewable content in the feed is equally distributed in all the products. Similar to the mass balance based on observed yield, the carbon balance method does not require any new equipment or additional testing as the liquid and gas streams are routinely monitored in a refinery and the measurement is easily integrated into the existing refinery setup (Schimmel et al., 2018). Similar to the mass balance method based on observed yields, the establishment of a baseline and the lack of chemical interactions between the biogenic and fossil components needs to be ensured. Consequently, this method has the same shortcomings as the mass balance method. Past work has shown that the renewable fraction is not distributed equally between all fractions (Pinho et al., 2015, 2017).

Carbon 14 tracking

The C14 carbon dating method is used to identify the amount of renewable carbon present in a fuel or product. It involves post-production analysis and reflects the renewable content in individual fuel products after co-processing. It is based on the principle that the C14 isotope is present in living organisms and has a half-life of

79

~5700 years. Fossil carbon therefore has no C14 and the ratio of C14/C13 is a considered as an accurate reflection of the biogenic content.

In 2004, ASTM International published a standard method for determining the biobased content of solid, liquid and gaseous samples using radiocarbon analysis (ASTM D6866). ASTM D6866 provides two methods for the quantification of bio-based content, including guidelines for sample preparation, analysis and reporting. Method B of this standard utilizes Accelerated Mass Spectrometry (AMS) along with Isotope Ratio Mass Spectrometry (IRMS) techniques to quantify the biogenic content of a given product. As stated in the standard, "Instrumental error can be within 0.1-0.5% (1 relative standard deviation (RSD)), but controlled studies identify an inter-laboratory total uncertainty up to ±3% (absolute)." Method C of the standard uses Liquid Scintillation Counting (LSC) techniques to quantify the biobased content of a product using sample carbon that has been converted to benzene. Method C also has a maximum total error of ±3% (absolute), according to the text in the standard. Method A was removed from the most recent revision of ASTM D6866 due to its low precision.

The advantage of the C14 method is that it is based on the actual measurement of biogenic carbon for each product fraction and does not rely on assumptions used in the other methods. The methodology is clearly described in the ASTM D6866 standard and can be consistently applied. Strict laboratory conditions are required to avoid contamination. It has been reported that the LSC method is less sensitive than AMS (not accurate at low concentrations (below 1-2%), but other techniques are more expensive and more time consuming (Schimmel et al., 2018). Analysis is typically carried out at specialized laboratories, at a significant cost. Although in-house testing is possible, it requires investment in equipment and training of staff. As a result, smaller refineries are unlikely to have in-house facilities.

Apart from the two methods described in the ASTM D6866 standard, researchers have established a modified Direct LSC analysis method with faster sample preparation, good sensitivity and lower cost (termed Method D by the authors) (Edler and Kaihola, 2010; Norton, Cline and Thompson, 2012). However, this method is not in accordance with the current ASTM D6866 standard and has the significant drawback that it is influenced by the colour of the fuel samples. A

80

summary of the various methods covered by ASTM D6866 is outlined in Table 10, and this provides an insight into the costs and requirements of each method (Edler & Kaihola, 2010). While current instrument and analysis cost may be out of date, it is useful as a comparison between the methods.

Table 10. Comparison of different C14 methods (modified from Edler & Kaihola (2010)

	Sample preparation time (h)	Analysis time (min)	Analysis cost (USD)	Instrument cost (000)	Sample size (g)	Contamination risk	Precision (%)
Method B (AMS)	2	20	400	2000	0.001	High	<1
Method C (LSC)	3	1300	250	150	2-10	Low	<2
Method D (Direct LSC)	0.1	360	150	100	5-10	Low	<6

The biggest concern about the C14 method is the $\pm 3\%$ absolute error, as stipulated in ASTM D6866. The origin of the absolute 3% error cited in the ASTM D6866 standard stems from a study conducted by the Iowa State University in 2003 (Oasmaa and Peacocke, 2010). The study comprised of 300-500 bio-based material samples that were sent to several different laboratories within the U.S. for testing. An absolute deviation of 2.6% across all laboratories was found and this was rounded to 3%. However, it has been argued that this absolute error is not justified as the AMS Method B has a much lower standard deviation, less than 1% (Oasmaa and Peacocke, 2010). The researchers who developed the Direct LSC method, which is not currently included in the ASTM standard, found much lower errors in measurement. Companies have made submissions to the California Air Resources Board regarding the most appropriate method for the determination of biogenic content in fuels. They have raised the absolute error of the ASTM 6866 methods as a key concern. As a result, CARB is carrying out a review of the ASTM C14 methods and the validity of the 3% absolute error. Companies such as REG argue that the error is overestimated (Haverly, Fenwick, Patterson and Slade, 2019). The final determination from CARB is still uncertain at the time of writing, although some companies are currently required to use C14.

Another concern for C14 analysis is the practicality of the method. There are no standard procedures for the frequency of sampling or which streams should be measured (not every stream can be easily sampled). Additional sampling not only adds a further burden to the refinery, but also may be a safety hazard if gas samples are required.

Carbon 13

The Los Alamos National Laboratory has been evaluating an alternative method known as stable carbon isotopes (13C/12C, or δ13C) (Mora, Claudia; Li, Zhenghu; Vance, 2016). The method is not ASTM certified and has not been widely applied due to the overlapping of stable C isotope of fossil fuels and bio-oil/biocrudes from C3-type plants that can serve as feedstocks (pine, rice, wheat, etc.). However, the biggest advantages are that the isotope radio mass spectrometers (IRMS) are less expensive than AMS systems (~400k USD vs. millions of dollars). Although a strong correlation between C14 and δ13C (13C/12C) shows promise, more studies are needed to test its applicability to different sources of feedstocks. As Li et. al stated, "the method is only valid when the difference in δ13C values of the feedstocks is significant relative to the precision of the analytical method" (Li et al., 2020).

9.2 DETERMINATION OF CARBON INTENSITY IN THE HYDROTREATER

Co-processing lipids in a diesel hydrotreater is currently the most common co-processing configuration that is used globally. The concept is very close to the processing of lipids in a stand-alone renewable diesel plant and it should result in the reduction of GHG emissions similar to a standalone plant. The processing scheme is shown in Figure 7.
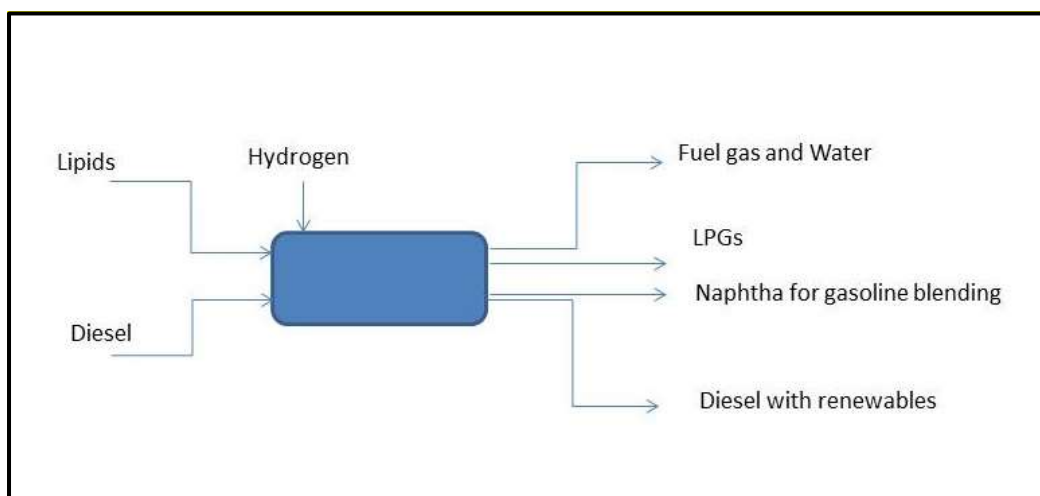
Figure 7 Processing scheme for hydrotreated lipids.

As most of the carbon intensity of the hydrotreating of lipids is from the production of hydrogen, accurate assessments of the incremental hydrogen requirements during co-processing will be critical in determining an accurate assessment of the carbon intensity of the co-processed lipids. The source of hydrogen will therefore have a significant impact on the carbon intensity of the co-processed fuel.

The issue of the incremental hydrogen flow rate is more problematic than determining the distribution of the biogenic carbon in the product streams. This quantification must be done with a mass balance approach which requires a stable baseline. Changes in the sulphur and nitrogen levels of the diesel stream between the diesel-only operations and the co-processing operations will influence the hydrogen demand and will result in an inaccurate assessment of the hydrogen demand for the biogenic portion of the feedstock. Similarly, changes in the finished diesel fuel properties could also impact the calculated hydrogen demand if less cracking or isomerization occurs during the baseline operations compared to the co-processing operations. However, this scenario is less likely to exist than varying sulphur levels in the diesel feed over time (Saddler, Dyk, O'Connor, Ebadian and Su, 2020).

While 75% to 85% of the mass of the biogenic feedstock will end up in the finished diesel stream, there will be some biogenic carbon in the naphtha, LPG, and fuel gas streams. These streams are all co-products and should carry some of the

83

emissions burden of the process. There are three possible approaches to allocation. The streams could receive a credit for displacing the emissions, including combustion emissions, of a fossil fuel equivalent product. The streams could also have a portion of the system emissions allocated to them on a mass or energy content basis. The choice of the best approach depends, in part, on how the co-products are used and on the regulatory requirements (Saddler et al., 2020).

For example, if the fuel gas is used to supply a portion of the energy for hydrogen , then it is most appropriate to give it credit for displacing refinery fuel gas or natural gas. If the naphtha is used as a gasoline blending component and the gasoline is used in a regulatory program such as a clean fuel standard where the emission benefits of the combustion of a biofuel are captured, then allocation by energy content would be the best approach. However, if the naphtha is used to displace a fuel in a jurisdiction that does not recognize the combustion emission benefit, then an argument can be made that it too should be given a displacement credit. In this way, the full emission benefits from the "project" are recognized when determining the emission benefits of the co-processed diesel fuel. Using displacement credits for some or all of the co-products will result in a lower CI than using an energy allocation approach since the displacement approach factors in the difference in combustion emissions between a fossil and biogenic fuel (Saddler et al., 2020).

It should be noted that there is also some hydrogen in the fuel gas stream. The California Air Resources Board considers the net hydrogen demand when they assess the carbon intensity of renewable diesel and co-processed lipids. This provides a larger emission credit for the fuel gas stream than any of the normal allocation approaches since hydrogen is more emission-intensive than natural gas or refinery fuel gas. The carbon intensity of co-processed lipids will be a function of the feedstock carbon intensity and the carbon intensity of the co-processing step. In GHGenius 5.0, the carbon intensity of the processing step for renewable diesel is in the 10 to 12 g CO_2eq/MJ (HHV) and co-processing should be in a similar range.

In summary, determining the LCA of co-processed lipids via hydrotreating should be one of the easier options and it is currently carried out in a number of refineries in the United States and Europe. The C14 approach is being used by the refiners to determine the biogenic content of at least the diesel portion of the

output. Hydrogen consumption is the largest driver of the CI of the finished product and there are standalone facilities that allow a check on the co-processing LCA results. However, the first CARB application (CARB, 2019) for a carbon intensity for co-processing tallow at a refinery (BP Cherry Point) requested a CI that implied a hydrogen consumption rate that was 20 to 30%. This is lower than found at a typical stand-alone renewable diesel plant. This indicates that determining an accurate incremental hydrogen flow rate in an industrial setting may not be straightforward.

Co-processing biocrudes, as opposed to lipids, through a hydrotreater is problematic since most biocrudes are not miscible with diesel fuel without the use of surfactants. Co-processing would likely require some hydrotreating of the biocrude alone before the product would be soluble in a petroleum oil stream. Conceptually the processing system would be the same as the lipid co-processing in a hydrotreater. However, where the hydrotreated lipids provide mostly diesel fuel, the hydrotreated biocrude will provide a range of hydrocarbons from gasoline to heavy fuel oil (D. O'Connor, personal communication).

With the high oxygen content of some biocrudes the hydrogen requirements will be much higher than for lipids, resulting in higher carbon intensities. The hydrogen requirement for standalone renewable diesel plants is about 4 wt% of the renewable diesel produced. The hydrogen requirements for producing an almost oxygen-free refined biocrude ranged from 12 to 20 wt% (Van Dyk, Su, Ebadian, Connor and Lakeman, 2019). Although the products that were produced still required some further processing to meet specifications, the carbon intensity of the production-only stage of the hydrotreated biocrudes ranged from 28 to 52 g CO_2eq/MJ for the hydrotreating stage without any allocation of the emissions to the co-products (or the feedstock production). This is three to five times higher than the emissions for hydrotreating lipids. It should be noted that these results are for a stand-alone hydrotreater facility.

In previous work, which assessed the possible co-processing of biocrudes, surfactants and other chemicals were used to create a stable emulsion of heating oil. The GHG emissions, therefore, included the emissions associated with the production of the chemicals used for the emulsion. As a result, the carbon intensity (CI) of the co-processed fuel is similar to the fossil-based fuel with no real CI reductions obtained (Van Dyk, Su, Ebadian, et al., 2019).

9.3 DETERMINATION OF CARBON INTENSITY IN THE FCC

The processing scheme for an FCC is much more complex than a hydrotreater with the minimum co-processing system boundaries for undertaking an effective LCA summarised in Figure 8.
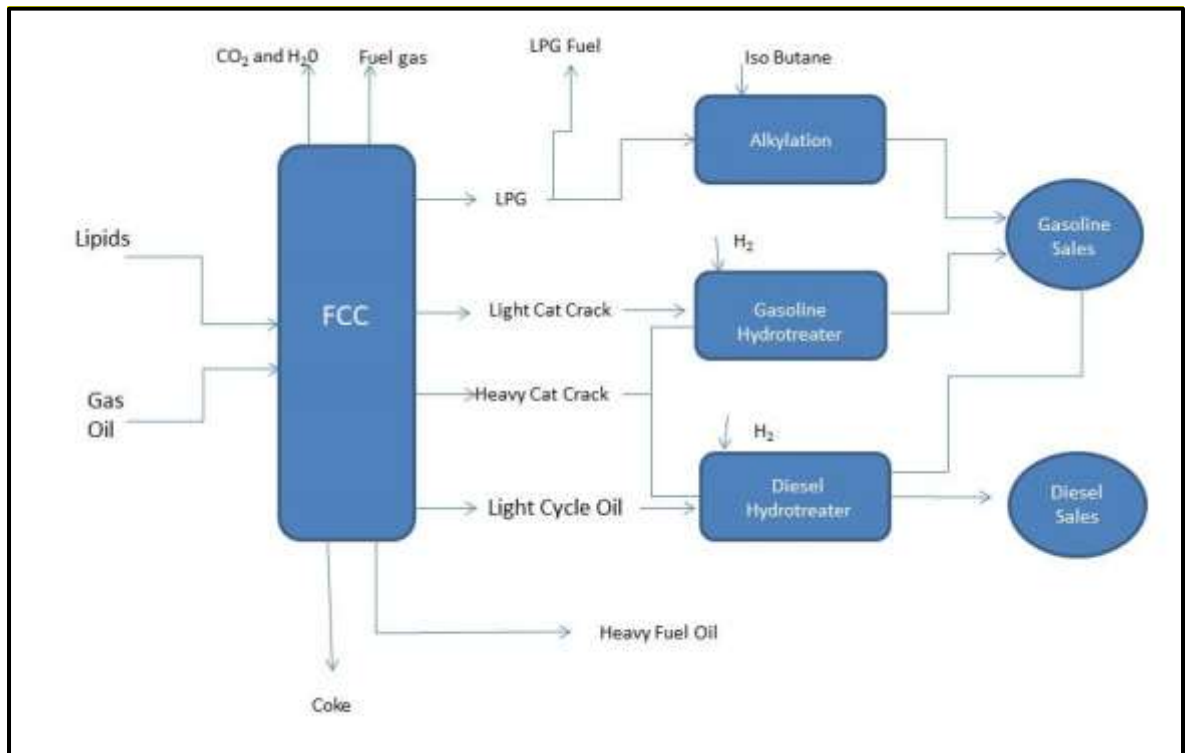

Figure 8 Processing scheme for lipids through the FCC

As mentioned earlier, using a mass balance approach for a commercial FCC unit can be challenging as the noise from the petroleum baseline can be bigger than the signal generated by co-processing biogenic feedstocks (Su et al., 2021).

Although there are relatively few papers in the literature that cover this processing system, some researchers have co-processed canola oil with bitumen in a bench-scale FCC (Ng et al., 2015; Ng, Heshka, Zheng, Wei and Ding, 2019), while others looked at lipids and biocrudes processed through both hydrotreaters and FCC units (Bezergianni et al., 2018). This latter work reported that increased conversion rates could be observed during FCC processing of blends of lipids and petroleum oil compared to processing only petroleum. This is an important observation with implications for the LCA analysis. As indicated earlier, the processing system is much more complex than a hydrotreater system as more streams will need to be measured,

86

including the incremental flow rates and biogenic content. The previous observation that conversion rates can be increased when co-processing means that a mass balance approach, where the change in flow rates is used to determine the biogenic flow rates, will result in incorrect results (Bezergianni et al., 2018). Thus, it is likely that the C14 approach will be needed in this case. However, with biogenic feed rates in the 5 to 10% range and more than a half dozen streams that the biogenic carbon could end up in, the concentration of the biogenic carbon in some of the product streams may be quite low and therefore difficult to quantify with any precision.

It is also likely that the overall biogenic carbon yield in the various products will be slightly lower than it is with a hydrotreater. This is because some of the oxygen in the feed is removed as carbon dioxide and carbon monoxide rather than as water. The ranges for the oxygen balances for different operating conditions reported by Ng are summarized in Table 11 (Ng et al., 2019). However, as the hydrogen requirements are lower than when using a hydrotreater, this should have positive implications for the carbon intensity.

Table 11. Oxygen Balance (Ng et al, 2019)

Component	Low Value	High Value
O_2 as CO	2.9	5.0
O_2 as CO_2	8.0	18.8
O_2 as H_2O	73.8	90.0
Total	84.8	111.4

Measuring the carbon in the oxygenated products indicates that 3.4 to 7.3% of the biogenic carbon in the feedstock is lost through the deoxygenation process. This yield loss will translate into a higher CI as more biogenic C will be required in the feedstock (and therefore more feedstock) for the finished fuels. However, the contribution should be lower than the CI of the hydrogen that is required for hydrotreating the same feedstock. The other factors that impact the carbon intensity of the finished products are the incremental hydrogen requirements in the gasoline and diesel hydrotreaters that follow the FCC. If the refinery has an alkylation unit, the fossil feed to that unit will have to be accounted for if the C14 measurements are taken at the FCC rather than in the finished product tanks.

The allocation approach used for the co-products will have a significant impact on the carbon intensity of the gasoline and diesel fuel, and there is the possibility that some biogenic carbon will be present in the heavy fuel oil (HFO). However, heavy fuel oil use is not included in the California or BC LCFS programs at this time. If the displacement method is used for co-products, then there will be a large co-product credit from the displacement of the bio-HFO compared to fossil HFO. A program like the proposed CFS will presumably use an energy allocation method as all of the refinery products will be included in the program.

The critical data that is required for this pathway is the C14 analysis of all of the output streams from the FCC and/or all of the finished fuel streams. As mentioned previously, the mass balance approach cannot be used due to the chemical reactions that occur in the FCC between the fossil and biogenic feedstocks. As the biogenic content of some of the streams may be quite low, this will make an accurate accounting of the biogenic carbon difficult. Although the contribution of the incremental hydrogen used in the downstream hydrotreaters will be smaller than when the hydrotreating co-processing route is used, there will still be challenges in accurately determining the incremental hydrogen demand when dealing with a potentially varying baseline.

The little information that is available on co-processing biocrudes in an FCC unit (Pinho et al., 2015, 2017) uses a processing system and data requirements that are identical to co-processing lipids. For example, the mass flow rates for all streams need to be measured so that the biogenic carbon yield can be determined. This earlier work only briefly mentions the use of C14 to determine the flows and relies more on a mass balance approach to determine the flow rates (Pinho et al., 2015, 2017). However, there is poor closure of both the oxygen and carbon when the mass balance is used. The U.S. DOE Bioenergy Technologies Office (BETO) gave a presentation based on this work (Chum and Pinho, 2015) and the reported yields based on the mass balance approach are shown in Table 12.

Table 12. BETO Stream Yields (Chum and Pinho, 2015). All values are per kilogram of pyrolysis oil.

	VGO alone (wt. %)	Pyrolysis oil alone at 5% feed rate (calculated wt. %)	Pyrolysis oil alone at 10% feed rate (calculated wt. %)
Dry gas	3.70%	-10.5%	-3.50%
LPG	16.20%	13.8%	0.80%
Gasoline	41.50%	53.9%	28.90%
LCO	17.90%	6.3%	9.30%
Bottoms	13.75%	-17.9%	-0.90%
Coke	6.75%	-1.6%	7.40%
CO	0.10%	18.1%	16.10%
CO_2	0.00%	8.0%	6.00%
H_2O	0.00%	28.0%	35.00%
Total	99.90%	98.10%	99.10%

As mentioned earlier, two of the conditions for applying a mass balance approach is a stable baseline and an absence of chemical reactions between the two classes of feedstock. Several researchers have shown that hydrogen transfer takes place in an FCC between the fossil and renewable components (Mercader, 2010; Pinho et al., 2015). As there were large discrepancies in the results between the 5 and 10% feed rates, this indicated that the mass balance approach was problematic. Thus, there is a need to do carbon and oxygen balances around the inputs and the implied outputs in order to determine the mass balance (Table 13).

Table 13. Biogenic Carbon Balance

	Biogenic Input	Biogenic Output
Feedstock	0.4180	
Dry gas		-0.090
LPG		0.119
Gasoline		0.464
LCO		0.054
Bottoms		-0.154
Coke		-0.014
CO		0.078
CO_2		0.022
Total	0.4180	0.479

Since there is more biogenic carbon coming out of the system than going into the system this is evidence that the mass balance approach does not work for co-processing in an FCC unit. The large negative numbers are also an indication that chemical reactions must be occurring between the fossil and biogenic carbon. About 25% of the biogenic carbon is lost through the deoxygenation process. When a similar analysis was done using oxygen (Table 14) it was apparent that not all of the oxygen is accounted for in the products, although there could be small amounts of oxygen in the hydrocarbon schemes.

Table 14. Oxygen Balance

	Biogenic Input	Biogenic Output
Feedstock	0.5070	
LPG		0.0000
Gasoline		0.0000
LCO		0.0000
Bottoms		0.0000
Coke		0.0000
CO		0.1034
CO_2		0.0582
Water		0.2489
Total	0.5070	0.4105

The data in Table 14 indicate that about half of the oxygen is removed as water and that twice as much is removed as CO as compared to CO_2. Thus, it is reasonable to conclude that essentially all of the carbon shown as CO or CO_2 in the previous table is biogenic carbon.

In earlier work, although Pinho et al. (2017) reported some C14 data, this was not reported for all of the individual streams. Approximately 30% of the biogenic ended up in the liquid products and the other 70% of the biogenic carbon was unaccounted for. As some of the biogenic carbon is removed as CO and CO_2, the rest must be in the solids and gases. However, only a reduction in coke and dry gas was reported, with only the LPG in the non-liquid streams showing an increase.

Thus, the critical data that is required for this pathway is the C14 analysis of all of the output streams from the FCC and/or all of the finished fuel streams. As

90

mentioned earlier, the mass balance approach cannot be used due to the chemical reactions that occur in the FCC between the fossil and biogenic feedstocks. Consequently, there is very little information on the biogenic content of the individual streams, making it very difficult to speculate on even the range of carbon intensities of the derived fuels. If the biogenic carbon is divided approximately equally between the carbon lost in deoxygenation, the carbon in the liquid products and the carbon in the co-products, the choice of which allocation approach to use will have a large impact on the calculated carbon intensity (CI) of the final fuels.

10. The critical role of hydrogen in drop-in biofuel production

The conversion of biogenic feedstocks into drop-in biofuels requires the removal of oxygen and the addition of large amounts of hydrogen, depending on the concentration of oxygen in the feedstock. As mentioned earlier, lipid feedstocks contain about 11% oxygen while biocrudes can contain up to 50% oxygen. Removal of oxygen can take place through the addition of hydrogen (hydrodeoxygenation) or through the removal of CO_2 (decarboxylation) or CO (decarbonylation). Although deoxygenation and decarbonylation can take place without hydrogen, this leads to loss of carbon through CO_2 or CO removal and hydrogen addition.

The higher the oxygen level in the starting feedstock, the more hydrogen will be required to upgrade it into drop-in fuels that are fully fungible with existing vehicles and infrastructure. This principle is illustrated in the hydrogen to carbon "staircase" (Figure 9).
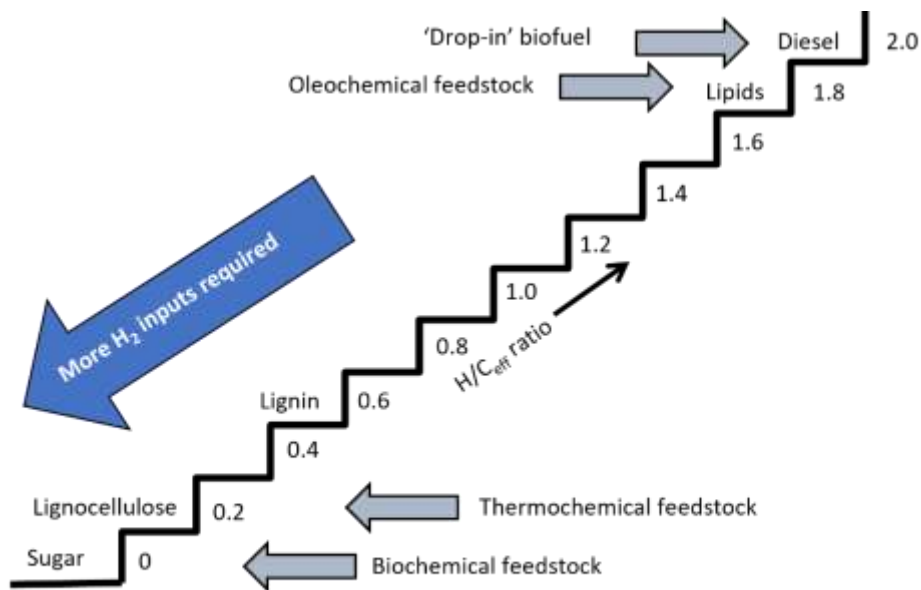
Figure 9: The effective Hydrogen to Carbon ratio "staircase" (Karatzos, Mcmillan and Saddler, 2014)

Large volumes of hydrogen are already used in the petroleum refining sector to upgrade crude oils into finished fuels. Crude oil contains negligible amounts of oxygen and the main use of hydrogen in refineries is to remove sulfur, nitrogen and metals in crudes, as well as hydrocracking heavy crudes into shorter hydrocarbons. As crude oils can differ substantially in sulfur and nitrogen concentration, low quality "sour" crudes have higher sulfur and nitrogen levels and thus require higher hydrogen consumption. The extent of sulfur removal also depends on minimum standards for sulfur and nitrogen in finished fuels to reduce tailpipe emissions of SOx and NOx as more extensive hydrotreating is required. At this point in time, the majority of hydrogen is used for applications in the chemical industry, including ammonia and methanol manufacture. Ammonia manufacture uses about 51% of all commercial hydrogen, while oil refining only uses about 31% (Yukesh Kannah et al., 2021). Thus, competing uses must be considered when estimating the availability of hydrogen for drop-in biofuel production. For example, the development and commercialisation of hydrogen vehicles and hydrogen airplanes will increase hydrogen demand in the future. Similarly, the development of power-to-liquids (PtL) fuels, particularly for aviation, is expected to have a very significant impact on the demand for renewable hydrogen. Ammonia is also considered one of the most promising options as a

92

renewable fuel for the shipping sector, which will also impact demand for sustainable hydrogen.

In summary, the critical impacts of hydrogen in low carbon intensity fuels production are two-fold. Higher consumption of hydrogen leads to increased costs and the source of the hydrogen will have a significant impact on the carbon intensity of the fuel. Thus, hydrogen consumption and the source of hydrogen will have a significant impact on the final carbon intensity of the fuel, based on a life cycle assessment.

As global climate mitigation ambitions increase, it is likely that there will be increased demand for low or zero carbon intensity hydrogen, such as hydrogen produced via the electrolysis of water-based on renewable electricity. Currently, the most economical and most efficient way to produce hydrogen is via steam reforming of natural gas. However, although the production of hydrogen using coal gasification results in considerable carbon emissions, hydrogen obtained via the steam reforming of natural gas also results in significant carbon emissions. The large-scale commercialisation of very low or zero carbon intensity hydrogen will be critical if we are to produce low CI transportation fuels.

10.1 HYDROGEN DEMAND

According to the IEA, the demand for hydrogen is currently around 90 Mt per year, produced predominantly from natural gas and coal ([IEA] - International Energy Agency, 2021). About 76% of dedicated hydrogen production is based on natural gas and almost all the rest is based on coal. Global hydrogen production is responsible for almost 900 $MtCO_2$/y of carbon emissions. Electrolysis only accounts for about 2% of global hydrogen production. If all current dedicated hydrogen production were produced via water electrolysis, it would require an annual electricity demand of 3,600 TWh. This is more than the annual electricity capacity of the European Union, with 617 million m3 of water (hydro) required ([IEA] - International Energy Agency, 2019). To meet the worlds ambitious climate targets by 2050, low carbon intensity hydrogen will need to replace all of the fossil-based hydrogen that is currently used in the refining, chemical and other industries with the electrolysis production route requiring renewable electricity. This will not only result in competing demands for

93

renewable hydrogen, it will also increase competition for the renewable electricity needed by electric vehicles, etc.

As discussed previously, more hydrogen will be needed if co-processing and freestanding production of drop-in biofuels are to expand. A comparison of hydrogen demand for various refinery processing units compared with the hydrogen required for biofuel production is summarised in Table 15, showing that significantly higher renewable hydrogen volumes will be needed to decarbonise transportation fuels.

Table 15. Typical hydrogen consumption for various refinery processes compared with hydrogen demand for green fuels production (AFPM, 2020)

Process	Typical H2 use in scf H2/bbl
Gasoline hydrotreating	450-650
Diesel hydrotreating	450-1,200
Hydrocracking	1,800-2,000
Biofuels	**1,700-2,900**

According to the IRENA Coalition for Action, about 21,000 TWh of renewable electricity will be needed by 2050 if the world is to meet its electrification end-uses and green hydrogen supply chain goals (IRENA Coalition for Action, 2021). Several reports have projected the 2050 demand for renewable electricity, and this ranges from almost 15,000 TWh (IEA) to about 35,000 TWh (Bloomberg New Energy Finance) (IRENA Coalition for Action, 2021). According to the IRENA, nearly 5,000 GW of electrolysing capacity will be needed by 2050 to produce approximately 400 million metric tonnes of green hydrogen per year (IRENA Coalition for Action, 2021).

10.2 PRODUCTION METHODS OF HYDROGEN

Hydrogen has been "colour coded" into grey hydrogen (produced from natural gas forming H_2 and CO_2), blue hydrogen (produced from natural gas to form H_2 and CO_2 but with carbon capture of the CO_2) and green hydrogen (produced using electrolysis and renewable electricity), with other categories also suggested. Some of

the advantages and disadvantages of the three main types of hydrogen are listed in Table 16.

Table 16. Comparison between grey, blue and green hydrogen (Ewing, Israel, Jutt, Talebian and Stepanik, 2020)

	Grey hydrogen	Blue hydrogen	Green hydrogen
Carbon intensity	Highest carbon intensity (94.8-101.4 gCO2eq/MJ)	Low carbon intensity (19.6-34.5 gCO2eq/MJ)	Lowest carbon intensity (0-5.3 gCO2/MJ)
Cost	Lowest cost	Medium cost	Highest cost
Other	Abundant feedstock, but no climate benefits Large scale and centralised production	Abundant feedstock Continued use of fossil industry Suitable areas for CCS must be present	Abundant H20 feedstock Sufficient renewable electricity required Decentralised production and small scale

It has been noted that replacing high-carbon hydrogen with low-carbon hydrogen is an effective way to decrease GHG emissions in the short term ([IEA] - International Energy Agency, 2020). However, at this time, the main process used to produce hydrogen is via the steam reforming of methane (SMR) using natural gas. The two main reactions involved in this conversion are:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{(water gas shift reaction)}$$
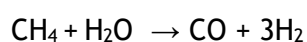
In the first reaction, methane reacts with high-temperature steam to form syngas (CO and H_2). In the second reaction (also called the "water-gas shift" reaction) the CO reacts with steam to produce hydrogen and CO_2. Although methane, usually derived from natural gas, is the predominant feedstock, because of its availability and relatively low cost, a variety of compounds, such as propane, methanol and many light gases, can be used to produce hydrogen. In facilities producing hydrotreated vegetable oils from triglycerides, renewable propane is formed as a by-product. This can be used to produce renewable hydrogen that can be

used for hydroprocessing[22]. Renewable hydrogen can also be produced from methane derived from anaerobic digestion and using steam reforming technology.

Many alternative hydrogen production pathways exist, including electrolysis, partial oxidation, gasification, aqueous phase reforming and biological methods such as dark fermentation. Several types of water electrolysis technologies are at various stages of development, including alkaline (commercial), proton exchange membrane (PEM), solid oxide electrolyser cells (SOEC), and Anion Exchange Membrane (AEM), all having various advantages and disadvantages (International Renewable Energy Agency, 2021). Hydrogen supply is generally divided into "captive" hydrogen, produced at refineries for the production of fuels and chemicals, and "merchant" hydrogen, produced for trading purposes. While both use similar methods for hydrogen production, merchant hydrogen has the added cost of compression/ liquefaction and transportation due to its low energy density.

Various hydrogen sourcing options are available to a biofuel production facility. These include: (1) increasing or building the infrastructure needed for internal hydrogen production; (2) purchasing merchant hydrogen; (3) co-locating the biofuel facility next to a petroleum refinery or facility with excess hydrogen production capacity, called "over-the-fence" hydrogen; or (4) sourcing by-product (waste) hydrogen from an industrial facility.

While the cost of the hydrogen will be a significant concern, the carbon intensity of the hydrogen will be, arguably, more important. Where policies reward low carbon intensity fuels, renewable hydrogen may be economical. It is very likely that the cost of green hydrogen will be linked to the cost of renewable electricity.

10.3 COST OF HYDROGEN PRODUCTION

The cost of hydrogen production depends on the type of technology used and the region of production. As mentioned earlier, the lowest cost hydrogen is produced

---

[22] Neste has used propane, derived from hydrotreating of triglycerides, as a source of hydrogen in their refineries

via the steam transformation of natural gas without carbon capture and utilisation or storage (CCUS). Costs will vary depending on the price of natural gas in that region. Electrolysis is a low carbon option but only becomes competitive with natural gas and CCUS at prices of USD10-40/MWh ([IEA] - International Energy Agency, 2019). However, a region with low cost, renewable electricity (or nuclear power) may cheaply produce hydrogen through electrolysis, especially when natural gas is expensive.

The cost of hydrogen via steam reforming of natural gas varies from $1.43/kg H2 to $2.27/kg H2 with CCUS (USDOE, 2020). The cost of hydrogen production via electrolysis is estimated to be between $5/kg-to-$6/kg H2 with electricity derived from nuclear or wind resources (USDOE, 2020). As a key challenge in the development of drop-in biofuels will be finding cheap, sustainable sources of hydrogen, there is an opportunity to synergise with existing refineries. This could be done through increased integration, such as co-processing or co-location of a biorefinery with a petroleum refinery, to share hydrogen infrastructure or access "over-the-fence" hydrogen.

11. Conclusions

The production and use of drop-in biofuels will be essential if the world is to meet its carbon reduction targets, specifically for hard-to-decarbonise sectors such as aviation and marine. However, the production of lower-carbon-intensive (CI) fuels must rapidly increase if targets, such as those outlined in COP26, are to be met. Development of drop-in biofuels has been slow and only limited volumes are currently available. The only **fully** commercial process that is currently used to produce drop-in biofuels is via the hydrotreatment of lipids, using the oleochemical pathway (hydrotreated vegetable oils, HVO, or hydrotreated esters and fatty acids, HEFA). Other drop-in biofuel technologies are moving towards commercialisation, with many facilities under construction or planned, but at a slow pace.

Co-processing biogenic feedstocks (lipids, biocrudes, etc.) within existing petroleum refineries can provide an alternative, fast and effective way to rapidly increase the volumes of drop-in, lower carbon-intensive fuels. Co-processing has the potential to produce large volumes of drop-in, lower-CI fuels but will require significant volumes of biogenic feedstocks.

Two main feedstocks can be used for co-processing: lipids (fats, oils and greases (FOGs)) and biomass derived biocrudes produced via technologies such as fast pyrolysis and hydrothermal liquefaction. The most likely insertion points of these feedstocks within refineries will be at the hydrotreater or the fluid catalytic cracker, depending on the desired products and risk mitigation. Lipids are currently co-processed at a commercial scale in various locations around the world and this will expand. However, in the longer term, feedstock availability, cost and sustainability will place a limitation on the growth lipid co-processing. Thus, it is likely that biocrude liquid intermediates will become significant co-processing feedstocks.

Co-processing biogenic feedstocks in a refinery poses some risks for the refiner in terms of operational challenges, fuel quality issues, corrosion of metallurgy, inactivation of catalysts, increased hydrogen demand, etc. Risk mitigation requires an understanding of the potential impacts of biogenic feeds and the steps that need to be taken to reduce and overcome risks. Commercial experience has indicated that co-processing lipids at low ratios (e.g. 5%) has a relatively minor impact on refinery operations and the associated risks can be managed with limited investment in new and modified infrastructure. However, as

98

co-processing ratios increase it is likely that much greater investment will be required and more extensive refinery modifications will be needed. Although some infrastructure and operational modifications will be required to facilitate co-processing at an existing refinery, the cost is likely to be significantly lower than building dedicated standalone biorefinery.

Determining the actual renewable content in the final fuel is essential and the methods used to track the biogenic content (green molecules) of co-processed fuels need to be refined. Although the quantification of the carbon intensity of feedstocks is relatively well-established, the life cycle assessment (LCA) of the co-processed fuels is more complex. Typically, life cycle analysis is not carried out for the whole refinery, but rather only for the processing unit where the co-processing takes place.

Although carbon 14 measurements are considered to be the "gold standard" way of determining renewable carbon content, this assessment requires expensive equipment, skilled technicians, etc., and is usually done offsite. At low biofeed concentrations, the carbon 14 (ASTM D6866) method also has a high uncertainty.

Other methods, such as the mass balance based on observed yields, (also known as the step-change mass balance method), can be used to assess the effectiveness of co-processing compared to fossil feedstock baseline. Although this method is cheaper and easier for refiners to carry out using existing equipment, it has several shortcomings such as the need for a stable baseline and an accurate closure of the mass balance. It also assumes that no interaction occurs between fossil and biogenic molecules. These conditions are not met during co-processing in the FCC and further work is necessary to refine the methods for measuring carbon intensity in this processing unit.

While co-processing of biocrudes will become more significant in the future, significant research and extensive data will be needed to resolve associated challenges.

References

[IEA] - International Energy Agency. (2019), *The future of hydrogen*., https://doi.org/10.1016/S1464-2859(12)70027-5.

[IEA] - International Energy Agency. (2020), "Hydrogen – Analysis - IEA," https://www.iea.org/reports/hydrogen (accessed February 8, 2021).

[IEA] - International Energy Agency. (2021), *Global Hydrogen Review*., Paris.

R. Abhari et al. (2013), "US9523041B2 - Reducing pressure drop buildup in bio-oil hydroprocessing reactors - Google Patents," https://patents.google.com/patent/US9523041B2/en (accessed May 4, 2021).

AFPM. (2020), "Getting the Most From Your Hydrogen Plant, Part 1 | American Fuel & Petrochemical Manufacturers," *webinar*, https://www.afpm.org/node/13876 (accessed May 14, 2021).

F. A. Agblevor et al. (2012), "Co-processing of standard gas oil and biocrude oil to hydrocarbon fuels," *Biomass and Bioenergy*, Vol. 45, pp. 130–137, Elsevier Ltd, https://doi.org/10.1016/j.biombioe.2012.05.024.

M. Al-Sabawi and J. Chen. (2012), "Hydroprocessing of Biomass-Derived Oils and Their Blends with Petroleum Feedstocks: A Review," *Energy & Fuels*, Vol. 26/9, pp. 5373–5399, American Chemical Society, https://doi.org/10.1021/ef3006405.

M. Al-Sabawi, J. Chen and S. Ng. (2012), "Fluid catalytic cracking of biomass-derived oils and their blends with petroleum feedstocks: A review," *Energy and Fuels*, Vol. 26/9, pp. 5355–5372, https://doi.org/10.1021/ef3006417.

S. Arbogast et al. (2017a), "Commercialization of pyrolysis oil in existing refineries - Part II," *Hydrocarbon Processing*, Vol. b/FEBRUARY, pp. 29–38.

S. Arbogast et al. (2017b), "Commercialization of pyrolysis oil in existing refineries - Part 1," *Hydrocarbon Processing*, Vol. a/JANUARY, pp. 27–30.

Argusmedia. (2021), "Demystifying Global Sustainable Aviation Fuel."

M. Argyle and C. Bartholomew. (2015), "Heterogeneous Catalyst Deactivation and Regeneration: A Review," *Catalysts*, Vol. 5/1, pp. 145–269, https://doi.org/10.3390/catal5010145.

ASTM. (2018), "Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration," https://www.astm.org/Standards/D664.htm.

S. M. Banerjee and R. K. Hoehn. (2014), "Hydrotreating methods and hydrotreating systems,"

Patent US 8,911,514 B2, Vol. 2/12.

B. Van De Beld et al. (2021), *Polar and non-polar components in Fast Pyrolysis Bio-Oil in relation to REACH registration . Polar and non-polar components in Fast Pyrolysis Bio-Oil in relation to REACH registration .*

F. Bertoncini and K. Marchand. (2011), "Methods of hydrotreating a mixture made up of oils of animal or vegetable origin and of petroleum cuts with intermediate stripping," *Patent US 7,872,165 B2*, Vol. 2/12.

S. Bezergianni et al. (2018), "Refinery co-processing of renewable feeds," *Progress in Energy and Combustion Science*, Vol. 68, pp. 29–64, https://doi.org/10.1016/j.pecs.2018.04.002.

S. Bezergianni, V. Dagonikou and S. Sklari. (2016), "The suspending role of H2O and CO on catalytic hydrotreatment of gas-oil; Myth or reality?," *Fuel Processing Technology*, Vol. 144, pp. 20–26, Elsevier B.V., https://doi.org/10.1016/j.fuproc.2015.12.007.

P. Biller and A. Roth. (2017), "Hydrothermal liquefaction: A promising pathway towards renewable jet fuel," *Biokerosene: Status and Prospects* (pp. 607–635), https://doi.org/10.1007/978-3-662-53065-8_23.

K. Bitnere and S. Y. Searle. (2017), *Effective Policy Design for Promoting Investment in Advanced Alternative Fuels.*, http://www.theicct.org/sites/default/files/publications/Advanced-alternative-fuels_ICCT-white-paper_21092017_vF.pdf.

M. P. Brady et al. (2017), "Corrosion of stainless steels in the riser during co-processing of bio-oils in a fl uid catalytic cracking pilot plant ☆," *Fuel Processing Technology*, Vol. 159, pp. 187–199, Elsevier B.V., https://doi.org/10.1016/j.fuproc.2017.01.041.

A. Brown et al. (2020), "Advanced Biofuels – Potential for Cost Reduction, IEA Bioenergy: Task 41: 2020:01," pp. 1–88, https://www.ieabioenergy.com/wp-content/uploads/2020/02/T41_CostReductionBiofuels-11_02_19-final.pdf.

California Air Resources Board. (2017), *Draft discussion paper*.

D. Castello and L. Rosendahl. (2018), *Coprocessing of pyrolysis oil in refineries*, *Direct Thermochemical Liquefaction for Energy Applications*, Elsevier Ltd., https://doi.org/10.1016/B978-0-08-101029-7.00008-4.

D Castello and L. Rosendahl. (2018), "Direct Thermochemical Liquefaction for Energy Applications Coprocessing of pyrolysis oil in refineries," https://doi.org/10.1016/B978-0-08-101029-7.00008-4.

A. Centeno, A. Laurent and B. Delmon. (1995), "Influence of the Support of CoMo Sulfide Catalysts and of the Addition of Potassium and Platinum on the Catalytic Performances for the Hydrodeoxygenation of Carbonyl, Carboxyl, and Guaiacol-Type Molecules," *Journal of Catalysis*, Vol. 154/2, pp. 288–298, https://doi.org/10.1006/jcat.1995.1170.

J. Chen, H. Farooqi and C. Fairbridge. (2013), "Experimental study on co-hydroprocessing canola oil and heavy vacuum gas oil blends," *Energy and Fuels*, Vol. 27/6, pp. 3306–3315, https://doi.org/10.1021/ef4005835.

E. Christensen et al. (2016), "Acid Number Determination of Pyrolysis Bio-oils using Potentiometric Titration Laboratory Analytical Procedure (LAP) Acid Number Determination of Pyrolysis Bio-oils using Potentiometric Titration Laboratory Analytical Procedure," March.

H. L. Chum and A. Pinho. (2015), "U.S. DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review Excerpt* 2.4.2.303 Brazil Bilateral: Petrobras-NREL CRADA."

K. Y. Cole, P. Hanks and W. E. Lewis. (2011), "Reducing hydrogen consumption in hydrotreating of biocomponent feeds," *Patent No.: US 2011/0054230 A1*, Vol. 1/19.

CONCAWE. (2020), *Exploring possible pathways for the EU refining system to contribute to a low co2 economy in the 2030-2050 time frame*.

J. Cooper. (2017), *Statistical Report.*, *FuelsEurope*, https://www.fuelseurope.eu/wp-content/uploads/2017/06/20170704-Graphs_FUELS_EUROPE-_2017_WEBFILE.pdf.

S. Czernik and A. Bridgwater. (2004), "Overview of applications of biomass fast pyrolysis oil," *Energy & Fuels*, 12, pp. 590–598.

Dan Szeezil. (2021), "COPROCESSING BIOCRUDES IN AN FCC TO PRODUCE RENEWABLE FUELS," *SINTEF coprocessing workshop*.

Q. Debuisschert et al. (2014), "Two-step hydrotreating of a feed derived from a renewable source using a first, metallic catalyst and a second, sulphurized, catalyst," *Patent No.: US 8,674,151 B2*, Vol. 2/12.

A. Dimitriadis et al. (2021), "Bio-based refinery intermediate production via hydrodeoxygenation of fast pyrolysis bio-oil," *Renewable Energy*, Vol. 168, pp. 593–605, https://doi.org/10.1016/j.renene.2020.12.047.

B. Donnis et al. (2009), "Hydroprocessing of bio-oils and oxygenates to hydrocarbons. Understanding the reaction routes," *Topics in Catalysis*, Vol. 52/3, pp. 229–240, https://doi.org/10.1007/s11244-008-9159-z.

V. P. Doronin et al. (2013), "Catalytic cracking of vegetable oils and vacuum gas oil," *Fuel*,

Vol. 106, pp. 757–765, https://doi.org/10.1016/j.fuel.2012.11.027.

S. van Dyk et al. (2019), "Potential synergies of drop-in biofuel production with further co-processing at oil refineries," *Biofuels, Bioproducts and Biorefining*, John Wiley & Sons, Ltd, https://doi.org/10.1002/bbb.1974.

S. Van Dyk, J. Su, J. D. Mcmillan et al. (2019), *"DROP-IN" BIOFUELS: The key role that co-processing will play in its production*.

S. Van Dyk, J. Su, M. Ebadian et al. (2019), "Potential yields and emission reductions of biojet fuels produced via hydrotreatment of biocrudes produced through direct thermochemical liquefaction," *Biotechnology for Biofuels*, pp. 1–12, BioMed Central, https://doi.org/10.1186/s13068-019-1625-2.

S. Van Dyk and et al. (2019), *Assessment of likely maturation pathways for production of biojet fuel from forest residue.*, http://task39.sites.olt.ubc.ca/files/2019/11/GARDN-NEC-21-ATM-project-final-report-public-release.pdf.

N. Economides et al. (2017), *chevron*.

R. Edler and Kaihola. (2010), "Differentiation between fossil and biofuels by liquid scintillation beta spectrometry – direct method," Vol. 55/September 2009, pp. 127–131.

R. Egeberg et al. (2011), "Industrial-scale production of renewable diesel," *Petroleum Technology Quarterly*, Vol. 16/3.

R. G. Egeberg, N. H. Michaelsen and L. Skyum. (2010), "Novel hydrotreating technology for production of green diesel," p. 21, http://www.topsoe.com/business_areas/refining/~/media/PDF files/Refining/novel_hydrotreating_technology_for_production_of_green_diesel.ashx.

D. C. Elliott. (2013), "Transportation fuels from biomass via fast pyrolysis and hydroprocessing," *Wiley Interdisciplinary Reviews: Energy and Environment*, Vol. 2/5, pp. 525–533, https://doi.org/10.1002/wene.74.

M. Ewing et al. (2020), *Hydrogen on the path to net-zero emissions*.

M. Ferrari et al. (2001), "CoMo/carbon hydrodeoxygenation catalysts: influence of the hydrogen activity of a CoMo/carbon catalyst," *Catalysis Today*, Vol. 65/2-4, pp. 257–264.

J. Ferrell, M. V Olarte and A. Padmaperuma. (2015), "DOE BETO 2015 Project Peer Review: Conversion R&D," March.

G. Fiori et al. (2021), "Eni ' s approach on co-processing for Biofuel production," *SINTEF coprocess*.

G. Fogassy et al. (2010), "Biomass derived feedstock co-processing with vacuum gas oil for second-generation fuel production in FCC units," *Applied Catalysis B: Environmental*, Vol. 96/3–4, pp. 476–485, Elsevier B.V., https://doi.org/10.1016/j.apcatb.2010.03.008.

G. Fogassy et al. (2012), "The fate of bio-carbon in FCC co-processing products," *Green Chemistry*, Vol. 14/5, p. 1367, https://doi.org/10.1039/c2gc35152h.

B. A. Freel and G. Robert. (2015), "Fluidized catalytic cracker riser quench system," *US Patent No.: US 2015/006576.0 A1*, Vol. 1/19.

C. Freeman, S. Jones and A. Padmaperuma. (2013), "Initial assessment of US refineries for purposes of potential bio-based oil insertions," April, http://www.pnl.gov/main/publications/external/technical_reports/pnnl-22432.pdf.

J. R. Gomes et al. (2013), "Process for hydrotreating biomass oil diluted in a refinery stream of petroleum hydrocarbons," *US Patent no: US8,507,738 B2*, Vol. 2/12.

K. Gong et al. (2014), "Integrated FCC/biomass pyrolysis," *Pub. No.: US 2014/0341784 A1*, Vol. 1/19.

M. B. Griffin et al. (2018), "Driving towards cost-competitive biofuels through catalytic fast pyrolysis by rethinking catalyst selection and reactor configuration," *Energy & Environmental Science*, Vol. Accepted w, https://doi.org/10.1039/C8EE01872C.

P. Guay et al. (2016), "Method of removing a contaminant from a contaminant-containing biological composition useful as a biofuel feedstock," *US Patent no: 2016/0340605 A1*, Vol. 1/9.

N. J. Gudde and J. W. Shabaker. (2014), "Methods and units for mitigation of carbon oxides during hydrotreating," *US patent US 8,668,823 B2*, Vol. 2/12.

Haldor Topsoe. (2021), *Avoid pressure drop build-up and premature reactor shutdowns.*, https://www.topsoe.com/processes/pressure-drop-control (accessed May 4, 2021).

K. Hauge and R. Allen. (2021), "Co-processing experience and a first view on pyrolysis oil," *SINTEF coprocessing workshop*.

M. R. Haverly et al. (2019), "Biobased carbon content quantification through AMS radiocarbon analysis of liquid fuels," *Fuel*, Vol. 237/October 2018, pp. 1108–1111, Elsevier, https://doi.org/10.1016/j.fuel.2018.10.081.

P. Havlik et al. (2013), "Methods for the removal of phosphorous," *Patent No.: US 8,575,409 B2*, Vol. 2/12.

J. Hoffmann, C. U. Jensen and L. A. Rosendahl. (2016), "Co-processing potential of HTL bio-crude at petroleum refineries – Part 1: Fractional distillation and characterization,"

104

Fuel, Vol. 165, pp. 526–535, Elsevier, https://doi.org/10.1016/J.FUEL.2015.10.094.

G. W. Huber, S. Iborra and A. Corma. (2006), "Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering," *Chemical Reviews*, Vol. 106/9, pp. 4044–4098, https://doi.org/10.1021/cr068360d.

G. W. Huber, P. O'Connor and A. Corma. (2007), "Processing biomass in conventional oil refineries: Production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures," *Applied Catalysis A: General*, Vol. 329, pp. 120–129, https://doi.org/10.1016/j.apcata.2007.07.002.

A. Ibarra et al. (2016), "Synergy in the Cracking of a Blend of Bio-oil and Vacuum Gasoil under Fluid Catalytic Cracking Conditions," *Ind. Eng. Chem. Res.*, Vol. 55/7, pp. 1872–1880, https://doi.org/10.1021/acs.iecr.5b04502.

ICF. (2021), *Fueling Net Zero*.

International Renewable Energy Agency. (2021), *Supply Hydrogen*, International Renewable Energy Agency, Abu Dhabi.

IRENA Coalition for Action. (2021), *Decarbonising end-use sectors. Practical Insights on green hydrogen.*, Abu Dhabi, https://doi.org/10.1007/978-3-030-33554-0_11.

J. Jacobs. (2018), "Unlocking Billions of Gallons of Installed Capacity for the Production of Cellulosic Fuels," November.

J. Jechura. (2016), "Hydroprocessing: Hydrotreating & Hydrocracking," *Colorado School of Mines Lectures*.

Ł. Jęczmionek and K. Porzycka-Semczuk. (2014), "Hydrodeoxygenation, decarboxylation and decarbonylation reactions while co-processing vegetable oils over a NiMo hydrotreatment catalyst. Part I: Thermal effects - Theoretical considerations," *Fuel*, Vol. 131, pp. 1–5, https://doi.org/10.1016/j.fuel.2014.04.055.

C. U. Jensen, J. Hoffmann and L. A. Rosendahl. (2015a), "Co-processing potential of HTL bio-crude at petroleum refineries. Part 2: A parametric hydrotreating study," *Fuel*, Vol. 165, pp. 536–543, Elsevier Ltd, https://doi.org/10.1016/j.fuel.2015.08.047.

C. U. Jensen, J. Hoffmann and L. A. Rosendahl. (2015b), "Co-processing potential of HTL bio-crude at petroleum refineries. Part 2: A parametric hydrotreating study," *Fuel*, Vol. 165, pp. 536–543, Elsevier Ltd, https://doi.org/10.1016/j.fuel.2015.08.047.

D. S. J. Jones and P. P. Pujadó. (2006), *Handbook of petroleum processing*, Springer Science & Business Media.

B. I. Kamara and J. Coetzee. (2009), "Overview of high-temperature Fischer-Tropsch gasoline

and diesel quality," *Energy and Fuels*, Vol. 23/4, pp. 2242–2247, https://doi.org/10.1021/ef800924z.

S. Karatzos, J. D. McMillan and J. N. Saddler. (2014), *The Potential and Challenges of Drop-in Biofuels The Potential and Challenges of Drop-in Biofuels*, IEA Bioenergy Task Force (Volume 39).

S. Karatzos, J. Mcmillan and J. Saddler. (2014), "The potential and challenges of 'drop in' biofuels," *IEA Bioenergy Task*, August 2013, p. 21, https://doi.org/10.1016/j.cattod.2008.07.001.

J. R. Keiser et al. (2014), "Bio-Oil Properties and Effects on Containment Materials," *Corrosion conference* (pp. 1–12).

J. R. Keiser et al. (2016), "Materials Issues in Thermochemical Production, Processing, and Utilization of Bio-Oil," *Corrosion conference*, 7867, pp. 1–16.

G. Kothandaraman, S. Uppili and J. Yao. (2011), "Production of hydrocarbon from high free fatty acid containing feedstock," *US Patent No. US 2011 / 0152588 A1*, Vol. 1/19, pp. 21-24.

D. Kubička and J. Horáček. (2011), "Deactivation of HDS catalysts in deoxygenation of vegetable oils," *Applied Catalysis A: General*, Vol. 394/1–2, pp. 9–17, https://doi.org/10.1016/j.apcata.2010.10.034.

T. Lammens. (2021), "Advanced Biofuels from Fast Pyrolysis Bio-Oil," *SINTEF coprocessing workshop*, http://www.etipbioenergy.eu/images/WS_Emerging_Technologies_Presentations/04 Advanced Biofuels from Fast Pyrolysis Bio-Oil - Lammens.pdf.

D. Lamprecht, L. P. Dancuart and K. Harrilall. (2007), "Performance synergies between low-temperature and high-temperature Fischer-Tropsch diesel blends," *Energy and Fuels*, Vol. 21/5, pp. 2846–2852, https://doi.org/10.1021/ef0701283.

I. Landälv and L. Waldheim. (2017), "Building up the future - Cost of Biofuel."

J. Lange. (2015), "Renewable Feedstocks : The Problem of Catalyst Deactivation and its Mitigation," *Angewandte*, pp. 13186–13197, https://doi.org/10.1002/anie.201503595.

L. Leng et al. (2018), "Biodiesel microemulsion upgrading and thermogravimetric study of bio-oil produced by liquefaction of different sludges," *Energy*, Vol. 153/x, pp. 1061–1072, Elsevier Ltd, https://doi.org/10.1016/j.energy.2018.04.087.

E. Lewis, T. Mizan and Z. Hou. (2013), "Staged co-processing of biofeeds for manufacture of diesel range hydrocarbons," *Patent No. US 8,551,327 B2*, Vol. 2/12.

Z. H. Li et al. (2020), "Quantitative Determination of Biomass-Derived Renewable Carbon in Fuels from Coprocessing of Bio-Oils in Refinery Using a Stable Carbon Isotopic Approach," *ACS Sustainable Chemistry and Engineering*, Vol. 8/47, pp. 17565–17572, https://doi.org/10.1021/acssuschemeng.0c07323.

M. B. Linck. (2016), "Co-processing for control of hydropyrolysis processes and products thereof," *International patent W O 2016/176255 A1*, 12.

C. Lindfors et al. (2014), "Fractionation of bio-oil," *Energy and Fuels*, Vol. 28/9, pp. 5785–5791, https://doi.org/10.1021/ef500754d.

C. Lindfors et al. (2015), "Co-processing of dry bio-oil, catalytic pyrolysis oil, and hydrotreated bio-oil in a micro activity test unit," *Energy and Fuels*, Vol. 29/6, pp. 3707–3714, https://doi.org/10.1021/acs.energyfuels.5b00339.

P. Manara, S. Bezergianni and U. Pfisterer. (2018), "Study on phase behavior and properties of binary blends of bio-oil/fossil-based refinery intermediates: A step toward bio-oil refinery integration," *Energy Conversion and Management*, Vol. 165/November 2017, pp. 304–315, https://doi.org/10.1016/j.enconman.2018.01.023.

T. Marker. (2005), "Opportunities for biorenewables in oil refineries," *US Department of Energy. Contract number DE-FG36-05GO15085*, Vol. Final tech, https://doi.org/10.1016/0165-1633(91)90054-O.

T Marker. (2015), "Refinery Upgrading of Hydropyrolysis Oil from Biomass," *US DOE Technical Report Award DE-EE-0005992*.

Terry Marker. (2015), "Refinery Upgrading of Hydropyrolysis Oil from Biomass," *Presentation DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review*, Gas Technology Institute, Des Plaines, IL (United States).

D. Meier et al. (2013), "State-of-the-art of fast pyrolysis in IEA bioenergy member countries," *Renewable and Sustainable Energy Reviews*, Vol. 20, pp. 619–641, Elsevier, https://doi.org/10.1016/j.rser.2012.11.061.

Juan A Melero et al. (2010), "Storage stability and corrosion studies of renewable raw materials and petrol mixtures : A key issue for their co-processing in refinery units," *Fuel*, Vol. 89/3, pp. 554–562, Elsevier Ltd, https://doi.org/10.1016/j.fuel.2009.09.026.

Juan A. Melero et al. (2010), "Production of biofuels via the catalytic cracking of mixtures of crude vegetable oils and nonedible animal fats with vacuum gas oil," *Energy and Fuels*, Vol. 24/1, pp. 707–717, https://doi.org/10.1021/ef900914e.

J. A. Melero, J. Iglesias and A. Garcia. (2012), "Biomass as renewable feedstock in standard

refinery units. Feasibility, opportunities and challenges," *Energy & Environmental Science*, Vol. 5/6, p. 7393, https://doi.org/10.1039/c2ee21231e.

F. D. M. Mercader. (2010), *Pyrolysis oil upgrading for co-processing in standard refinery units*, https://doi.org/10.3990/1.9789036530859.

B. J. Mezza, A. Bhattacharya and S. Lupton. (2014), "Process for removing metals from tallow," *Patent No.US 8,912,351 B2*, Vol. 2/12.

F. de Miguel Mercader et al. (2010), "Production of advanced biofuels: Co-processing of upgraded pyrolysis oil in standard refinery units," *Applied Catalysis B: Environmental*, Vol. 96/1–2, pp. 57–66, Elsevier B.V., https://doi.org/10.1016/j.apcatb.2010.01.033.

F. De Miguel Mercader et al. (2011), "Hydrodeoxygenation of pyrolysis oil fractions: Process understanding and quality assessment through co-processing in refinery units," *Energy and Environmental Science*, Vol. 4/3, pp. 985–997, https://doi.org/10.1039/c0ee00523a.

Z. Mora, Claudia; Li, Zhenghu; Vance. (2016), *Bio-Carbon Accounting for Bio-oil Co-processing: 14C and 13C/12C*.

S. H. Ng et al. (2015), "FCC coprocessing oil sands heavy gas oil and canola oil . 1 . Yield structure," *Fuel*, Vol. 156, pp. 163–176, Elsevier Ltd, https://doi.org/10.1016/j.fuel.2015.03.077.

S. H. Ng et al. (2019), "FCC coprocessing oil sands heavy gas oil and canola oil. 3. Some cracking characteristics," *Green Energy and Environment*, Vol. 4/1, pp. 83–91, Elsevier Ltd, https://doi.org/10.1016/j.gee.2018.03.004.

G. A. Norton, A. M. Cline and G. C. Thompson. (2012), "Use of radiocarbon analyses for determining levels of biodiesel in fuel blends – Comparison with ASTM Method D7371 for FAME," *Fuel*, Vol. 96, pp. 284–290, Elsevier Ltd, https://doi.org/10.1016/j.fuel.2012.01.026.

A. Oasmaa and C. Peacocke. (2010), *Properties and fuel use of biomass-derived fast pyrolysis liquids. A guide*.

OPEC. (2017), *World oil outlook*, *The Leading Edge* (Volume 4), https://doi.org/10.1190/1.1439163.

OPEC. (2020), *World oil outlook.*, *World Oil Outlook*, Vienna, Austria, https://doi.org/10.1190/1.1439163.

V. Paasikallio, B. Toukoniitty and J.-P. Pasanen. (2019), "Enhancing co-processing of lignocellulose by pyrolysis oil by enhancing its compatibility with typical oil refinery

hydrocarbon feed," *International Patent no: WO 2019/002445 Al*, 12.

H. De Paz Carmona et al. (2019), "Co-processing of straight run gas oil with used cooking oil and animal fats," *Fuel*, Vol. 254/February, p. 115583, Elsevier, https://doi.org/10.1016/j.fuel.2019.05.166.

F. Pelardy et al. (2016), "Hydrodésulfuration profonde de coupes essences de FCC et gazoles. Comparaison de l'effet du CO, un sous-produit de transformation de la biomasse," *Comptes Rendus Chimie*, Vol. 19/10, pp. 1266–1275, https://doi.org/10.1016/j.crci.2015.12.006.

A. Pinheiro et al. (2011), "Impact of the presence of carbon monoxide and carbon dioxide on gas oil hydrotreatment: Investigation on liquids from biomass cotreatment with petroleum cuts," *Energy and Fuels*, Vol. 25/2, pp. 804–812, https://doi.org/10.1021/ef1012769.

A. D. R. Pinho et al. (2014), "Production of lignocellulosic gasoline using fast pyrolysis of biomass and a conventional refining scheme," *Pure and Applied Chemistry*, Vol. 86/5, pp. 859–865, https://doi.org/10.1515/pac-2013-0914.

A. D. R. Pinho et al. (2015), "Co-processing raw bio-oil and gasoil in an FCC Unit," *Fuel Processing Technology*, Vol. 131, pp. 159–166, Elsevier B.V., https://doi.org/10.1016/j.fuproc.2014.11.008.

A. de R. Pinho et al. (2009), "Catalytic Cracking Process for the Production of Diesel From Vegetable Oils," *US Patent No.: US 7,540,952 B2*, Vol. 1/12, pp. 0–9, https://doi.org/10.1057/9780230607156.

A. de R. Pinho et al. (2017), "Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production," *Fuel*, Vol. 188, pp. 462–473, The Authors, https://doi.org/10.1016/j.fuel.2016.10.032.

R. Pujro et al. (2019), "Hydrogen Transfer between Hydrocarbons and Oxygenated Compounds in Coprocessing Bio-Oils in Fluid Catalytic Cracking," *Energy & Fuels*, Vol. 33, pp. 6473–6482, research-article, American Chemical Society, https://doi.org/10.1021/acs.energyfuels.9b01133.

M. M. Ramirez Corredores and V. S. Iglesias. (2016), "Production of renewable biofuels," *US Patent no: US9,447,338 B2*.

J. A. Ramirez, R. J. Brown and T. J. Rainey. (2017), "Liquefaction biocrudes and their petroleum crude blends for processing in conventional distillation units," *Fuel Processing Technology*, Vol. 167/August, pp. 674–683, Elsevier, https://doi.org/10.1016/j.fuproc.2017.08.022.

B. S. Rana et al. (2013), "Transportation fuels from co-processing of waste vegetable oil and gas oil mixtures," *Biomass and Bioenergy*, Vol. 56, pp. 43–52, Elsevier Ltd, https://doi.org/10.1016/j.biombioe.2013.04.029.

A. Ray and S. M. Banerjee. (2016), "Methods and apparatuses for co-processing pyrolysis oil," *International patent no: WO 2016/100003 A2*, 12.

G. F. Rispoli et al. (2015), "Biorefinery and method for revamping a conventional refinery of mineral oils into said biorefinery," *International patent no: WO 2015/181279 Al*, 12.

P. Robinson. (2006), *Practical Advances in Petroleum Processing*, https://doi.org/10.1007/978-0-387-25789-1.

J. (Jack) Saddler et al. (2020), *A technical and costing assessment of producing and processing lipids and biocrudes in petroleum refineries.*, Ottowa.

L. Sauvanaud et al. (2018), "Applied Catalysis A , General Co-processing of lignocellulosic biocrude with petroleum gas oils," *Applied Catalysis A, General*, May 2017, pp. 1–7, Elsevier, https://doi.org/10.1016/j.apcata.2017.09.029.

M. Schimmel et al. (2018), "Determining the renewability of co-processed fuels Final report Determining the renewability of co- processed fuels: Final report," p. 30, www.ecofys.com.

J. Su et al. (2021), "Challenges in determining the renewable content of the final fuels after co-processing biogenic feedstocks in the fluid catalytic cracker (FCC) of a commercial oil refinery," *Fuel*, Vol. 294, pp. 1–25, https://doi.org/10.1016/j.fuel.2021.120526.

M. Talmadge et al. (2021), "Techno-economic analysis for co-processing fast pyrolysis liquid with vacuum gasoil in FCC units for second-generation biofuel production," *Fuel*, Vol. 293, Elsevier Ltd, https://doi.org/10.1016/j.fuel.2020.119960.

C. Templis et al. (2012), "Effect of Palm Oil Content on Deep Hydrodesulfurization of Gas Oil – Palm Oil Mixtures," https://doi.org/10.1021/ef300413f.

C. Tóth et al. (2010), "Producing diesel fuel by co-hydrogenation of vegetable oil with gas oil," *Chemical Engineering Transactions* (Volume 21, pp. 1219–1224), https://doi.org/10.3303/CET1021204.

D. Uner. (2017), *Advances in Refining Catalysis*, CRC Press.

USDOE. (2020), *Hydrogen Strategy - Enabling A Low-Carbon Economy.*, https://www.energy.gov/sites/prod/files/2020/07/f76/USDOE_FE_Hydrogen_Strategy_July2020.pdf.

E. T. C. Vogt and B. M. Weckhuysen. (2015), "Fluid catalytic cracking: recent developments

on the grand old lady of zeolite catalysis," *Chem. Soc. Rev.*, Vol. 44/20, pp. 7342–7370, Royal Society of Chemistry, https://doi.org/10.1039/C5CS00376H.

A. Vonortas, D. Kubicka and N. Papayannakos. (2014), "Catalytic co-hydroprocessing of gasoil – palm oil / AVO mixtures over," Vol. 116, pp. 49–55, https://doi.org/10.1016/j.fuel.2013.07.074.

A. Vonortas and N. Papayannakos. (2014), "Kinetic Study of the Hydrodesulfurization of a Heavy Gasoil in the Presence of Free Fatty Acids Using a CoMo / γ -Al 2 O 3 Catalyst," https://doi.org/10.1021/ie5006492.

C. Wang, R. Venderbosch and Y. Fang. (2018), "Co-processing of crude and hydrotreated pyrolysis liquids and VGO in a pilot scale FCC riser setup," *Fuel Processing Technology*, Vol. 181/September, pp. 157–165, https://doi.org/10.1016/j.fuproc.2018.09.023.

S. Wang. (2013), "High-Efficiency Separation of Bio-Oil," *Biomass Now - Sustainable Growth and Use*, InTech, https://doi.org/10.5772/51423.

B. Watkins and M. Lansdown. (2012), "Understanding Cloud Point and Hydrotreating Relationships," 112.

T. Xing et al. (2019), "Co-hydroprocessing HTL Biocrude from Waste Biomass with Bitumen-Derived Vacuum Gas Oil," *Energy & Fuels*, Vol. 33/11, pp. 11135–11144, https://doi.org/10.1021/acs.energyfuels.9b02711.

É. Yáñez et al. (2021), "Assessing bio-oil co-processing routes as CO2 mitigation strategies in oil refineries," *Biofuels, Bioproducts and Biorefining*, pp. 1–29, https://doi.org/10.1002/bbb.2163.

G. Yildiz et al. (2016), "Challenges in the design and operation of processes for catalytic fast pyrolysis of woody biomass," *Renewable and Sustainable Energy Reviews*, Vol. 57, pp. 1596–1610, Elsevier, https://doi.org/10.1016/j.rser.2015.12.202.

R. Yukesh Kannah et al. (2021), "Techno-economic assessment of various hydrogen production methods – A review," *Bioresource Technology*, Vol. 319, p. 124175, Elsevier, https://doi.org/10.1016/J.BIORTECH.2020.124175.

A. Zacher. (2015), "DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review Optimizing Co-Processing of Bio-Oil in Refinery Unit Operations Using a Davison Circulating Riser (DCR)."

A. H. Zacher et al. (2014), "A review and perspective of recent bio-oil hydrotreating research," *Green Chemistry*, Vol. 16/2, pp. 491–515, https://doi.org/10.1039/c3gc41382a.

P. Zeuthen and H. Rasmussen. (2016), "Future fuel," *Digital refining*, May, pp. 1–5.

G. Zhou, S. H. Roby and C. Kuehler. (2015), "Removal of metals from liquid pyrolysis oils," *US patent No. US 2015 / 0337087 A1*, Vol. 1/19.

IEA Bioenergy
Technology Collaboration Programme