Co-processing of biogenic feedstocks in petroleum refineries

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1. Introduction

Co-processing refers to the simultaneous transformation of biogenic feedstocks and intermediate petroleum distillates such as vacuum gas oil (VGO) in existing petroleum refinery process units to produce renewable hydrocarbon fuels. Co-processing has recently received attention due to its potential to provide low carbon renewable fuels at economically competitive prices by utilizing existing refining, transport and storage infrastructure. Several entities including national labs and universities are involved in co-processing research and development, and a few commercial refiners are exploring both pilot and commercial production.

Current research is mostly directed at the potential of fluid catalytic cracking (FCC) and hydrocracking/hydrotreating units in refineries for co-processing. Research to date suggests that co-processing of up to 20 percent (wt.) biogenic oils with VGO may be possible in FCC units[1]. The US Department of Energy estimates that more than 8 billion gallons of renewable hydrocarbon fuels could potentially be produced from co-processing in 110 FCC units in the USA.[2]

Air Resources Board (ARB) staff recognize the potential of co-processing to produce low carbon hydrocarbon fuels in-state. With no blending constraints and the ability to use existing fuel transport and distribution infrastructure, co-processed fuels offer a significant opportunity to contribute to the 10 percent reduction in the carbon intensity of transportation fuels under the Low Carbon Fuel Standard (LCFS) program. In addition, with the adoption of SB32[3] in 2016, staff is considering additional reductions from this program through 2030[4]. To incentivize the commercial production of co-processed fuels, a technical work group established by staff is exploring technical and logistical aspects related to co-processing operations and finished fuel production in-state. The work group includes invited technical experts (from National Laboratories, Universities and Technology companies) together with stakeholders representing oil companies, other fossil industries, co-processing technology companies, co-processing feedstock producers, and environmental NGOs. Because the primary focus of the LCFS program is the reduction of life-cycle greenhouse gas (GHG) emissions from transportation fuels, the work group efforts are focused on the technical issues related to the quantification of renewable fuel volumes from co-processing in petroleum refineries. In addition, since credits are generated based on carbon intensity of co-processed streams, the work group will also evaluate lifecycle approaches to estimating greenhouse gas emissions for such fuels on a well-to-wheel basis.

Research and exploratory work related to co-processing is a fairly new area, with the potential to grow rapidly in the near future. Existing methods and guidelines used to estimate carbon intensities for renewable product streams are limited. Additionally, the biogenic fractions of the

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[1] Fogassy, Gabriella, et al. "Biomass derived feedstock co-processing with vacuum gas oil for second-generation fuel production in FCC units." *Applied Catalysis B: Environmental* 96.3 (2010): 476-485.

[2] DOE. "New Pilot Plant Demonstrates the Potential to Co-Process Biomass Streams with Petroleum." October 11, 2016. https://energy.gov/eere/bioenergy/articles/new-pilot-plant-demonstrates-potential-co-process-biomass-streams-petroleum

[3] https://leginfo.legislature.ca.gov/faces/billNavClient.xhtml?bill_id=201520160SB32

[4] ARB. *The 2017 Climate Change Scoping Plan Update: The Proposed Strategy for Achieving California's 2030 Greenhouse Gas Target*. Scoping Plan Document. Sacramento: ARB, 2017. https://www.arb.ca.gov/cc/scopingplan/2030sp_pp_final.pdf

co-processed liquid products and process unit emissions will be important to other ARB regulatory programs, including the Regulation for the Mandatory Reporting of Greenhouse Gas Emissions (MRR) and the Cap-and-Trade Program. The primary objective of this draft white paper is to review and evaluate current industry and academic research related to co-processing and details a few options for:

a) the quantification of renewable content in produced fuels; and
b) estimation of carbon intensities for renewable hydrocarbon fuels

This paper also identifies additional technical issues that may need to be resolved (i.e., catalyst deactivation). As part of on-going stakeholder engagement, staff will explore operational, institutional and logistical challenges to sourcing and processing biogenic feedstocks in FCC, hydrocracking, and hydrotreating process units in commercial refineries.

2. Objectives

The objectives of this paper are to:

- Identify and summarize existing research literature on co-processing;
- Identify advantages and issues related to co-processing;
- Describe a few renewable content quantification methodologies; and
- Detail a few Life Cycle Analysis methodologies for co-processing.

3. Literature Review

3.1. Co-processing

Co-processing refers to the simultaneous transformation of biogenic feedstocks and intermediate petroleum products such as vacuum gas oil (VGO) in existing petroleum refinery process units to produce renewable hydrocarbon fuels. Co-processing involves cracking, hydrogenation, or other reformation of semi-processed biogenic oils, vegetable oils and fats in combination with petroleum intermediates to obtain finished fuels such as diesel, gasoline and jet fuels. Research literature suggests that co-processing may provide a significant pathway for utilizing existing refining infrastructure to process biomass, mainly lignocellulosic feedstocks, and increase the supply of drop-in biofuels to the market.[5] Semi-processed biogenic feedstocks that have been identified as likely to be suitable for co-processing include pyrolysis oil from pyrolysis, and triglycerides such as virgin vegetable oils, used cooking oils, and fat-based oils. In addition, lignin and sugars may be co-processed in existing refineries.

Refining processes that could potentially be utilized for co-processing include (1) thermal cracking (visbreaking and coker unit), (2) catalytic cracking, (3) hydrotreating, and (4) hydrocracking. Thermal cracking of biogenic feedstocks results in products with high oxygen content and is generally not considered practical for producing renewable diesel and gasoline.[6]

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[5] Freeman, C., et al. "Initial assessment of US refineries for purposes of potential bio-based oil insertions." (2013).

[6] Melero, J. A., et al. "Production of biofuels via catalytic cracking." *Handbook of biofuels production: processes and technologies* (2011): 390-419.

Over the last decade, refiners have explored co-processing options mainly to evaluate compliance scenarios related to biofuel and GHG reduction mandates in North America and Europe. Companies such as Chevron and Petrobras, and research organizations such as National Renewable Energy Laboratory and Pacific Northwest National Laboratory are pursuing co-processing research and development efforts. A consortium consisting of Ensyn, Chevron, and Tesoro is investigating commercial scale co-processing of pyrolysis oil derived from forest residues.

Technologies and research outcomes associated with co-processing are described below.

3.1.1. Co-processing of Pyrolysis Oil in a typical FCC Unit

Pyrolysis oil derived from either pyrolysis or liquefaction of biomass is made of several oxygenated organic compounds including acids, aldehydes, ketones, alcohols, glycols, esters, phenols, carbohydrates, and lignin-based oligomers and water.[6] Pyrolysis oil is reported to have high oxygen content ranging from 8 to 63 percent (dry basis) depending on feedstocks and pyrolysis conditions,[7] although typical values may range from 28 to 50 percent (Table 1). The higher oxygen content of pyrolysis oil is responsible for its lower stability, poor miscibility with oil, higher acidity and lower energy content. In comparison, triglycerides (vegetable oil and animal fat) have favorable chemical properties for co-processing such as lower oxygen content and negligible water content. The energy content of raw pyrolysis oil is usually about half of petroleum fuels. An extensive literature review carried out by Gollakota et al.[7] suggests that energy content of pyrolysis oil can vary from 8-37 MJ/kg (LHV) for lignocellulosic feedstocks, although typical values may range from 13 to 30 MJ/kg. Typical chemical and physical properties of pyrolysis oil and vegetable oil are shown in Table 1. For comparison, similar properties for VGO and diesel oil are also included in Table 1.

Co-processing in FCC units is a promising method of transforming pyrolysis oil into renewable gasoline and diesel fuels. Since most refineries in the U. S. are equipped with FCC units, the infrastructure for co-processing pyrolysis oil already exist in the country. Figure 1 provides a schematic of a typical FCC process unit. The FCC unit provides an environment for cracking heavier molecular weight pyrolysis oil, as it is more selective and can be carried out under milder reaction conditions. Catalytic cracking removes oxygen present in feedstocks in the form of water, CO and CO_2 via simultaneous dehydration, decarboxylation, and decarbonylation. Co-processing in an FCC unit has an advantage compared to other processing units in a refinery because additional hydrogen or energy inputs are typically not required, saving both costs and additional GHG emissions.

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[7] Gollakota, Anjani RK, et al. "A review on the upgradation techniques of pyrolysis oil." *Renewable and Sustainable Energy Reviews* 58 (2016): 1543-1568.

Table 1. Typical chemical and physical properties of biogenic feedstocks summarized from various sources

Fuel Property	Unit	Pyrolysis oil[8]	Vegetable oil[9]	Vacuum gas oil	Diesel oil
Density@ 15°C	kg/L	1.05-1.25	0.9-0.93	1.22	0.85
Kinematic viscosity@50°C	CP	40-100	<38 at 40°C		2.5
Lower heating value	MJ/kg	13-30	36-37	42	42.9
Ash	% wt.	<0.2	<0.01	<1%	<0.01
Water content	% wt.	15-30	<0.075		0.1
Elemental analysis					
Carbon	% wt.	55-65	~80	84.6[10]	86.3
Hydrogen	% wt.	5-7	~12	10.7	12.8
Oxygen	% wt.	28-54	~9	0.4	0.9
Sulfur	% wt.	<0.05	Negligible	3.6	0.15-0.30
Nitrogen	% wt.	<0.4	Negligible		

The final makeup of products from co-processing is determined by feedstock type and reaction conditions. Cracking at an FCC unit is carried out at temperatures ranging from 350-500°C and one atmosphere of pressure in the presence of zeolite catalysts. Studies have shown that a portion of pyrolysis oil ends up as coke, petroleum gases (LPG), CO_2, CO, and water.[11] This is attributed to lower thermal stability of pyrolysis oil, resulting in the formation of larger amounts of coke, CO_2, CO, and LPG, compared to cracking VGO alone. Due to higher oxygen content of pyrolysis oil, more water is also produced during the reaction, compared to the processing of VGO only. In-addition, co-processing of pyrolysis oil in FCC units results in higher amounts of oxygenated and phenolic compounds in liquid products.

Recently, a pilot scale study by Pinho et al.[11] utilized a tracer technique (C^{14}) to quantify the relative proportion of pyrolysis oil-originating products in a pilot scale FCC unit. The study revealed that 30 percent of renewable carbon in pyrolysis oil would end up in total liquid products (gasoline, light cycle oil (LCO) and bottoms). This suggests that an appreciable amount of carbon in pyrolysis oil ends up as LPG, coke, CO, and CO_2, thereby reducing overall liquid product yields. These results are consistent with yield trends (Figure 2) reported by Lindfors et al. which show that as the mass percent of pyrolysis oil feedstock increases, yields of gases and coke also increase, which come at the expense of lower liquid fuel yields.[12]

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[8] Vivarelli, Silvia, and Gianluca Tondi. "Pyrolysis oil: an innovative liquid biofuel for heating The COMBIO Project." *International Workshop. Bioenergy for a sustainable development, Casino Vin a del Mar e Chile*. 2004.

[9] Toscano, Giuseppe, and Eleonora Maldini. "Analysis of the physical and chemical characteristics of vegetable oils as Fuel." *Journal of Agricultural Engineering 3*8.3 (2007): 39-47.

[10] Chen, Jinwen, Hena Farooqi, and Craig Fairbridge. "Experimental study on co-hydroprocessing canola oil and heavy vacuum gas oil blends." *Energy & Fuels* 27.6 (2013): 3306-3315.

[11] Pinho, Andrea de Rezendo et al. "Co-processing raw bio-oil and gasoil in an FCC unit." *Fuel Processing Technology* 131 (2015): 159-166.

[12] Lindfors, Christian, et al. "Co-processing of Dry Bio-oil, Catalytic Pyrolysis Oil, and Hydrotreated Bio-oil in a Micro Activity Test Unit." *Energy & Fuels* 29.6 (2015): 3707-3714.
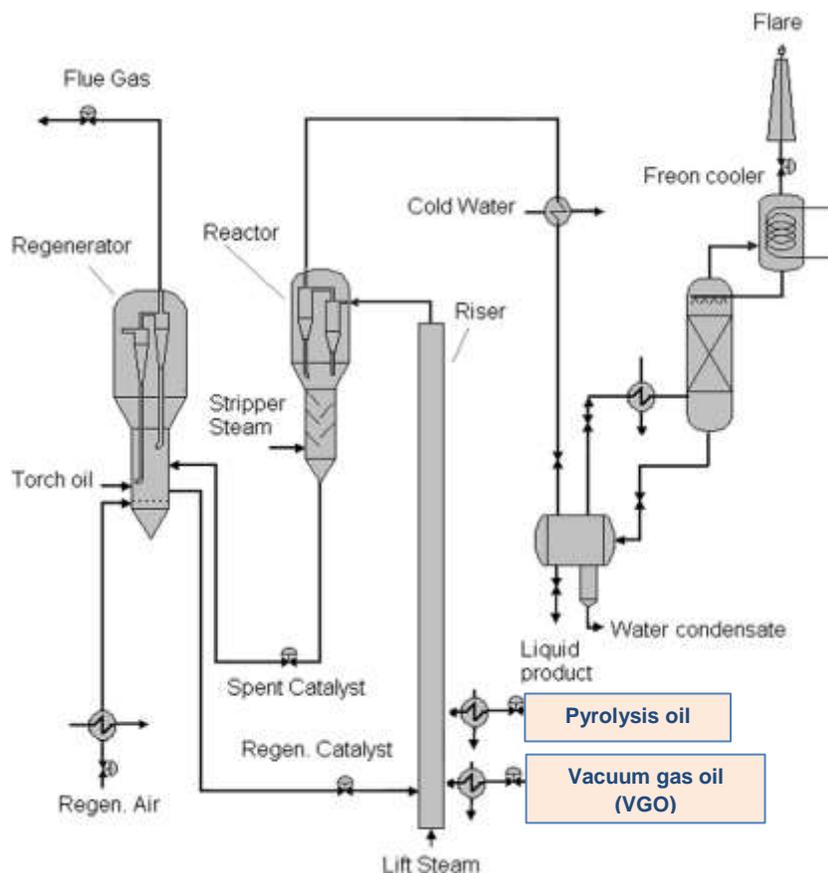
Figure 1. A schematic of an FCC unit for co-processing[11]

Previous pilot-scale studies suggest carbon conversion efficiencies in the range of 15-20 percent.[11] However, the conversion efficiency of pyrolysis oil to renewable diesel and renewable gasoline, and coke formation behavior are expected to be different in commercial scale FCC plants. Pinho et al. pointed out that blending pyrolysis oil with VGO feed may not be possible at a commercial scale FCC unit, due to excess polymerization in blends during storage and coke formation under FCC conditions.[11] Hence, the study suggests that pyrolysis oil and VGO would need to be injected separately into a riser reactor at different heights, to increase thermal cracking and prevent these undesirable reactions.

Research also demonstrates that it is possible to improve renewable gasoline yields to levels comparable to that of 100 percent VGO, if raw pyrolysis oil is upgraded to hydrodeoxygenated oil (HDO) and then co-processed with VGO. A study by Fogassy et al. simulating FCC conditions found that co-processing 20 percent HDO with 80 percent VGO resulted in gasoline yields comparable to that of the conventional FCC feedstock (VGO).[1] Lower oxygen content and higher aliphatic and aromatic content of HDO resulting from upgrading may have contributed to improved gasoline yields. Similar results were reported by Lindfors et al.[12] where hydrogenated pyrolysis oil yielded 74% (by weight) liquid products compared to 69% for dry pyrolysis oil (Table 2).
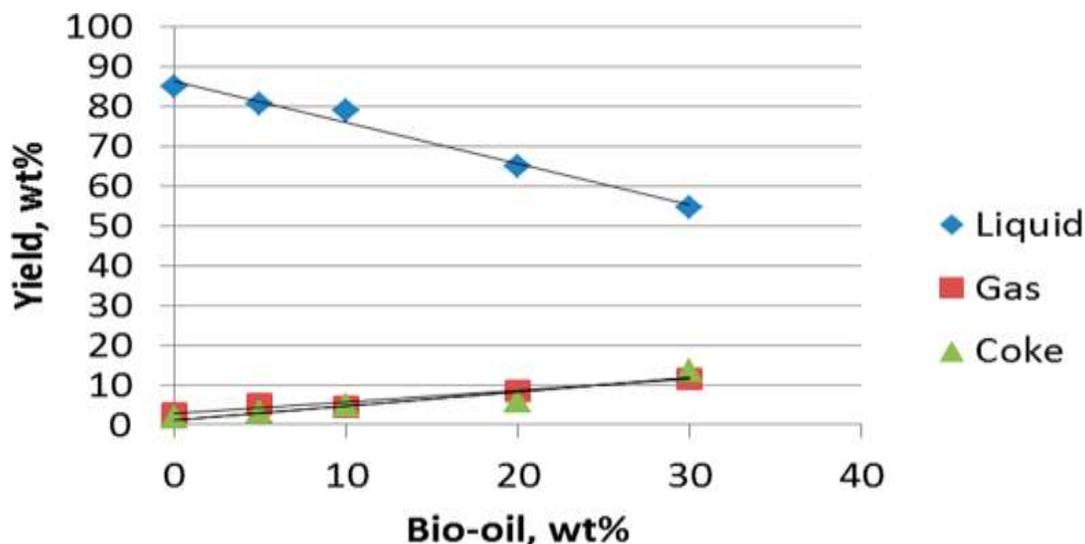
Figure 2. Product yield trends at various bio-oil to VGO ratios (source: Lindfors et al, 2015)[12]

Table 2. Impact of upgrading of pyrolysis oil on liquid product yields (Source: Lindfors et al.[12])

Products	VGO	VGO+ 20% dry pyrolysis oil	VGO + 20% HDO
Liquid (wt. %)	85	69	74
Gas (wt. %)	10	14	12
Coke (wt.%)	5	10	10

3.1.2. Co-processing of Lignin and Glycerol in a typical FCC unit

Lignin: Co-processing of lignin in an FCC unit in the presence of zeolite catalysts and at temperatures 500-650°C produces liquid fuels primarily consisting of aromatic hydrocarbons such as toluene, benzene, and xylene.[13] In addition CO, CO_2, light hydrocarbon gases, water, and coke are produced. The lignin co-processing with VGO is shown to increase the crackability of VGO and shift yields towards light end products. At a temperature of 500°C, about a 50 percent (by weight) conversion rate of lignin to coke and char has been reported.[6] The same study reports that at higher temperatures (~650°C), the lignin conversion to coke declines to 25 percent.[6] The high aromatic content in the liquid products (including renewable diesel) differentiates co-processing of lignin from pyrolysis oil. It is likely that the high coke yield from lignin co-processing may make lignin unsuitable in a majority of FCC units.[6]

Glycerol: Glycerol obtained from sugar fermentation and trans-esterification of vegetable oils and fats can be co-processed with VGO in an FCC unit to obtain renewable diesel and gasoline. Depending on the types of catalyst used, glycerol co-processing provides different product yields. A ZSM-5 catalyst is shown to yield more olefins (unsaturated hydrocarbons such as propene and butene) and aromatics but less than 20 percent coke. The use of other catalysts in

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[13] Thring, Ronald W., Sai PR Katikaneni, and Narendra N. Bakhshi. "The production of gasoline range hydrocarbons from Alcell® lignin using HZSM-5 catalyst." *Fuel Processing Technology* 62.1 (2000): 17-30.

an FCC unit leads to higher levels of coke, in the range of 30-50 percent.[14] Given that glycerol is currently an expensive feedstock, its use for co-processing may be limited.

3.1.3. *Co-processing of Triglycerides (vegetable oil and animal fat)*

As with co-processing of pyrolysis oil in FCC units, co-processing of triglycerides such as vegetable oil and animal fat with VGO in FCC units appears to be an attractive option. Unlike in thermal cracking, FCC catalysts remove oxygen from final products in the form of CO_2, CO, and water yielding products similar to processing 100 percent VGO in FCC units. Studies performed using conditions that attempt to simulate FCC operating conditions have reported negligible amounts of oxygenated hydrocarbons in the final products.[15,16,17] Since triglycerides primarily comprise paraffinic and olefinic hydrocarbons, the resulting product slate is likely to lead to an increased amount of gasoline.

Research carried out to date on co-processing of triglycerides with VGO under FCC conditions points to the following trends in the product outputs:[15,18,19,20]

As the percentage of triglycerides in the co-processed mixture increases:
- The percentage of liquid products (gasoline, light cycle oil (LCO), and decanted oil (DO) in the final product slate declines.
- The percentage of light petroleum gas (LPG) increases. The higher yields of LPG and dry gases are attributed to better crackability of triglycerides as there are no aromatics in triglycerides.
- The percentage of coke increases. This is because there is an accelerated removal of hydrogen from hydrocarbon molecules in the presence of triglycerides.
- The percentage of CO and CO_2 increases due to the presence of oxygen in the biogenic feedstock.
- While polyaromatic content decreases, there is an increase in monoaromatic and diaromatic content. Triglycerides have no monoaromatic and diaromatic compounds to begin with but they are easily produced from triglycerides during co-processing

These trends are succinctly captured in Figure 3 which shows varying product outputs from co-processing of palm oil (PO) with VGO under FCC conditions.

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[14] Corma, Avelino, et al. "Processing biomass-derived oxygenates in the oil refinery: Catalytic cracking (FCC) reaction pathways and role of catalyst." *Journal of Catalysis* 247.2 (2007): 307-327.

[15] Melero, Juan A., et al. "Production of biofuels via the catalytic cracking of mixtures of crude vegetable oils and nonedible animal fats with vacuum gas oil." *Energy & Fuels* 24.1 (2009): 707-717.

[16] Li, Hong, et al. "Enhancing the production of biofuels from cottonseed oil by fixed-fluidized bed catalytic cracking." *Renewable Energy* 34.4 (2009): 1033-1039.

[17] Chew, Thiam Leng, and Subhash Bhatia. "Effect of catalyst additives on the production of biofuels from palm oil cracking in a transport riser reactor." *Bioresource technology* 100.9 (2009): 2540-2545.

[18] Pinho, A. D. R., et al. *Catalytic Cracking Process and Catalysts for Production of Diesel Fuel from Pure and Waste Vegetable Oils. PBSA* (Petrobras), Brazil, US 7176, 2007.

[19] Bormann, K., H. Tilgner, and H-J. Moll. "Rape seed oil as a feed component for the catalytic cracking process." *Erdol Erdgas Kohle* 109 (1993): 172-172.

[20] Buchsbaum, A., et al. *The challenge of the biofuels directive for a European refinery*. OMW Refining and Marketing, ERTC 9th Annual Meeting, Prague, Czech Republic, Nov. 15-17, 2004.
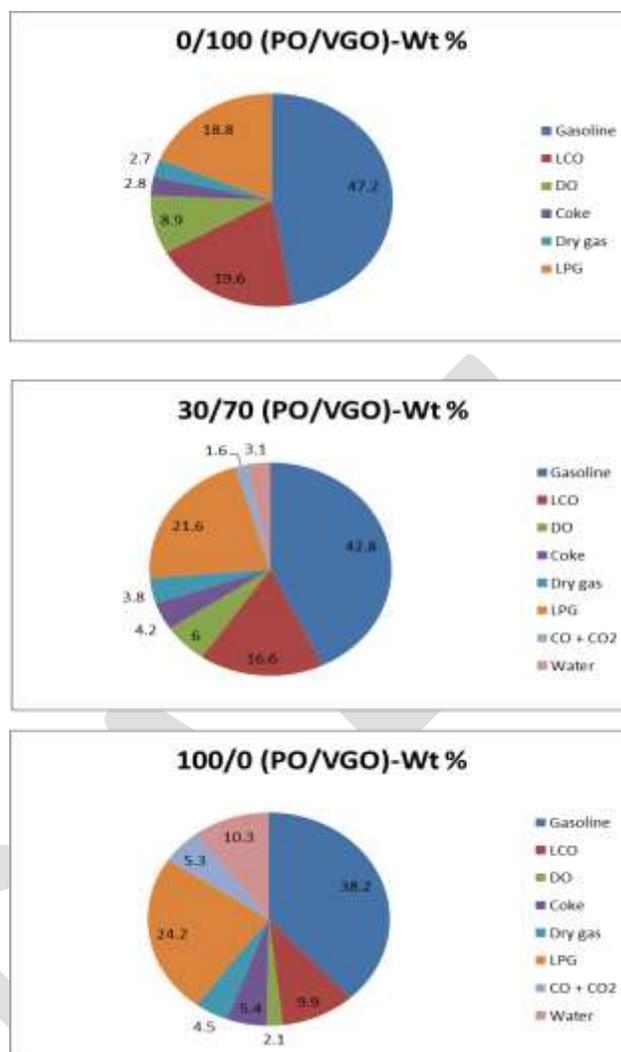
Figure 3. Product outputs from catalytic cracking as a function of feedstock composition[6]

Although co-processing of triglycerides in existing FCC units holds promise due to its beneficial properties, such as lower oxygen content, higher hydrogen index, and similar physical properties to conventional feedstock in FCC units, it is still in the research and development phase. There has been a limited effort in co-processing of triglycerides under real FCC conditions at a pilot plant scale.[6]

Currently, co-processing in FCC units is not being utilized on a commercial scale due to concerns about feedstock stability during storage, and corrosiveness of biomass feedstock under high temperatures. Refiners are also likely reluctant to take catalyst and runtime risks that may result from co-processing such feedstocks in large processing units.[6]

3.2 Co-processing in hydrotreaters

Co-processing of biogenic feedstocks with petroleum distillate fractions is also possible in hydrotreating (HT) units. Triglycerides can be co-processed with middle distillates or VGO in

hydrotreaters.[21,22] Typical catalysts used in hydrotreatment of triglycerides include $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$. Figure 4 illustrates the co-processing of triglyceride oils and diesel and jet fuel middle distillates in a hydrotreater. Plant oils and animal fats comprised primarily of triglycerides can be converted to renewable diesel, renewable jet fuel, biopropane and renewable naphtha (which can be converted to gasoline) in the presence of hydrogen and catalysts and under mild temperatures (300-350°C). Conversion occurs through decarboxylation, decarbonylation and hydro-deoxygenation reactions. During cracking of larger hydrocarbon molecules into lighter fuel fractions, small amounts of renewable naphtha and hydrocarbon gases such as biopropane are also produced. Bio-propane can be used as a renewable and non-fossil input to the refinery's fuel gas to provide heat to process units. In addition to hydrotreaters, hydrocrackers may also be used for co-processing of triglycerides.

Research provides good evidence of the technical and economic viability of hydrotreating of triglyceride feedstocks on a commercial scale. Operating conditions and catalyst selection have been shown to influence product yields and quality. Satyarthi et al. found that co-processing straight run diesel with a vegetable oil (Jatropha) had no effect on the desulfurization of the fossil fraction, and did not deactivate the hydrotreater catalyst.[22] Additionally, the final fuel product contained virtually no oxygenated compounds. Chen et al. also found that co-processing heavy VGO with canola oil did not affect desulfurization, and produced intermediate fuel fractions with less aromatics, and higher levels of saturates, favoring the diesel fraction and improving the cetane number for diesel.[10] Similar results were obtained by Rana et al. who found that catalysts can be selected to improve the production of either the diesel or jet fraction of produced fuels, allowing adjustments to meet market demand.[23] Further research and development of the hydrotreating approach may provide additional information on desirable catalysts, throughput conditions that optimize energy and hydrogen inputs, and any potential drawbacks to commercial scale production such as equipment corrosion from the use of biogenic feedstock.

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[21] Dimitriadis, Athanasios, and Stella Bezergianni. "Co-hydroprocessing gas-oil with residual lipids: effect of residence time and H 2/Oil ratio." *Journal of Cleaner Production* 131 (2016): 321-326.

[22] Satyarthi, J. K., et al. "Studies on co-processing of jatropha oil with diesel fraction in hydrodesulfurization." *Fuel Processing Technology* 118 (2014): 180-186.

[23] Rana, Bharat S., et al. "Transportation fuels from co-processing of waste vegetable oil and gas oil mixtures." *Biomass and Bioenergy* 56 (2013): 43-52.
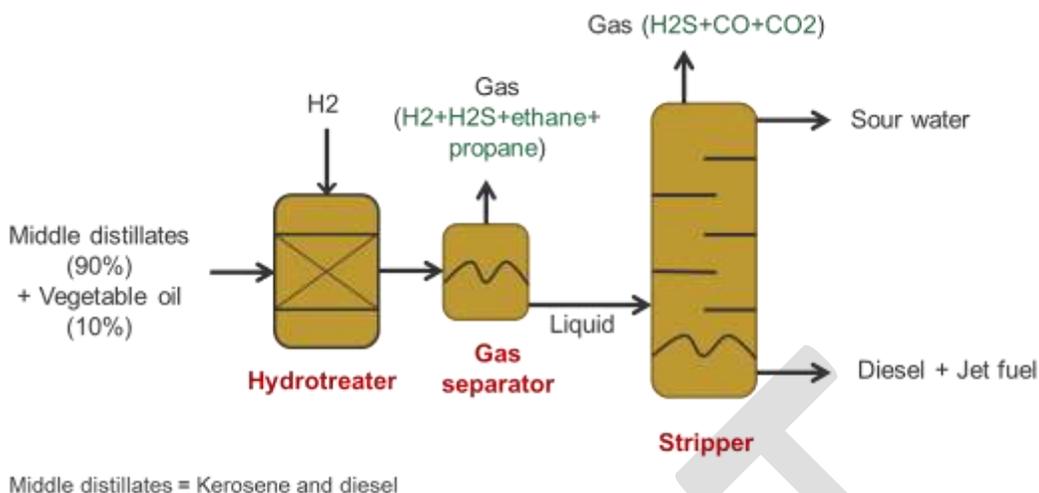
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Figure 4. Schematic of co-processing in a hydrotreater

4. Issues related to co-processing

Several issues may affect the economic and operational viability of co-processing. Some of these include:
- Differences in the stability of biogenic feedstocks during storage and handling;
- The presence of water and oxygenated organic compounds in biogenic feedstocks which can cause equipment corrosion and can affect yields and conversion rates;
- The potential for alkali metals in biogenic feedstocks to deactivate catalysts; and
- Differences in yields between pilot and commercial scale projects.

However, some of these problems can be mitigated based on findings from ongoing research and development activities. Additional detail on some of these issues with potential solutions are discussed below.

Triglycerides and pyrolysis oil have lower thermal and oxidative stability, which may pose storage problems such as changes in density, viscosity, acidity, and increase in polymer formation.[24] The instability of pyrolysis oil is mainly attributed to lignin oligomers formed during pyrolysis.[25] The polymer formed during the storage of triglycerides can lead to gumming in heat exchanger tubes and transfer lines. Triglycerides also have corrosive properties attributable to carboxylic acids. Likewise, the corrosiveness of pyrolysis oil is contributed by oxygenated compounds such as phenols, aldehydes, and carboxylic acids. Raw pyrolysis oil typically has a pH value of about 2-3.[25] The corrosivity of these feedstocks may pose problems in storage units.

However, storage problems listed above may be limited for mixtures of triglycerides and petroleum intermediates. A recent study carried out by Melero et al.[26] to test the oxidative and

[24] Geller, Daniel P., et al. "Storage stability of poultry fat and diesel fuel mixtures: specific gravity and viscosity." *Fuel* 87.1 (2008): 92-102.
[25] Vispute, Tushar. "Pyrolysis oils: characterization, stability analysis, and catalytic upgrading to fuels and chemicals." (2011).
[26] Melero, Juan A., et al. "Storage stability and corrosion studies of renewable raw materials and petrol mixtures: A key issue for their co-processing in refinery units." *Fuel* 89.3 (2010): 554-562.

thermal stability of various mixtures of vegetable oils, animal fats, used cooking oil and petroleum feedstocks suggest these mixtures can be stable for a period of at least 180 days. Likewise, a leaching experiment found a limited amount of metal leaching in storage tanks, suggesting the mixtures are not as corrosive as 100 percent triglycerides.[6] In addition, stability of pyrolysis oil can be improved through processes such as aqueous phase reforming, hydrotreating, and zeolite upgrading.[25] These processes remove oxygen from oxygenated compounds, reduce moisture and increase the paraffin and aromatic content thereby improving the overall stability of pyrolysis oil.

The presence of trace components in biogenic feedstocks could have undesirable effects on reactor performance. Alkali metals present in pyrolysis oils can deactivate FCC catalysts by two mechanisms:
(1)   Loss of cracking activity due to poisoning of acid sites via neutralization.
(2)   The alkali metal oxides can react with silica and/or alumina present as part of the catalyst matrix to form salts. These reactions can cause damage to zeolite and reduce the catalytic activity.

The deactivation of zeolite catalysts by poisoning by impurities may require higher catalyst makeup rates. In addition, biogenic feedstocks contain oxygenated compounds (e.g. water, phenols, organic acids, etc.) that may corrode process equipment. This may limit the amount of biogenic-feedstocks which can be co-processed with petroleum intermediates. To-date, research and development efforts have focused on co-processing with up to 20 percent biogenic feedstocks.

5. Co-processing Potential in California

In 2016, EIA reported total capacities of 729,700 bpsd[27] and 723,000 bpsd were available for FCC and heavy gas oil hydrotreaters respectively in California.[28] The same report listed capacity for hydrotreaters units that could potentially be used for co-processing triglycerides with middle distillates (kerosene/jet, diesel and other distillate) as 659,500 bpsd. In addition, in-state refineries offer a hydrocracking capacity of 488,400 bpsd which can be used to co-process triglycerides with middle distillate including gas oil. Assuming renewable liquid product yields vary between 65%-85% (by volume) and a co-processing ratio of five percent (on a volumetric basis), approximately 1.5 billion gallons of renewable hydrocarbon fuels including renewable diesel and renewable gasoline could potentially be produced in California (Table 3).

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[27] Bpsd refers to barrels per stream day
[28] EIA, US. "Refinery Capacity Report 2016." EIA website http://www.eia.gov/petroleum/refinerycapacity/ accessed January 24, 2017

Table 3. Co-processing capacity and renewable hydrocarbon fuel production potential in California Refineries

Co-processing units	Capacity (BPSD)[28]	Biogenic feedstock to petroleum ratio	Biogenic Feedstock	Assumed % liquid renewable fuel yields (v/v biogenic feedstock)	Renewable hydrocarbon fuel potential (gallons/year)
Catalytic cracking	729,700	5%	Pyrolysis oil	65%	3.6E+08
Hydrotreater (heavy gas oil)	723,000	5%	Vegetable oil + tallow	85%	4.7E+08
Hydrotreater (jet+ kerosene+diesel +other distillate)	659,500	5%	Vegetable oil + tallow	85%	4.3E+08
Hydrocracker (gas oil)	296,600	5%	Pyrolysis oil	70%	1.6E+08
Hydrocraker (distillate)	191,800	5%	Vegetable oil + tallow	85%	1.2E+08
Total					**1.5E+09**

6. Approaches to Renewable Content Quantification

For the LCFS, a critical issue in co-processing is the quantification of renewable fuel volumes. This is because volumes of renewable streams from such operations have the potential to generate credits under this program.

Table 1 compares pyrolysis oil and vegetable oil (both biogenic) with VGO and diesel oil (both fossil). Although biogenic feedstocks have lower hydrogen and sulfur content compared to fossil feedstocks, they typically have an abundance of oxygen. This oxygen is converted to CO, CO_2, and water in FCC or hydrotreating units. In addition, during co-processing in FCC units, biogenic feedstocks, especially pyrolysis oil, may tend to preferentially precipitate as coke onto the catalyst, compared to petroleum feeds.[11] There is also a tendency for biogenic feedstocks to produce additional LPG when compared to fossil feedstocks. This alters the mass and volume ratios of liquid fuels and emissions produced from the unit, when compared to processing 100% fossil feed. Robust methods are therefore needed to quantify the biogenic (renewable) fractions of valuable liquid fuels and associated GHG emissions produced during co-processing. For quantifying GHG emissions under other ARB programs, such as MRR and the Cap-and-Trade Program, a separate rulemaking process would need to be conducted if those programs were to incorporate new methods.

This section describes several methods to quantify renewable fuel volumes produced when using biogenic feedstocks in conventional petroleum refineries. The approaches presented in this discussion paper are preliminary and staff is soliciting feedback from stakeholders. Specifically, support and/or concerns related to quantification methods presented in the discussion paper, or alternate methods of quantification are being requested.

6.1. C^{14} isotopic method

One approach for the determination of renewable fraction of liquid fuels from co-processing is the use of C^{14} carbon isotope analysis. Analysis of C^{14} has been used for decades to determine the percent fraction of biogenic materials in mixtures, and also to determine the age of artifacts based on the rate of C^{14} decay.

Samples of co-processed fuels could be analyzed on a periodic basis to determine the amount of biogenic-sourced carbon in the fuel. Since co-processing changes both the total mass of carbon in the combined feedstocks and the rate at which fossil-based feedstocks are converted to liquid fuels (compared to a fossil-only feedstock), such an approach would allow a post-reaction analysis of the biogenic fraction of fuels using an established methodology.

6.2. Total mass balance approach

A mass balance approach is predicated on the conservation of mass principle. In any system, the total mass of inputs should equal the total mass of outputs. The total mass balance method does not directly measure the renewable fuel products, instead a reasonable method of allocation needs to be applied to indirectly and conservatively determine the renewable fractions of fuel products after a mass balance analysis is performed.

The total mass-based allocation discussed takes into consideration the amounts of CO, CO_2, and H_2O produced during co-processing, and adjusts the mass of biogenic feedstock to exclude the mass of biogenic feedstock that ends up as CO, CO_2, and H_2O. The CO, CO_2, and H_2O lost from the biogenic feedstock can be estimated by considering the mass difference of these components between the petroleum-only baseline and co-processing, and the co-processing ratio. Alternatively, if the production CO, CO_2 and H_2O from 100% petroleum intermediates such as VGO is shown to be negligible, all CO_2, CO and H_2O produced from co-processing can be assumed to come from the biogenic feedstock. Any H_2O introduced externally as steam is excluded to only account for water from the biogenic feedstock and petroleum intermediate.[29]

The total mass-based allocation involves the following steps. The approach described herein is applicable to FCC co-processing but can be modified to make it applicable to co-processing in hydrotreaters.

1. Analyze the chemical composition of biogenic feedstocks and petroleum intermediates to determine their elemental composition (C, O, H, S, and N), water content, and ash content. These data are used to inform and corroborate the mass-balance analysis. An example of chemical composition analysis is shown in Table 4.
2. Establish mass balance using a baseline 100 % petroleum intermediate in a co-processing unit (e.g., FCC or hydrotreater).

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[29] In FCC, water is introduced as dispersion steam, annular steam and stripping steam. Because these streams are monitored, it is possible to subtract out the steam addition to get produced water from the biogenic feedstock. However, this may add uncertainty in estimates since the amounts of steam that are added are very large and this method may need to be tested against real refinery data.

Table 4. Chemical composition analysis of feedstocks

Fuel composition	Unit	Pyrolysis oil	VGO
Ash	% wt.	0.13	Negligible
Water content	% wt.	20.5	<1%
Carbon	% wt.	48.5	84.6%
Hydrogen	% wt.	6.4	10.7%
Oxygen (dry basis)	% wt.	42.5	0.4%
Sulfur	% wt.	0	3.6%

3. Perform a mass-balance analysis using co-processed renewable and petroleum inputs to the co-processing unit. Quantify the mass of each input and product stream to demonstrate conservation of mass. The mass of CO + H_2O + CO_2 needs to be determined separately from other outputs.
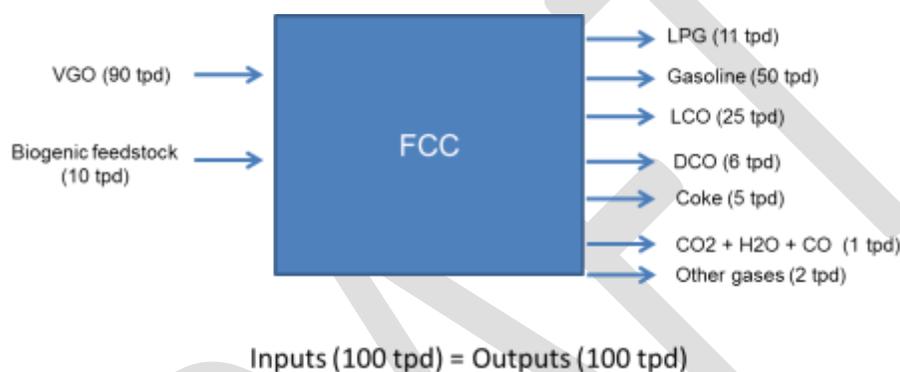

Figure 5 Illustration of total mass balance analysis (tpd = ton per day)

4. Determine the mass fraction that ends up as CO, CO_2 and H_2O as shown in Equation 1.

$$F_{CO+CO2+H2O} = \frac{M_{CO+CO2+H2O}}{M_{total}}$$ **Equation 1**

Where,
$F_{CO+CO2+H2O}$ = Mass fraction of CO+CO_2+H_2O
$M_{CO+CO2+H2O}$ = Mass of CO+CO_2 +H_2O from the reactor gases
M_{total} = Total mass of outputs

For example based on Figure 5,
$F_{CO+CO2+H2O}$ = 1 tpd/ 100 tpd = 0.01

The factor of 0.01 in this example implies that only 9% of the biogenic input out of 10% co-processed initially ends up in the remaining product streams including catalyst coke. The remaining 1% amount that is lost as CO+ CO_2+ H_2O is assumed to uniformly lower the renewable content in the remaining product streams relative to the petroleum intermediate. This assumption is necessary to estimate renewable factions of product streams indirectly (baseline runs may be able to establish mass of CO, CO_2 and H_2O when using 100% petroleum intermediates and appropriate adjustments may be necessary).

Calculate the mass allocation factor as shown in Equation 2.
$X = Input_{biogenic} - (F_{CO+CO2+H2O})$ *Equation 2*

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Where,

X = mass allocation factor

Input$_{biogenic}$ = Weight fraction of biogenic feedstock in co-processing, which is 0.10 in this example

5. Estimate the renewable mass of each product stream (excluding CO+ CO_2+ H_2O) as shown in Equation 3.

$P_{i,ren} = M_i \times X$ **Equation 3**

Where,

$P_{i,ren}$ = Renewable mass of ith product

M_i = Mass of ith product

Table 5 summarizes the results of renewable mass estimates of co-processed products for the example described above in Figure 5.

Table 5. Estimation of renewable mass of co-processed products (10% pyrolysis oil + 90% VGO example)

Product	M_i (tpd)	X	Renewable mass (tpd) Mi × Xa$_{di}$ (%)
LPG	11	0.09	0.99
Gasoline	50	0.09	4.5
LCO	25	0.09	2.25
DCO	6	0.09	0.54
Coke	5	0.09	0.45
Other gases	2	0.09	0.18

If a renewable product undergoes further treatment in processing units such as alkylation unit or hydrotreater, the mass balance approach needs to be extended to quantify the renewable content in finished fuels from those units that would be delivered for end uses. Any such mass balance should correspond to the amount of renewable fuels estimated above using equation 3.

6.2.1. Other mass balance approaches

One approach, proposed by the National Renewable Energy Laboratory (NREL), uses a carbon mass balance method which relies on the carbon content of biogenic feedstock and measurements of carbon that would be lost as CO and CO_2 during co-processing. The difference between the biogenic carbon content and lost carbon provides the biogenic carbon that would end up in renewable products. Using appropriate conversion factors, it may be possible to convert biogenic carbon content to the amount of finished renewable fuels. The carbon mass approach is similar to the total mass balance approach described in section 6.2. By avoiding the quantification of H_2O lost from the biogenic feedstock, this method eliminates any uncertainty associated with H_2O quantification in the total mass balance approach.

A second mass balance approach proposed by NREL requires measuring overall product yields from co-processing as well as 100% petroleum-only refining. The renewable product yield is calculated as follows.

Renewable Product Yield (RPY) = OPY–(PY× PI %)   ***Equation 4***

where,

OPY = Overall product yield from co-processing (sum of liquid product, gaseous product and solid product)
PY = Petroleum only yield (baseline)
PI% = percent contribution of a petroleum intermediate used in co-processing

% Renewable product = (RPY/ OPY) * 100   **Equation 5**

This method assumes that the yields from a petroleum intermediate such as VGO remain constant. It does not require CO, CO_2 and H_2O measurements. However, if the fossil carbon that goes into coke in the baseline is converted to liquid fuel in co-processing, the fossil carbon can be characterized as renewable.[30]

6.3.   Biogenic feedstock energy content method

Presence of oxygenated compounds and water lowers the energy content of biogenic feedstocks as well as liquid product yields from co-processing. For example, while VGO has energy content of about 42 MJ/kg, raw pyrolysis oil has energy content of about 20 MJ/Kg. It may be possible to use the relative percent energy contribution of biogenic feedstock in co-processing to overall energy content of the co-processed feed as proxy to get approximate but conservative estimate of the renewable content of liquid products steams. This approach assumes a linear collinearity between the energy content of biogenic feedstocks and renewable content of liquid products from co-processing. The % renewable energy contribution from biogenic feedstock ($RE_\%$) can be calculated as:

$$RE_\% = \frac{BF_E \times Wt_{B\%}}{BF_E \times Wt_{B\%} + PF_E \times Wt_{P\%}}$$ **Equation 6**

Where,
BF_E = Energy content of biogenic feedstock (MJ/kg)
PF_E = Energy content of petroleum intermediate (MJ/kg)
$Wt_{B\%}$ = Weight fraction of biogenic feedstock in percent
$Wt_{p\%}$ = Weight fraction of petroleum intermediate in percent

Finally, $RE_\%$ would be multiplied by the amount of total liquid hydrocarbon fuel produced in MJ to calculate the amount of renewable hydrocarbon fuel produced in MJ from co-processing.

The advantage of this approach is that data requirements and administrative burden are minimal as only the weight fraction of biogenic feedstock and its energy content has to be reported. The disadvantage is that it may be less accurate than the mass balance approach described above and hence it may require limiting the biogenic mass percentage to no more than 10% and use of biogenic feedstocks with lower oxygen and moisture content such as vegetable oils. More research is required to validate the accuracy of this method.

Note: For all mass, carbon or energy content method, applicants may be required to demonstrate the presence of renewable carbon through C^{14} analysis for co-processed fuels if requested by staff.

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[30] Talmadge et al. Analysis for co-processing fast pyrolysis oil with VGO in FCC units for second generation fuel production. Presented at Co-Processing Working Group Sacramento, CA , December 13, 2016 (https://www.arb.ca.gov/fuels/lcfs/lcfs_meetings/12132016nrel.pdf)

7. Proposed LCA Methodology for Co-processing

Staff proposes to perform a well-to-wheel analysis to estimate carbon intensities of co-processed renewable fuels (Figure 6). This includes GHG emissions from feedstock production, harvest and processing, feedstock transport, co-processing, fuel transport/storage and end use. Where applicable, direct and indirect land use change GHG emissions will be assessed as part of feedstock production.
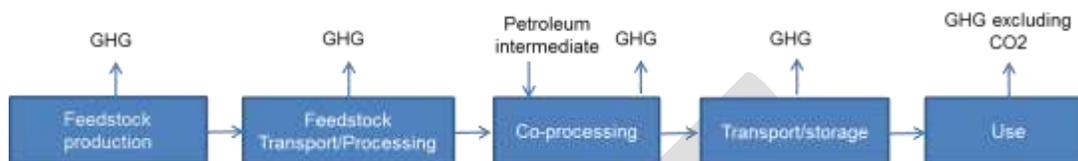
Figure 6. LCA system boundary for co-processing

Except for co-processing, all other steps are similar to regular fuel pathways and have been described elsewhere. Hence this paper focuses mainly on the co-processing step. Co-processing creates challenges in estimating refining emissions not only because co-processing may alter energy consumption and hence emissions in existing refineries but also because there is a need to allocate emissions between renewable and non-renewable fractions in the finished fuel.

This section describes several approaches to estimate carbon intensities of renewable fuel volumes produced from co-processing biogenic feedstocks in petroleum refineries. The approaches presented in this discussion paper are preliminary and staff is soliciting feedback from stakeholders. Specifically, support and/or concerns related to LCA methods presented in the discussion paper or alternate methods are being requested.

For discussion purpose, staff is presenting two approaches:
- Default value approach that assigns petroleum gasoline or diesel refinery emissions obtained from the CA-GREET model to renewable gasoline or diesel.
- Quantify energy consumption and GHG emissions at process unit levels and allocate emissions based on the energy content of finished fuels.

Note that any emissions associated with pre-processing of biogenic feedstocks (e.g. pyrolysis oil production and upgrading) which occur prior to their introduction into refining units are not part of the refinery emissions and need to be accounted separately as shown in Figure 6 above.

7.1. Default value approach

The default value approach is predicated on the assumption that the refining emissions per unit of fuel from co-processed biofuels would be less than the refining emissions per unit of conventional fossil fuel produced at a complex conventional petroleum refinery. This assumption may be valid for co-processing ratios of up to 10% because co-processing bypasses carbon-intensive refining processes units such as distillation and coking.

Under this approach, applicants may use the default refinery carbon intensities of petroleum gasoline, diesel, and jet fuel obtained from CA-GREET model as proxy for carbon intensities of renewable gasoline, renewable diesel fuel and renewable jet fuel. The default value approach

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may provide conservative estimates (overestimation) of refining carbon intensities for co-processed renewable fuels because as mentioned above, co-processing bypasses some carbon-intensive refining processes units. The consideration of this approach will require demonstration that emissions from energy use, hydrogen requirements and other inputs are not higher for co-processed runs compared to baseline runs with 100% petroleum intermediates.
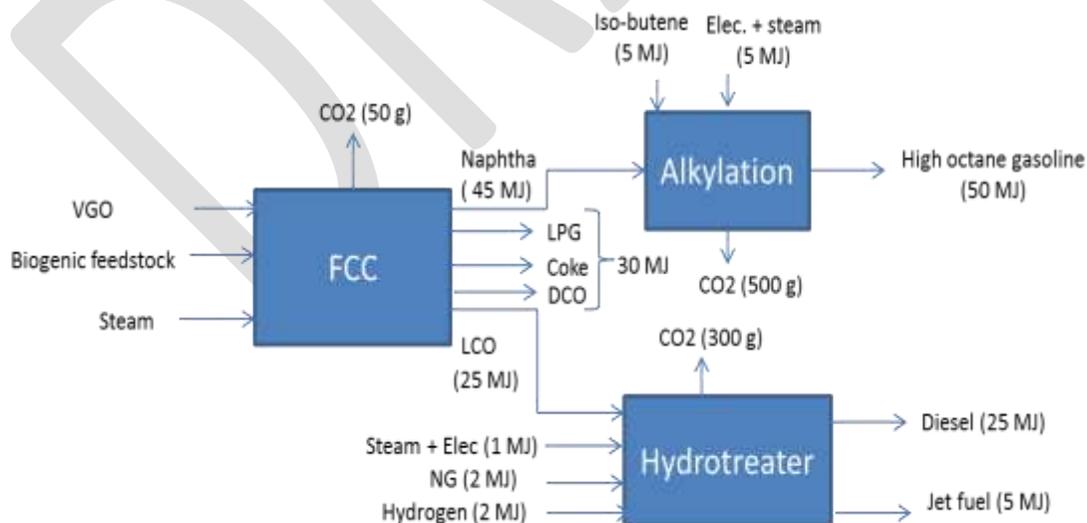
7.2.   Process unit level estimation

In this section, ARB staff is presenting two types of process unit level allocation for further evaluation- (1) energy content-based allocation and (2) hybrid marginal allocation.

7.2.1. Energy content–based allocation

Estimating GHG emissions at the refinery process unit level involves quantifying energy/hydrogen and chemical use and allocating GHG emissions among co-products at each process unit level which processes renewable fractions. In this approach, energy and emissions are allocated based on the energy content of output fuels. The process unit level approach is applicable irrespective of the mass ratio of biogenic feedstock to petroleum intermediate. However, it will entail rigorous modelling and data requirements on the part of an applicant. The applicant will be required to submit baseline emissions and energy use data in addition to energy requirements and emissions from co-processing for data corroboration.

Figure 7 provides an illustration of refinery units affected by co-processing. All the data related to the inputs, outputs and emissions are hypothetical.

The approach is detailed using an example of a biogenic feedstock co-processed with VGO to produce five major products: naphtha, LCO, DCO, coke and LPG. Naphtha is further processed in an alkylation unit to produce high octane gasoline feedstock. Likewise, LCO is further hydrotreated to produce diesel and jet fuel.

Figure 7. Process level energy inputs, outputs and CO$_2$ emissions for illustrating process unit level energy and CO$_2$ allocation

CO_2 emissions and carbon intensities associated with the finished fuels: gasoline, diesel and jet fuel- are calculated as follows:

1. The FCC unit releases 50 g CO_2 and produces 100 MJ of products, of which naphtha contributes 45 MJ and LCO contributes 25 MJ (Figure 7). The relative energy contributions of LCO and Naphtha to the total energy output are 25% and 45%, respectively. Hence, the CO_2 emissions are allocated accordingly in the same ratios.

   (a) Naphtha is allocated 45% of CO_2 emissions from FCC, which equals to 50 g CO_2 × 0.45 = 22.5 g CO_2
   (b) LCO is allocated 25% of CO_2 emissions from FCC, which equals to 50 G CO_2 × 0.25 = 12.5 g CO_2

2. The alkylation unit produces gasoline only (50 MJ). Hence all of the CO_2 emissions (500 g CO_2) from the alkylation unit are assigned to gasoline.

   The total CO_2 allocated to gasoline is the sum of the CO_2 emissions allocated to naphtha in the FCC and alkylation units (Figure 8).

   (a) Gasoline$_{CO2}$ = 22.5 g (step1a) + 500 g (step 2) = 522.5 g CO_2e

   Hence, carbon intensity of gasoline ($CI_{gasoline}$) = $\dfrac{Allocated\ CO2\ Emissions}{MJ\ of\ fuel\ produced}$ = Step 2a/50
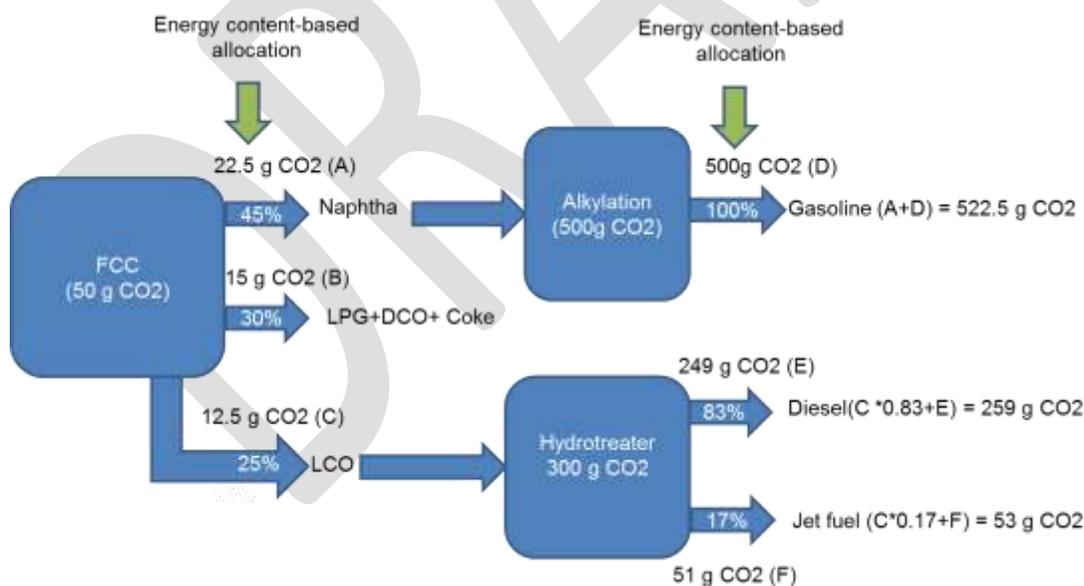
   = 522.5/50 = 10.45 g CO_2/MJ

Figure 8. Illustration of process unit level allocation

3. The hydrotreater unit produces 25 MJ of diesel and 5 MJ jet fuel while generating 300 g CO_2. Since diesel constitutes 83% of the total energy output and jet fuel constitutes 17% of the total energy output from hydrotreating, CO_2 emissions from the hydrotreater are allocated accordingly in the same ratios.

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(a) CO₂ allocated to diesel = 300 ✕ 0.83 = 249 g CO₂
(b) CO₂ allocated jet fuel = 300 ✕ 0.17 = 51 g CO₂

Hence, total CO_2 allocated to diesel or jet fuel would be the sum of the allocated emissions to LCO in the FCC unit and allocated emissions in the hydrotreating unit (Figure 8).

(c) Diesel_CO2 = 0.83 ✕ 12.5 g CO₂ (step 1b) + 249 g CO₂ (step 3a) = 259 g CO₂
(d) Jet fuel_CO2 = 0.17 ✕12. 5 g CO₂ (step 1b) + 51 g CO₂ (step 3b) = 53 g CO₂

Carbon intensity of diesel (CI_diesel) $\quad = \dfrac{Allocated\ CO2\ Emissions}{MJ\ of\ fuel\ produced}$ *= Step 3c/25 MJ*

$$= 259/25 = 10\ g\ CO_2/MJ$$

Carbon intensity of jetfuel (CI_jetfuel) $\quad = \dfrac{Allocated\ CO2\ Emissions}{MJ\ of\ fuel\ produced}$ *= Step 3d /5 MJ*

$$= 53/5 = 11\ g\ CO_2/MJ$$

Additionally, if co-products like renewable coke and LPG from co-processing are used in refinery processes on-site as process fuels, it will reduce the carbon intensities of renewable hydrocarbon fuels. In such cases it may be possible to assign fossil fuel displacement credits to renewable gasoline or diesel that would result when a renewable coproduct is used to replace fossil fuel on-site.

7.2.2. Hybrid marginal allocation

One possible drawback of the energy content based allocation for *co-processing* is that it may underestimate energy use and emissions when biogenic feedstock consumes disproportionately more energy and inputs like hydrogen. This limitation could be overcome by using the hybrid marginal allocation approach.

This approach requires the energy use and emissions data for the baseline with 100% petroleum feedstock which are then compared with the energy use and emissions from co-processing. Any incremental energy use and emissions relative to the baseline are attributed to the renewable fraction only. In addition, portions of energy use and emissions at the process unit level in the baseline are allocated to the renewable portion by subtracting emissions associated with the petroleum intermediate in co-processing from the baseline emissions. The latter is required to ensure that emissions attributable to renewable fuels are not underestimated. For example, even if there are no incremental emissions associated with co-processing relative to the baseline, there would emissions from co-processing units that would still be attributable to renewable fuels. The use of Linear Programming (LP) modelling can be a useful tool for calculating incremental emissions.

The hybrid marginal allocation approach is illustrated in Figure 9. The numbers used in Figure 9 are hypothetical and shown for the purposes of illustration.
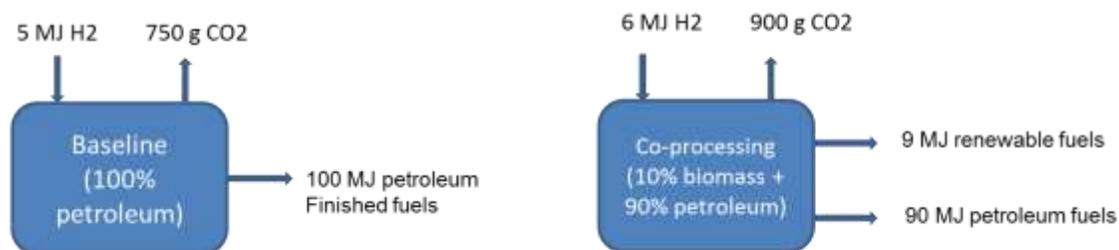
Figure 9. Illustration of the hybrid marginal approach

The steps to calculate the carbon-intensity of renewable fuels using the hybrid marginal allocation approach are as follows:

1. Incremental emissions (A) = $GHG_{CP} – GHG_B$
   Where,
   GHG_{CP} = GHG emissions in Baseline
   GHG_B = GHG emissions in Co-processing
   Hence,
   A = 900 – 750 = 150 g CO_2
2. Baseline emissions allocated to renewable output (B) = $GHG_B - GHG_B \times \%_{PI}$
   Where,
   $\%_{PI}$ = Percent contribution of petroleum intermediate on energy basis in co-processing
   Hence,
   B = 750 – (750 × 90/100) = 75
3. Total emissions allocated to renewable fuel output (C) = A + B = 150+75 = 225 g CO_2
4. Total renewable fuel output (D) = 9 MJ
5. Refinery carbon intensity of renewable fuel output = C/D = 225/9 = 25 gCO_2/MJ

8. Monitoring and verification

ARB is in the process of developing a monitoring and verification program targeted to begin in 2019. The complexity involved in co-processing such as pre-processing of feedstocks and co-processing of biogenic feedstocks with petroleum intermediates creates challenges in tracking, monitoring and verification. There is a need to develop a comprehensive monitoring and verification framework applicable to co-processing as ARB moves towards proposing an MVR program. Staff from the monitoring and verification team will outline steps for verification of co-processed renewable fuels. These will be made available at a future work group meeting. Feedback from stakeholders is solicited to develop protocols to ensure a robust monitoring and verification program can be established for co-processed fuels.

9. Summary

Co-processing of biogenic feedstocks is an emerging technology which has the potential to produce renewable and low carbon hydrocarbon fuels by utilizing sustainably sourced feedstocks. DOE estimates a FCC co-processing potential of 8 billion gallons per year. A preliminary analysis by staff indicates that about 1.5 billion gallons of renewable hydrocarbon fuel could potentially be produced in California petroleum refineries. Co-processing is appealing since it can utilize existing refining, transport, storage and distribution infrastructure. It offers an

opportunity to lower the costs of renewable hydrocarbon fuels as no significant additional upfront capital investments are required for refining, fuel transportation and distribution.

However, technological and market challenges remain. There are concerns regarding feedstock storage and handling owing to lower stability of pyrolysis and vegetable oils. Also, corrosive properties of biogenic feedstock and presence of impurities such as alkali metals may corrode process equipment and poison catalysts raising production costs. Relatively higher costs of biogenic materials in a period of low crude oil prices may impact economic competiveness of co-processing. However, these problems are not insurmountable. By limiting the amount of biogenic feedstocks to 10% or below and upgrading of pyrolysis oil, it may be possible to diminish the problems regarding material integrity and catalyst deactivation.

To facilitate the deployment of co-processing technologies, robust accounting methods for renewable mass quantification and GHG emissions from co-processing are crucial. This draft staff discussion paper presents a few approaches for consideration and feedback from stakeholders. They include mass-balance methods, the biomass feedstock energy content method and C^{14} isotopic analysis. Staff is seeking input on approaches presented and soliciting additional approaches from stakeholders on quantification of renewable fuel volumes.

This paper also presents LCA methodologies to estimate GHG emissions associated with co-processed renewable hydrocarbon fuels. The methodologies presented are preliminary and staff is soliciting feedback from stakeholders on the utility of the approaches presented here. Other approaches to estimating carbon intensities of co-processed renewable fuels are also solicited as part of stakeholder outreach through this discussion paper.

ARB staff is also developing a list of requirements with respect to co-processing that ARB may consider when implementing its monitoring and verification program. Stakeholder feedback to develop monitoring and verification plans is also being solicited.