

Co-processing of Low Carbon Feedstocks in Petroleum Refineries
Draft Discussion Paper



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California Air Resources Board

DRAFT

Contents

1.	Introduction	1
2.	Objectives	2
3.	Co-processed Fuel Pathway Certification	3
4.	Approaches to Low Carbon Fuel Quantification	3
4.1.	<i>Mass Balance Based on Observed Yields</i>	4
4.2.	<i>Carbon Mass Balance Method</i>	5
5.	Proposed LCA Methodology for Co-processing	8
5.1.	<i>Framework for Estimating Refinery Carbon Intensities of Co-processed Fuels</i> 8	
5.2.	<i>Process Unit Level Allocation for FCC Co-processing</i>	10
5.3.	<i>Incremental Allocation for Co-processing in Hydrotreaters</i>	15
6.	Co-processing of Renewable Hydrogen in Refineries.....	17
6.1.	<i>Proposed Amendment to the Renewable Hydrogen Credit Pilot Program</i> 17	
7.	Monitoring and Verification.....	19
8.	Conclusion	20
	Appendix.....	21
A.	Literature Review	21
A.1.	Co-processing.....	21
A.2.	Co-processing in Hydrotreaters	21
A.3.	Co-processing in a FCC unit	23
A.4.	Issues Related to Co-processing.....	30
A.5.	Co-processing Potential in California	32

List of Figures

Figure 1. FCC material flows (tpd = ton per day).....	7
Figure 2. LCA system boundary for co-processing.....	8
Figure 3. Framework for estimating refinery carbon intensity of co-processed fuels.....	9
Figure 4. Process level energy inputs, outputs and CO ₂ emissions for illustrating process unit allocation for FCC co-processing	11
Figure 5. Simplified illustration of process unit level allocation.....	13
Figure 6. Simplified illustration of the incremental allocation approach	15

List of Tables

Table 1. Estimation of renewable mass of co-processed products (10% pyrolysis oil + 90% VGO example)	7
Table A.1. Typical chemical and physical properties of potential co-processing feedstocks	24
Table A.2. Impact of upgrading of pyrolysis oil on liquid product yields.....	27
Table A.3. Co-processing capacity and low carbon hydrocarbon fuel production potential in California Refineries.....	32

1. Introduction

Co-processing refers to the simultaneous transformation of biogenic feedstocks or low carbon intensity (CI) non-biogenic feedstocks¹ and intermediate petroleum distillates such as vacuum gas oil (VGO) in existing petroleum refinery process units to produce low carbon hydrocarbon fuels. Co-processing has recently received attention due to its potential to provide low carbon 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.² The US Department of Energy estimates that more than 8 billion gallons of low carbon hydrocarbon fuels could potentially be produced from co-processing in 110 FCC units available in commercial refineries in the USA.³

Air Resources Board (ARB) staff recognizes the potential of co-processing to produce low carbon hydrocarbon fuel. 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 SB32⁴ in 2016, staff is considering additional greenhouse gas reductions from this program through 2030.⁵

A technical workgroup established by staff is exploring technical and logistical aspects of co-processing operations and finished fuel production. The invited members of the workgroup include technical experts from national laboratories, universities and technology companies. These experts have been presenting on co-processing issues [at public working meetings](#) attended by stakeholders representing oil companies, co-processing technology companies, co-processing feedstock producers, and environmental NGOs.

¹ Although co-processed fuel pathways will predominantly involve biogenic feedstocks, there is a possibility of co-processing low carbon intensity (CI) but non-biogenic feedstocks such as syncrude from recycled plastics. Tailpipe CO₂ emissions of fuels derived from non-biogenic but low CI feedstocks still need to be accounted for as part of fuel pathway CI certification.

² 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.

³ 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>

⁴ https://leginfo.legislature.ca.gov/faces/billNavClient.xhtml?bill_id=201520160SB32

⁵ 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

The workgroup's efforts are focused on the technical issues related to the quantification of low carbon fuel volumes from co-processing operations. In addition, since credits in the LCFS program are generated based on carbon intensity of co-processed streams relative to fossil gasoline and diesel, the workgroup 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/low carbon product streams are limited. Additionally, the biogenic fractions of the co-processed liquid products and process unit emissions will be important to ARB programs beyond the LCFS, including [the Mandatory Greenhouse Gas Reporting Regulation \(MRR\)](#) and the [Cap-and-Trade Program](#).

2. Objectives

The primary objective of this draft document is to review and evaluate current industry and academic research related to co-processing and to suggest options for:

- The quantification of low carbon fuel mass/volumes produced through co-processing; and
- Estimation of carbon intensities for fuels produced through co-processing.

Sub-objectives include:

- Identifying and summarizing existing research literature on co-processing;
- Suggesting guidelines for monitoring and verification of the key variables in co-processing projects; and
- Exploring operational, institutional and logistical challenges to sourcing and processing low carbon feedstocks in commercial petroleum refineries.

3. Co-processed Fuel Pathway Certification

Considering the complexity of co-processing operations, mixed feedstocks and unique challenges in quantifying low carbon fuel volumes and associated carbon intensities, all co-processed fuel pathways shall be handled as Tier 2 Fuel Pathways. This staff discussion paper aims to develop uniform quantification methods to estimate renewable fuel mass (or low carbon fuel mass in the case of low carbon intensity (CI) non-biogenic feedstocks) and well-to-wheel carbon intensities (CI) of co-processed fuels. The current LCFS regulation grants the Executive Officer authority to approve additional calculation methodologies that fall outside the scope of the CA-GREET framework. The co-processed fuel pathways are subject to all the applicable requirements for Tier 2 pathways described in section 95488 of the LCFS regulation. Section 95488 describes various requirements for obtaining and using fuel pathways including Tier 2 pathways. In addition, applicants shall be required to adhere to operating conditions listed by ARB staff for each co-processed fuel pathway to ensure that process is operating in the manner described in the fuel pathway applications.

4. Approaches to Low Carbon Fuel Quantification

For the LCFS, a critical issue in co-processing is the quantification of renewable fuel mass/volumes for the purposes of credit generation under this program.

As shown in Table A.1 in Appendix, 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, CO₂, and water in FCC or hydrotreating process 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. There is also a tendency for biogenic feedstocks to produce additional mixed C₄s (mixture of hydrocarbons consisting of four carbon atoms) 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 needed to quantify the low carbon fuel fractions of total liquid fuels produced and associated GHG emissions during co-processing to align with the requirements of the LCFS and potentially the MRR/Cap-and-trade regulatory frameworks.

This section describes the framework staff is considering to quantify low carbon fuel mass produced when co-processing biogenic/low CI feedstocks in conventional petroleum refineries. The approaches presented in this discussion paper are preliminary and address feedback from stakeholders and experts from co-processing workgroup meetings to-date. *The approaches discussed here are appropriate for co-processing with lower biogenic/low CI feedstock to petroleum feedstock ratios ($\leq 10\%$). For higher ratios ($>10\%$), these approaches may need to be modified.* Staff is soliciting additional 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.

While determining low carbon fuel content/yield, staff is considering requiring applicants to provide actual refinery material input and output data (material balance data). Applicants may choose to estimate of low carbon fuel yields using:

- (1) a mass balance approach based on observed yields,
or
- (2) a carbon balance method.

For the mass balance approach, a mass balance analysis, at minimum, should be performed on the unit where co-processing first occurs. If the composition and/or yield of the co-processed product(s) significantly change in downstream process units, applicants would likely be required to perform additional mass balance analyses on all units that receive low carbon streams downstream of the main co-processing unit. Any such mass balance should correspond to the amount of low carbon fuels estimated in the primary co-processing step. Stoichiometric calculations/theoretical modeling should also be used to verify that observed yields do not exceed maximum theoretical yields. If the observed yields exceed theoretical limits, adjustments may be suggested.

The mass balance based on observed yields and the carbon balance method are discussed in more detail in sections 4.1 and 4.2 below.

4.1. Mass Balance Based on Observed Yields

The “mass balance method based on observed yields” does not attempt to directly measure the amounts of low carbon fuel product produced. Instead it estimates the amount of low carbon fuel produced based on observing the changes in total yields when comparing co-processing scenarios to baseline scenarios with no low-carbon feedstock processed.

The low carbon product yield is calculated as follows.

$$LCM_i = CM_i - (M_p \times Y_i) \text{ Equation 1}$$

where:

LCM_i	=	Mass of i^{th} low carbon stream produced from co-processing
CM_i	=	Total mass of i^{th} fuel (low carbon + petroleum) produced from co-processing
M_p	=	Mass of petroleum feedstock used in co-processing
Y_i	=	Specific yield of i^{th} fuel in baseline (kg of i^{th} fuel/kg of petroleum feedstock)

CM_i , M_p and Y_i could be based on average yields utilizing data from a minimum of three months of operation with and without co-processing for provisional pathway applications.

The percent low carbon mass in i^{th} co-processed fuel ($\%LCM_i$) can be calculated as:

$$\%LCM_i = \frac{LCM_i}{CM_i} \quad \text{Equation 2}$$

This method assumes that yields from petroleum intermediates such as vacuum gas oil remain constant. This is a reasonable assumption for lower levels of biogenic/low CI feedstock addition.⁶ It does not require CO, CO₂ and H₂O measurements. However, one potential disadvantage of this approach is that if the fossil carbon that goes into coke in the baseline is converted to liquid fuel in co-processing, the fossil carbon could potentially be mischaracterized as renewable.⁷ However, at lower co-processing ratios, such a mischaracterization is expected to be small.

An example of calculating low carbon fuel yield from co-processing using the mass balance method based on observed yields is illustrated in the hydrotreater co-processing excel template available online on the LCFS website as part of materials posted for the June 2, 2017 Working Group meeting (https://www.arb.ca.gov/fuels/lcfs/lcfs_meetings/lcfs_meetings.htm).

4.2. Carbon Mass Balance Method

The carbon mass balance method is applicable for co-processing of biogenic feedstocks in general. The carbon mass balance method relies on the carbon content of biogenic feedstock and measurements of carbon lost as CO and CO₂ during co-processing.⁸ The difference between the biogenic carbon content and lost carbon provides the biogenic carbon that would end up in renewable products.

First, the renewable carbon correction factor of co-processed fuel is calculated as follows:

$$\%R_F = \frac{C_{biomass} - C_{CO_2} - C_{CO}}{C_{biomass}} \times 100 \quad \text{Equation 3}$$

where:

$$\%R_F = \text{Renewable carbon correction factor in percent}$$

⁶ The chemistry of co-processing has not been fully understood and it is possible that the presence of large amounts of oxygenates and water from bio-oil will have a significant impact on FCC chemistry - especially at higher levels of pyrolysis oil addition.

⁷ 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.

⁸ This method is based on the assumption that produced CO and CO₂ are biogenic. In reality, small portions of CO and CO₂ can come from petroleum feedstock. Since the amounts of CO₂ and CO produced from co-processing in FCC and in a hydrotreater are small relative to total output, e.g. (about 1-2% in FCC co-processing (Pinho et al., 2017)), this assumption will not introduce significant errors, especially at lower ratios of biogenic feedstock to petroleum feedstock. In addition, any error may lead to conservative yield estimates, which is an acceptable policy outcome.

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$C_{biomass}$	=	Mass of carbon in biogenic feedstock
C_{CO_2}	=	Mass of carbon lost as CO ₂
C_{CO}	=	Mass of carbon lost as CO

$\%R_F$ could be based on average data derived from minimum of three months of operation. $\%R_F$ can be used to convert the amount of fuels produced in co-processing into the amounts of renewable fuels (RM_i) as follows.

$$RM_i = \frac{M_{biomass}}{M_{total}} \times CM_i \times \%R_F \quad \text{Equation 4}$$

where:

RM_i	=	Mass of i^{th} renewable fuel from co-processing
$M_{biomass}$	=	Mass of biogenic feedstock
M_{total}	=	Total mass of feedstock co-processed (petroleum + biogenic)
CM_i	=	Mass of i^{th} fuel from co-processing

CM_i could be based on average yields utilizing data from a minimum of three months of operation.

In the example shown in Figure 1, 10 tons per day (tpd) of biogenic feedstock are co-processed with 90 tpd of VGO. The carbon content of the biogenic feedstock is 60%, which translates into 6 tpd of renewable carbon input. Since 1 tpd of C is lost as CO and CO₂ (Figure 1), the renewable carbon correction factor ($\%R_F$) is calculated to be = $(6-1)/6 * 100 = 83.3\%$.

The corresponding renewable amount for each individual fuel calculated using Equation 4 is shown in Table 1.

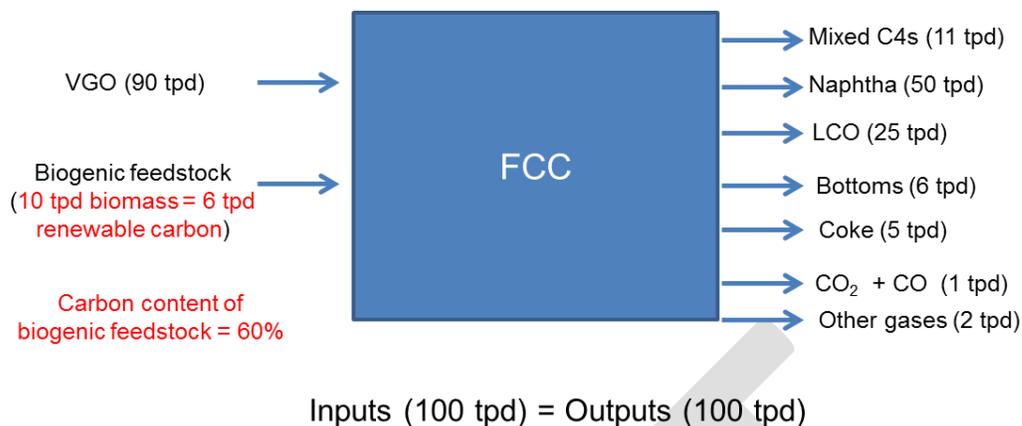


Figure 1. FCC material flows (tpd = ton per day)

Table 1. Estimation of renewable mass of co-processed fuels based on carbon mass balance method (10% pyrolysis oil + 90% VGO example)

Dry mass of biogenic feedstock ($M_{biomass}$) tpd	Total mass of feedstock (M_{total}) tpd	Product (CM_i)	CM_i (tpd)	$\%R_F$ (Equation 3)	Renewable mass (tpd) Equation 4
10	100	Mixed C4s	11	83.3%	0.9
		Naphtha	50	83.3%	4.2
		LCO	25	83.3%	2.1
		Bottoms (HCO+ Slurry oil)	6	83.3%	0.5
		Coke	5	83.3%	0.4

5. Proposed LCA Methodology for Co-processing

Similar to all other LCFS pathways, applicants for co-process pathways must perform a well-to-wheel analysis to estimate carbon intensities of co-processed low carbon fuels (Figure 2). 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.

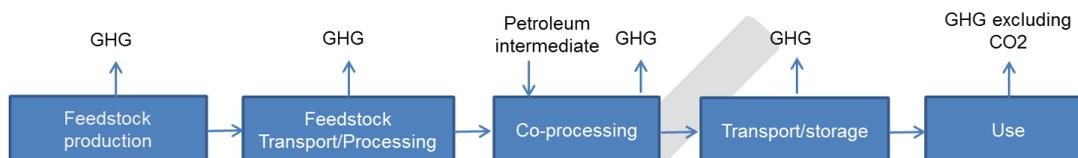


Figure 2. LCA system boundary for co-processing

Except for the refinery co-processing step, all other lifecycle steps are similar to fuel pathways for standalone biofuel production. Hence this paper focuses only 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 low carbon and petroleum fractions in the finished fuel.

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

5.1. Framework for Estimating Refinery Carbon Intensities of Co-processed Fuels

Staff is considering a framework for quantifying refinery carbon intensities of low carbon fuels for further discussion and feedback as shown in Figure 3.

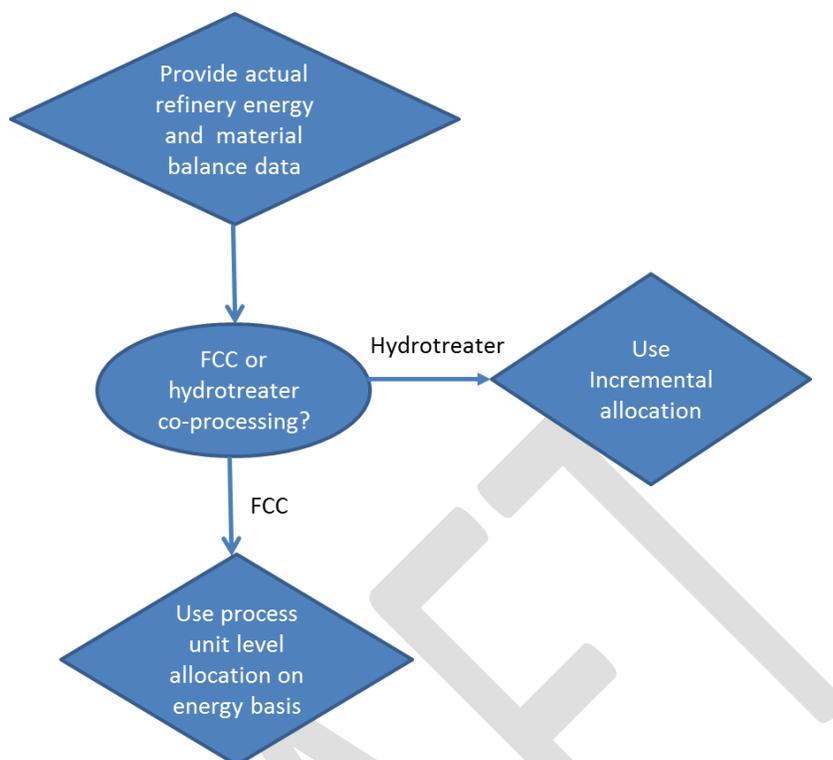


Figure 3. Framework for estimating refinery carbon intensity of co-processed fuels

Staff is considering the above framework as a guide for assessing carbon intensities of low carbon fuels obtained from co-processing. Since the energy and chemical requirements and method of assessment for FCC co-processing differs from hydrotreater co-processing, they are described separately below. In particular, co-processing of biogenic feedstocks in a hydrotreater is likely to consume disproportionately more hydrogen and hence a straightforward allocation of GHG emissions based on energy content would not fully capture the emissions attributable to low carbon fuels.

5.1.1. FCC Co-processing

Estimating carbon intensities of low carbon fuels obtained from FCC co-processing will likely involve the following steps:

- Determine the energy and material balance data for the FCC unit and other downstream units, which receive low carbon inputs (mainly the alkylation unit, and the diesel and naphtha hydrotreaters).
 - Data should cover yields and energy/chemical use in the FCC co-processing system boundary (see Figure 4).
- Allocate energy/chemical inputs and associated emissions step by step for each unit based on energy content allocation.

The method for estimating CIs of low carbon fuels obtained from co-processing in an FCC unit is described in section 5.2 below with an illustrative example. In addition, a detailed FCC co-processing template has been posted online (https://www.arb.ca.gov/fuels/lcfs/lcfs_meetings/lcfs_meetings.htm) to illustrate the process unit level allocation approach to estimate carbon intensities of various low carbon fuels.

5.1.2. Co-processing in Hydrotreaters

Staff is suggesting the following requirements in estimating carbon intensities of low carbon fuels obtained from hydrotreater co-processing:

- Determine the energy and material balance data for the hydrotreater unit. Data should cover production with and without co-processing.
- Allocate energy/chemical use and associated GHG emissions based on the incremental allocation approach. The incremental allocation approach is chosen because hydrotreating of biomass derived oil is expected to consume significantly more hydrogen and produce more propane relative to 100% fossil feedstock.

The method for estimating CIs of low carbon fuels obtained from co-processing in a hydrotreater is described in section 5.3 below using an illustrative example. In addition, a detailed hydrotreater co-processing template has been posted online (https://www.arb.ca.gov/fuels/lcfs/lcfs_meetings/lcfs_meetings.htm) to illustrate the incremental allocation method to estimate a refinery CI for low carbon diesel.

5.2. Process Unit Level Allocation for FCC Co-processing

Estimating GHG emissions at the FCC co-processing system boundary level involves quantifying material and energy balances (inputs and outputs) for each process unit and allocating GHG emissions among co-products at each process unit level where low carbon fuels are co-produced with petroleum fuels. In this approach, total energy and emissions associated with each process unit are allocated to individual products based on the energy content of products at each processing unit involved.

The process unit level approach is applicable irrespective of the mass ratio of biogenic feedstock (or low CI non-biogenic feedstock) to petroleum intermediates. The applicant would be required to submit baseline emissions and energy use data in addition to emission and energy data from co-processing for data corroboration.

Figure 4 represents a FCC co-processing system boundary.⁹ The process unit level approach is discussed using a simplified example of a biogenic feedstock co-processed with VGO in an FCC unit to produce five major products: light cracked naphtha (LCN), heavy cracked naphtha (HCN), light cycle oil (LCO), mixed C4s, and bottoms (heavy

⁹ All the data related to inputs, outputs and emissions in the illustrative examples are hypothetical and do not represent actual refinery operations.

cycle oil (HCO) and slurry oil). *Although the example presented here deals with the biogenic feedstock, the method is also applicable for low CI non-biogenic feedstocks.*

Fuel gas and coke produced are consumed internally and hence are not considered as co-products. LCN is further processed in a Merox unit which is primarily designed to remove sulfur from petroleum derived LCN. Since the renewable LCN contains a negligible amount of sulfur, no emissions from the Merox unit are assigned to the renewable component of LCN. Heavy cracked naphtha is processed in a heavy cracked naphtha hydrotreater to produce heavy naphtha. Likewise, LCO is further hydrotreated to produce diesel. Mixed C4s produced in the FCC goes to an alkylation unit where it reacts with isobutene to produce an alkylate, a gasoline blendstock. The alkylate is mixed with the naphtha obtained from the heavy cracked naphtha hydrotreater and the Merox unit to produce gasoline.

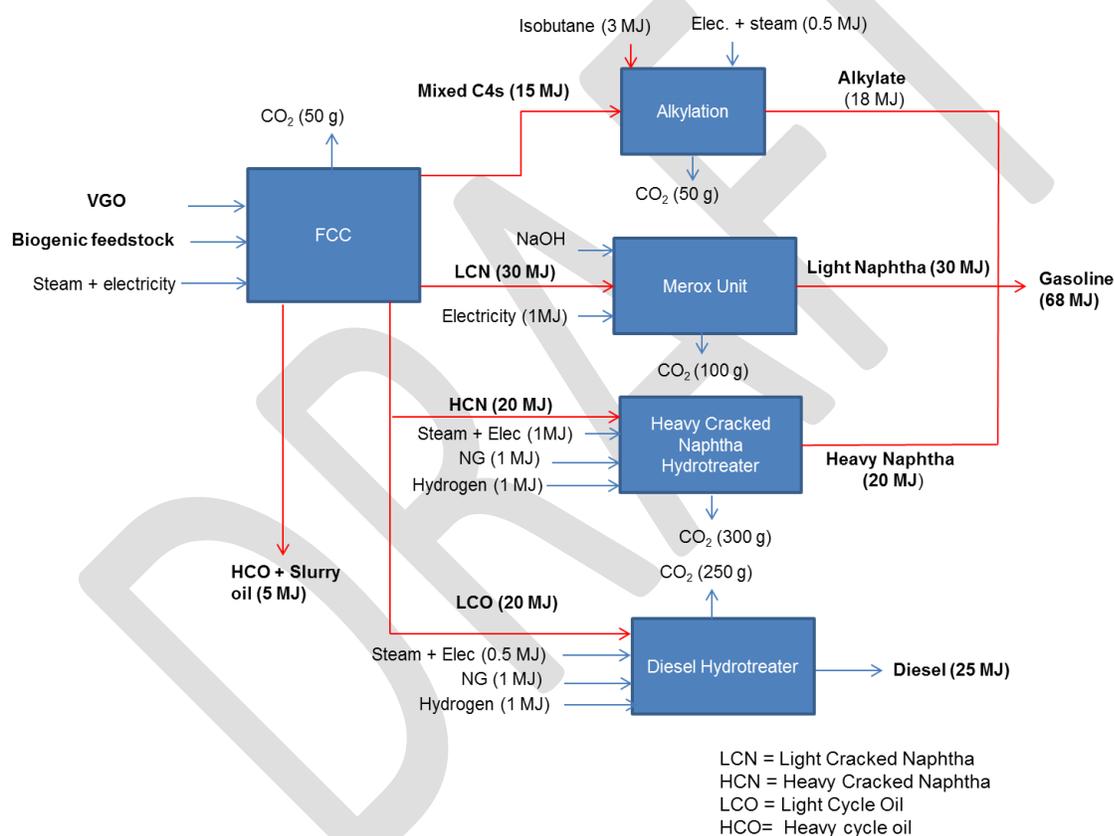


Figure 4. Process level energy inputs, outputs and CO₂ emissions for illustrating process unit allocation for FCC co-processing

CO₂ emissions and carbon intensities associated with the finished fuels (i.e. renewable carbon gasoline and renewable carbon diesel) are calculated as follows:

Low Carbon Gasoline

1. The FCC unit releases 50 gCO₂ and produces 90 MJ of products, of which LCN accounts for 30 MJ, HCN accounts for 20 MJ, LCO accounts for 20 MJ, bottoms (heavy cycle oil and slurry oil) accounts for 5 MJ, and mixed C4s accounts for 15 MJ (Figure 4). The relative energy contributions of LCN, HCN, LCO, bottoms and mixed C4s to the total energy output are 33%, 22%, 22%, 6% and 17%, respectively. Hence, the CO₂ emissions are allocated accordingly in the same ratios.
 - A. Mixed C4s is allocated 17% of CO₂ emissions from the FCC unit, which equals to $50 \text{ gCO}_2 \times 0.17 = 8.5 \text{ gCO}_2$
 - B. Light cracked naphtha (LCN) is allocated 33% of CO₂ emissions from the FCC unit, which equals to $50 \text{ gCO}_2 \times 0.33 = 16.5 \text{ gCO}_2$
 - C. Heavy cracked naphtha (HCN) is allocated 22% of CO₂ emissions from the FCC unit, which equals to $50 \text{ gCO}_2 \times 0.22 = 11 \text{ gCO}_2$
 - D. LCO is allocated 22% of CO₂ emissions from the FCC unit, which equals to $50 \text{ g CO}_2 \times 0.22 = 11 \text{ gCO}_2$
 - E. Bottoms (Heavy cycle oil + Slurry oil) is allocated 6% of CO₂ emissions from the FCC unit, which equals to $50 \text{ g CO}_2 \times 0.06 = 3 \text{ gCO}_2$
2. The alkylation unit produces an alkylate only (18 MJ).
 - F. Hence all of the CO₂ emissions (50 gCO₂) from the alkylation unit are assigned to the alkylate.

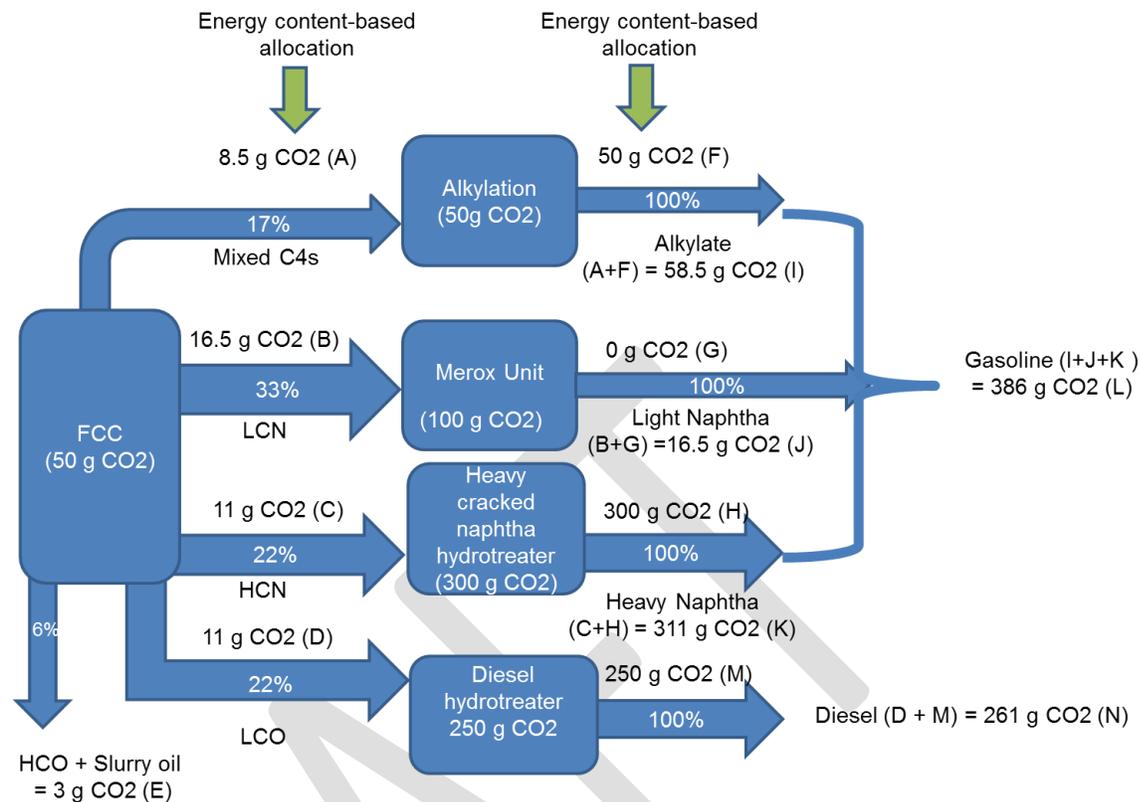


Figure 5. Simplified illustration of process unit level allocation

- The Merox unit produces 30 MJ of light naphtha while generating 100 gCO₂. Since the Merox unit is primarily designed to remove sulfur from petroleum naphtha and renewable light naphtha does not contain sulfur, none of the GHG emissions from the Merox unit are allocated to renewable light naphtha.

G. CO₂ allocated to light naphtha (renewable) = 0 gCO₂

- The heavy cracked naphtha hydrotreater unit produces 50 MJ of heavy naphtha (gasoline blendstock) while generating 300 gCO₂. Since the naphtha constitutes 100% of the total output, all of CO₂ emissions from the hydrotreater are allocated to the naphtha.

H. CO₂ allocated to heavy naphtha = 300 gCO₂

- Finally, the alkylate (18 MJ) is mixed with light and heavy naphtha (50 MJ) to produce 68 MJ of gasoline.
- Hence the total CO₂ allocated to gasoline is the sum of the CO₂ emissions allocated to the alkylate and light and heavy naphtha starting from the FCC unit (Figure 5).

$$\begin{aligned}
 I. \text{ Alkylate}_{CO_2} &= 8.5 \text{ g (A)} + 50 \text{ g (F)} = 58.5 \text{ gCO}_2\text{e} \\
 J. \text{ Light Naphtha}_{CO_2} &= 16.5 \text{ g (B)} + 0 \text{ g (G)} = 16.5 \text{ gCO}_2\text{e} \\
 K. \text{ Heavy Naphtha}_{CO_2} &= 11 \text{ g (C)} + 300 \text{ g (H)} = 311 \text{ gCO}_2\text{e}
 \end{aligned}$$

$$L. \text{ Gasoline}_{CO_2} = (I + J + K) = 386 \text{ gCO}_2\text{e}$$

Since 68 MJ of gasoline is produced, the carbon intensity of low carbon gasoline (CI_{gasoline})

$$= \frac{\text{Allocated CO}_2 \text{ Emissions}}{\text{MJ of fuel produced}}$$

$$= \text{Step (L)}/68 = 386/68 = 5.67 \text{ gCO}_2\text{e}/\text{MJ}$$

Low Carbon Diesel

7. The hydrotreater unit produces 25 MJ of diesel while generating 250 gCO₂. Since the diesel constitutes 100% of the total energy output, all of CO₂ emissions from the diesel hydrotreater are allocated to diesel from the hydrotreater.

$$M. \text{ CO}_2 \text{ allocated to diesel} = 250 \text{ gCO}_2$$

Hence, the total CO₂ allocated to diesel would be the sum of the allocated emissions to LCO in the FCC unit and the allocated emissions in the hydrotreating unit (Figure 5).

$$N. \text{ Diesel}_{CO_2} = 11 \text{ gCO}_2 \text{ (D)} + 250 \text{ gCO}_2 \text{ (M)} = 261 \text{ gCO}_2$$

The carbon of intensity of diesel is calculates as:

$$\begin{aligned}
 \text{Carbon intensity of low carbon diesel } (CI_{\text{diesel}}) &= \frac{\text{Allocated CO}_2 \text{ Emissions}}{\text{MJ of fuel produced}} = \\
 & \text{Step (N)}/25 \text{ MJ} \\
 & = 261/25 = 10.44 \text{ gCO}_2/\text{MJ}
 \end{aligned}$$

Additionally, if co-products like renewable coke and LPG from co-processing are used in refinery processes on-site as process fuels, it may further reduce the carbon intensities of renewable hydrocarbon streams.

For a detailed illustration of the process unit level allocation approach, refer to the FCC co-processing template posted online (https://www.arb.ca.gov/fuels/lcfs/lcfs_meetings/lcfs_meetings.htm June 2, 2017 meeting).

5.3. Incremental Allocation for Co-processing in Hydrotreaters

One possible drawback of the energy content-based allocation for co-processing is that it may underestimate energy use and emissions when a biogenic feedstock consumes disproportionately more energy and inputs such as hydrogen. This limitation could be overcome by using the incremental allocation approach. Since the co-processing of biogenic feedstock in hydrotreaters is likely to consume a disproportionate amount of hydrogen (and likely to generate a greater amount of propane), staff is considering the incremental allocation approach as a preferred method for co-processing in a hydrotreater.

This approach requires energy use and emissions data for the baseline (assuming 100% petroleum-derived 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 low carbon fuel fraction only. In addition, portions of energy use and emissions at the process unit level in the baseline are also allocated to the low carbon fuel portion. The latter is required to ensure that emissions attributable to low carbon fuels are not underestimated. For example, even if there are no incremental emissions associated with co-processing relative to the baseline, there would be emissions from co-processing units that would be attributable to the low carbon stream.

The incremental allocation approach is illustrated in Figure 6. The values used in Figure 6 are hypothetical and used only for illustration. *Although the example presented here deals with the biogenic feedstock, the method is also applicable to low CI non-biogenic feedstocks.*

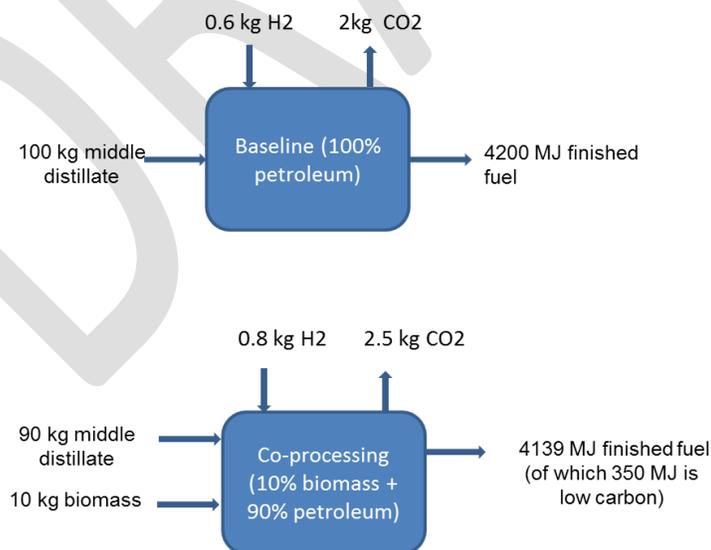


Figure 6. Simplified illustration of the incremental allocation approach

The steps to calculate the carbon-intensity of low carbon fuels using the incremental allocation approach are as follows:

- (1) Calculate incremental GHG emissions associated with low carbon fuel using Equation 5.

$$GHG_{LCF} = GHG_{cp} - (M_p \times Y_i) \quad \text{Equation 5}$$

where:

GHG_{LCF}	=	Incremental GHG emissions associated with low carbon fuel
GHG_{cp}	=	GHG of i^{th} fuel (low carbon + petroleum) produced from co-processing
M_p	=	Mass of middle distillate used in co-processing
Y_i	=	Specific emissions per unit middle distillate processed in the baseline (kg CO ₂ e/ kg-middle distillate)

In the above example (Figure 6),

$$\begin{aligned} GHG_{cp} &= 2.5 \text{ kg} \\ M_p &= 90 \text{ kg} \\ Y_i &= 2 \text{ kg CO}_2/100 \text{ kg middle distillate} = 0.02 \text{ kg CO}_2/\text{kg middle distillate} \end{aligned}$$

Hence, $GHG_{LCF} = 0.7 \text{ kg CO}_2$

- (2) Estimate a carbon intensity by dividing GHG_{LCF} with MJ of low carbon fuel produced which is 350 MJ. The low carbon fuel amount is determined using the method described in Section 4.

$$\text{Carbon intensity (low carbon fuel)} = 0.7 \text{ kg CO}_2/350 \text{ MJ} = 2.0 \text{ g CO}_2\text{e/MJ}$$

For a detailed illustration of the incremental allocation approach, refer to the hydrotreater co-processing template posted online (https://www.arb.ca.gov/fuels/lcfs/lcfs_meetings/lcfs_meetings.htm. June 2, 2017 meeting).

6. Co-processing of Renewable Hydrogen in Refineries

As part of the co-processing workgroup meetings, renewable hydrogen co-processing was initially included along with the biomass co-processing discussions to solicit stakeholder feedback on whether it was appropriate to consider renewable hydrogen as part of the co-processing Tier 2 pathway application framework. Stakeholders opined that it would be appropriate to address renewable hydrogen under the existing *Renewable Hydrogen Credit Pilot Program (Section 954489 (g))* of the LCFS regulation. Staff agrees and will therefore not consider renewable hydrogen used in hydrotreaters under co-processing pathway applications.

However, staff is also proposing to make an amendment to enhance the effectiveness of the Renewable Hydrogen Credit program by simplifying the methodologies and expanding the scope of eligible hydrogen pathways.

This program currently awards credits to refineries based on GHG reductions achieved by substituting renewable hydrogen for fossil hydrogen derived from natural gas via steam methane reforming (SMR). In the case of SMR-derived hydrogen, there is an opportunity to simplify the methodology and reduce administrative burden by considering carbon intensities of natural gas and renewable natural gas.

6.1. Proposed Amendment to the Renewable Hydrogen Credit Pilot Program

Staff is considering replacing the content of section 954489(g) (2) of the current Renewable Hydrogen Credit Pilot Program with the following text.

Calculation of Credits:

(A) For CARBOB or diesel fuel that is partially or wholly derived from renewable hydrogen produced from renewable natural gas (RNG) and which displaces fossil natural gas in a steam methane reforming (SMR) unit, the calculation of credits shall be as follows:

$$Credits_{RIC}^H = (CI_{NG} - CI_{RNG}) \times E_{RNG} \times C \quad \text{Equation 6}$$

where:

$Credits_{RIC}^H$ is the amount of LCFS credits generated (a zero or positive value), in metric tons, by renewable hydrogen;

CI_{NG} is the carbon intensity of North American CNG with a value of 78.37 gCO₂e/MJ. This carbon intensity score will be subject to updates;

CI_{RNG} is the carbon intensity of the renewable natural gas in gCO₂e/MJ delivered to a refinery and is estimated using the CA-GREET model. The process for obtaining CI_{RNG} will be similar to regular fuel pathway applications. The value of CI_{RNG} primarily

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depends on the type of biogenic feedstock, method of production, and transportation distance;

E_{RNG} is the amount energy of RNG in MJ delivered to a refinery; and

$$C = 1.0 \times 10^{-6} \frac{MT}{gCO2e}$$

(B) For CARBOB or diesel fuel that is partially or wholly derived from renewable hydrogen produced from other production processes such as electrolysis using renewable electricity and syngas from biomass gasification, the calculation of credits shall be as follows:

$$Credits_{RIC}^H = (CI_{Fossil}^H - CI_{Renewable}^H) \times D_{Renewable}^H \times V_{Renewable}^H \times C \quad \text{Equation 7}$$

where:

$Credits_{RIC}^H$ is the amount of LCFS credits generated (a zero or positive value), in metric tons, by renewable hydrogen;

CI_{Fossil}^H is the carbon intensity of fossil hydrogen (baseline) in gCO_2e/MJ delivered at the refinery, as estimated using the CA-GREET model. The process for obtaining CI_{Fossil}^H will be similar to regular fuel pathway applications;

$CI_{Renewable}^H$ is the carbon intensity of renewable hydrogen in gCO_2e/MJ delivered at the refinery, as estimated using the CA-GREET model. The process for obtaining $CI_{Renewable}^H$ will be similar to regular fuel pathway applications. The value of $CI_{Renewable}^H$ primarily depends on the type of feedstock, method of production, and transport distance;

$V_{Renewable}^H$ is the amount of renewable hydrogen in kg;

$D_{Renewable}^H$ is the energy density of hydrogen in MJ/kg; and

$$C = 1.0 \times 10^{-6} \frac{MT}{gCO2e}$$

7. 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/low CI 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. This framework may include documentation of refinery energy use within the co-processing system boundary and fuel production data: isotopic analysis of representative samples to verify the presence of renewable content in co-processed fuels; and similar steps. We welcome stakeholder feedback on if the calculation methodologies outlined in this paper are sufficiently clear to facilitate third-party verification.

With regard to biomass/low carbon CI feedstock supply, monitoring and verification requirements are expected to be similar to biomass-based diesel pathways.

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8. Conclusion

Co-processing of biogenic/low CI feedstocks is an emerging technology which has the potential to produce low carbon hydrocarbon fuels by utilizing sustainably sourced feedstocks. The Department of Energy (DOE) estimates FCC co-processing potential of 8 billion gallons per year.³ A preliminary analysis by staff indicates that about 1.5 billion gallons of low carbon 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 may offer an opportunity to lower the costs of low carbon hydrocarbon fuel production 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 competitiveness of co-processing. However, these problems are not insurmountable. Issues related with catalyst deactivation and material integrity can either be addressed by using smaller amounts of biogenic feedstocks or by upgrading of pyrolysis oil and other process improvements.

To facilitate the deployment of co-processing technologies, robust accounting methods for low carbon fuel mass quantification and GHG emissions from co-processing are critical. This draft document presents a preliminary framework and methods for estimating low carbon fuel content of co-processed fuels for consideration and feedback from stakeholders.

This document also presents LCA methodologies to estimate GHG emissions associated with co-processed low carbon hydrocarbon fuels. The methodologies presented are preliminary and staff is soliciting feedback from stakeholders to further refine and streamline the approaches presented here.

Staff is considering guidelines to include co-processed low carbon fuels under the mandatory monitoring and verification program being considered for the LCFS. Stakeholder feedback to develop monitoring and verification plans is also being solicited.

Appendix

A. Literature Review

A.1. Co-processing

Co-processing refers to the simultaneous transformation of biogenic or low CI feedstocks and intermediate petroleum products such as vacuum gas oil (VGO) in existing petroleum refinery process units to produce low carbon hydrocarbon fuels. Co-processing involves transformation (e.g., cracking and hydrogenation) of biogenic oils, vegetable oils and fats or other low CI non-biogenic feedstocks (e.g. syncrude from plastics) 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 pathway for utilizing existing refining infrastructure to process biomass—including lignocellulosic feedstocks—and increase the supply of drop-in biofuels to the market.¹⁰ 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.

Refining processes that could potentially be utilized for co-processing include (1) catalytic cracking, (2) hydrotreating, and (3) hydrocracking.¹¹

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.

A.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

¹⁰ Freeman, C., et al. "Initial assessment of US refineries for purposes of potential bio-based oil insertions." (2013).

¹¹ Co-processing of biogenic feedstocks in thermal cracking units (visbreaker and coker) may be possible. However, thermal cracking of biogenic feedstocks results in products with high oxygen content and is generally not considered practical for producing renewable diesel and gasoline (Source: Melero, J. A., et al. "Production of biofuels via catalytic cracking." *Handbook of biofuels production: processes and technologies* (2011): 390-419.)

VGO in hydrotreaters.^{12,13} Typical catalysts used in hydrotreatment of triglycerides include CoMo/Al₂O₃ and NiMo/Al₂O₃. Figure A 1 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.

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.¹⁴

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.¹⁵ 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.

¹² Dimitriadis, Athanasios, and Stella Bezergianni. "Co-hydroprocessing gas-oil with residual lipids: effect of residence time and H₂/Oil ratio." *Journal of Cleaner Production* 131 (2016): 321-326.

¹³ Satyarthi, J. K., et al. "Studies on co-processing of jatropha oil with diesel fraction in hydrodesulfurization." *Fuel Processing Technology* 118 (2014): 180-186.

¹⁴ 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.

¹⁵ 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.

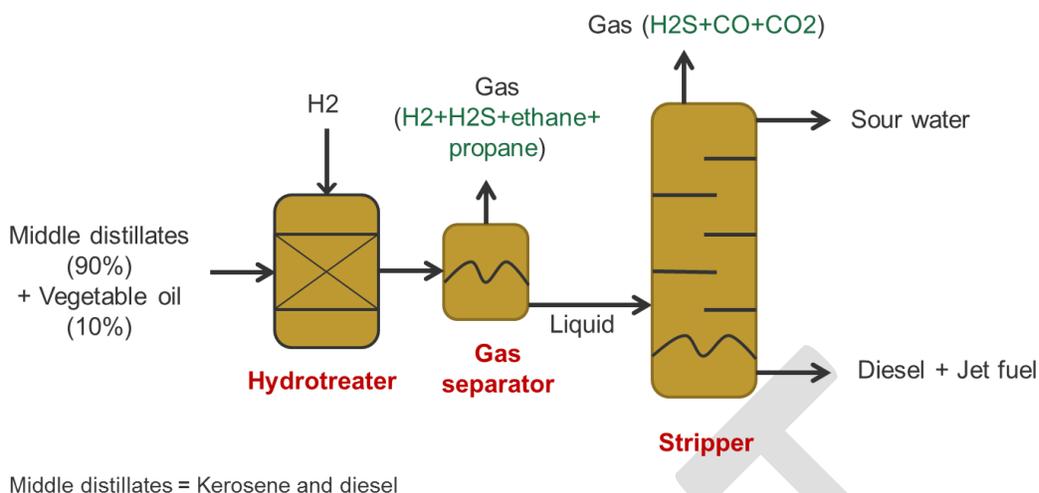


Figure A 1. Schematic of co-processing in a hydrotreater

A.3. Co-processing in a FCC unit

A.3.1. 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.¹⁶ Pyrolysis oil tends to have high oxygen content, ranging from 8 to 63 percent (dry basis) depending on feedstocks and pyrolysis conditions, although typical values may range from 28 to 50 percent (Table A.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.¹⁷ 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 A.1. For comparison, similar properties for VGO and diesel oil are also included in Table A.1.

Co-processing in FCC units is expected to be a promising route for transforming pyrolysis oil into low carbon gasoline and diesel fuels. Since most refineries in the U. S.

¹⁶ Melero, J. A., et al. "Production of biofuels via catalytic cracking." *Handbook of biofuels production: processes and technologies* (2011): 390-419.

¹⁷ Gollakota, Anjani RK, et al. "A review on the upgradation techniques of pyrolysis oil." *Renewable and Sustainable Energy Reviews* 58 (2016): 1543-1568.

are equipped with FCC units, the infrastructure for co-processing pyrolysis oil already exist in the country. Figure A 2 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 CO₂ 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.

Table A.1. Typical chemical and physical properties of potential co-processing feedstocks

Fuel Property	Unit	Pyrolysis oil ¹⁸	Vegetable oil ¹⁹	Vacuum gas oil ²⁰	Diesel oil ¹⁸
Density@ 15°C	kg/L	1.05-1.25	0.9-0.93	0.96-0.98	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 ¹⁴	86.3
Hydrogen	% wt.	5-7	~12	10.7-11.0	12.8
Oxygen	% wt.	28-54	~9	0.4	0.9
Sulfur	% wt.	<0.05	Negligible	2-3	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 in FCC units is carried out at temperatures ranging from 350-500°C at atmospheric pressure and in the presence of zeolite catalysts. Studies have shown that a portion of pyrolysis oil ends up as coke, mixed C4s, CO₂, CO, and water.²¹ This is attributed to lower thermal stability of pyrolysis oil, resulting in the formation of larger amounts of coke, CO₂, CO, and LPG, compared to cracking VGO alone. Due to higher oxygen content of pyrolysis oil, water is also produced during the reaction, in contrast when processing VGO only. In-addition, co-processing of pyrolysis oil in FCC units results in higher amounts of oxygenated and phenolic compounds in liquid products.

¹⁸ 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.

¹⁹ Toscano, Giuseppe, and Eleonora Maldini. "Analysis of the physical and chemical characteristics of vegetable oils as Fuel." *Journal of Agricultural Engineering* 38.3 (2007): 39-47.

²⁰ Derived from the Prelim model (<http://www.ucalgary.ca/lcaost/prelim>) and other sources.

²¹ Pinho, Andrea de Rezendo et al. "Co-processing raw bio-oil and gasoil in an FCC unit." *Fuel Processing Technology* 131 (2015): 159-166.

Recently, a pilot scale study by Pinho et al.²¹ utilized a tracer technique (C^{14}) to quantify the relative proportion of pyrolysis oil-originating products in a pilot scale FCC unit. The study found 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 CO₂, thereby reducing overall liquid product yields. These results are consistent with yield trends (Figure A 3) 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.²²

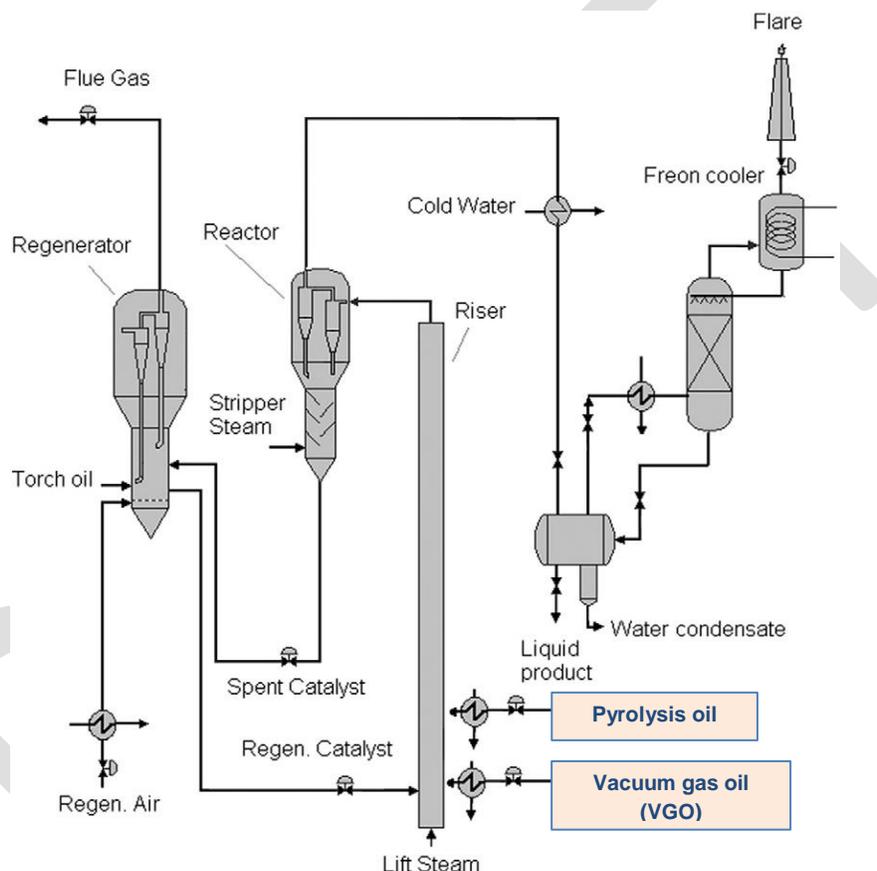


Figure A 2. A schematic of an FCC unit for co-processing²¹

Previous pilot-scale studies suggest carbon conversion efficiencies in the range of 15-20 percent.²¹ 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

²² 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.

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.²¹ 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).² 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.²² where hydrogenated pyrolysis oil yielded 74% (by weight) liquid products compared to 69% for dry pyrolysis oil (Table A.2).

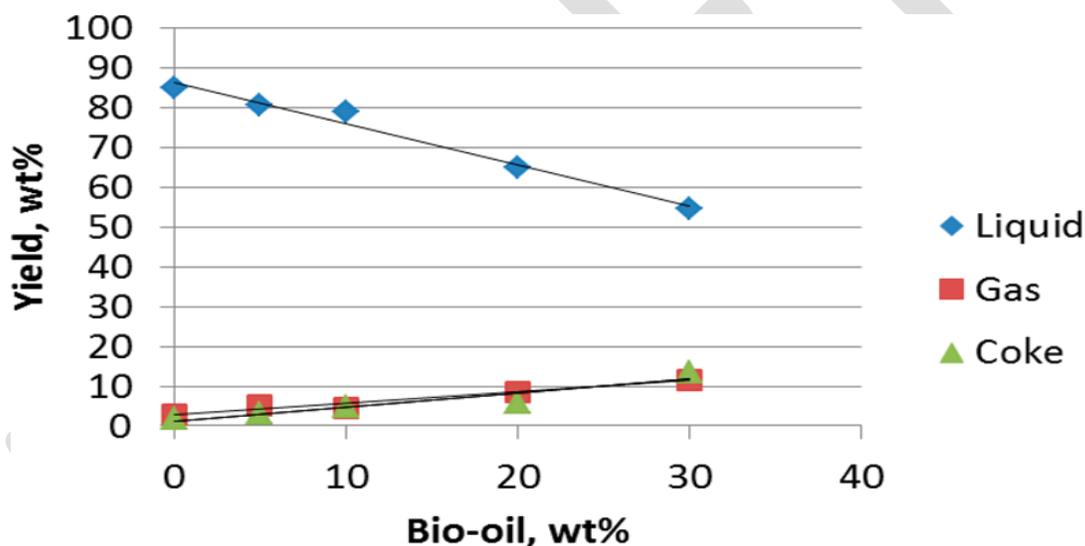


Figure A 3. Product yield trends at various bio-oil to VGO ratios (source: Lindfors et al, 2015²²)

With regard to coke yields, FCC co-processing studies show mixed results. Some studies including Lindfors et al. show an increase in coke production (Figure A 3) whereas a pilot-scale study by Pinho et al.²³ shows lower coke production, especially at higher conversion levels (wt %).

²³ Pinho, de Rezende Andrea, et al. "Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production." *Fuel* 188 (2017): 462-473.

Table A.2. Impact of upgrading of pyrolysis oil on liquid product yields
(Source: Lindfors et al.²²)

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

A.3.2. Co-processing of Glycerol in a Typical FCC unit

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 low carbon diesel and gasoline. Depending on the types of catalyst used, glycerol co-processing provides different product yields. A ZSM-5 catalyst²⁴ 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 an FCC unit leads to higher levels of coke, in the range of 30-50 percent.²⁵ Given that glycerol is currently produced in limited amounts, mainly as by-product of biodiesel, low carbon fuel production from glycerol co-processing can be constrained by its limited supply. .

A.3.3. 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 is technically possible. Unlike in thermal cracking, FCC catalysts remove oxygen from final products in the form of CO₂, 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.^{26,27,28} Since triglycerides primarily comprise paraffinic and olefinic hydrocarbons, the resulting product slate is likely to lead to an increased amount of gasoline.

²⁴ Zeolite Socony Mobil-5 (ZSM-5) is an aluminosilicate zeolite, a catalyst used primary in petroleum in refineries.

²⁵ 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.

²⁶ 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.

²⁷ 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.

²⁸ 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.

Research carried out to date on co-processing of triglycerides with VGO under FCC conditions points to the following trends in the product outputs:^{26,29,30,31}

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 liquefied petroleum gas (LPG) and dry gas. The higher yields of LPG and dry gas 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 CO₂ increases due to the presence of oxygen in the biogenic feedstock.
- While the polyaromatic content decreases, the monoaromatic and diaromatic content increases. 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 A 4 which shows varying product outputs from co-processing of palm oil (PO) with vacuum gas oil (VGO) under FCC conditions.

²⁹ 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.

³⁰ 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.

³¹ 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.

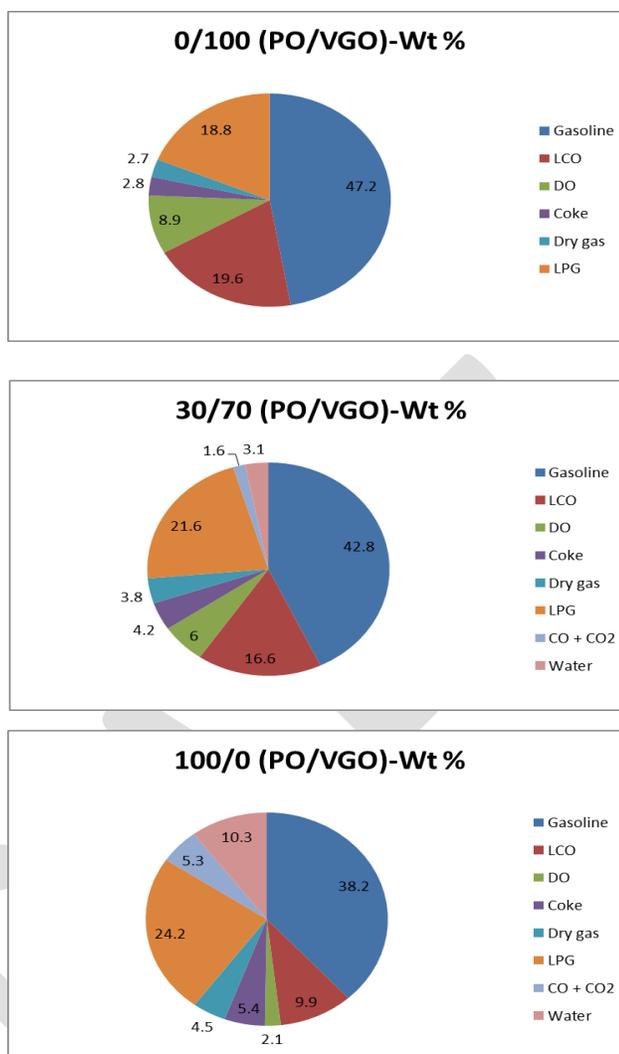


Figure A 4. Product outputs from catalytic cracking as a function of feedstock composition¹⁶

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, most of the reported information to-date has been from research and development projects. There have been a few reports of co-processing of triglycerides under real FCC conditions at a pilot plant scale.¹⁶ We are unaware of any co-processing in FCC units on a commercial scale, likely 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.¹⁶

A.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 details 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.³² The instability of pyrolysis oil is mainly attributed to lignin oligomers formed during pyrolysis.³³ 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 2-3.³³ 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.³⁴ to test the oxidative and 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.¹⁶ In addition, stability of pyrolysis oil can be improved through processes such as aqueous phase reforming, hydrotreating, and zeolite upgrading.³³ 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:

³² Geller, Daniel P., et al. "Storage stability of poultry fat and diesel fuel mixtures: specific gravity and viscosity." *Fuel* 87.1 (2008): 92-102.

³³ Vispute, Tushar. "Pyrolysis oils: characterization, stability analysis, and catalytic upgrading to fuels and chemicals." (2011).

³⁴ 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.

- (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 due to impurities may require higher catalyst makeup rates. However, it is possible to minimize catalyst deactivation by removing alkali metals from pyrolysis oil. A study by Baldwin and Feik used hot gas filtration to separate char from pyrolysis before condensation.³⁵ In doing so, the authors produced pyrolysis oil with near zero alkali metal content and improved its quality and stability.

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.

³⁵Baldwin, Robert M., and Calvin J. Feik. "Bio-oil stabilization and upgrading by hot gas filtration." *Energy & Fuels* 27.6 (2013): 3224-3238.

A.5. Co-processing Potential in California

In 2016, EIA reported total capacities of 729,700 bpsd³⁶ and 723,000 bpsd were available for FCC and heavy gas oil hydrotreaters respectively in California.³⁷ 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 could be used to co-process triglycerides with middle distillate, including gas oil. Assuming low carbon liquid product yields vary between 65%-85% (by volume) and a co-processing ratio of 5 percent (on a volumetric basis), approximately 1.7 billion gallons of low carbon hydrocarbon fuels including low carbon diesel and low carbon gasoline could potentially be produced in California (Table A.3).

Table A.3. Co-processing capacity and low carbon hydrocarbon fuel production potential in California Refineries

Co-processing units	Capacity (BPSD) ³⁷	Biogenic feedstock to petroleum ratio	Example Biogenic Feedstock	Assumed % liquid low carbon fuel yields (v/v biogenic feedstock)	Low carbon liquid fuel potential (gallons/year)
Catalytic cracking	729,700	5%	Pyrolysis oil	65%	3.60E+08
Hydrotreater (heavy gas oil)	723,000	5%	Vegetable oil + tallow	100%	5.54E+08
Hydrotreater (jet+ kerosene+diesel +other distillate)	659,500	5%	Vegetable oil + tallow	100%	5.06E+08
Hydrocracker (gas oil)	296,600	5%	Pyrolysis oil	70%	1.60E+08
Hydrocracker (distillate)	191,800	5%	Vegetable oil + tallow	95%	1.40E+08
Total					1.7E+09

³⁶ Bpsd refers to barrels per stream day

³⁷ EIA, US. "Refinery Capacity Report 2016." EIA website <http://www.eia.gov/petroleum/refinerycapacity/> accessed January 24, 2017