Full Length Article

Challenges in determining the renewable content of the final fuels after co-processing biogenic feedstocks in the fluid catalytic cracker (FCC) of a commercial oil refinery

Jianping Su [a], Liang Cao [b], Gary Lee [c], Jonathan Tyler [c], Anna Ringsred [d], Michael Rensing [d], Susan van Dyk [a], Don O'Connor [e], Robert Pinchuk [c], Jack (John) Saddler [a,*]

[a] Forest Products Biotechnology/Bioenergy Group, The University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada
[b] Data Analytics and Intelligent Systems Lab, The University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada
[c] Parkland Refining (B.C.) Ltd., 2025 Willingdon Ave, Burnaby, BC V5J 0J3, Canada
[d] Ministry of Energy, Mines, and Low Carbon Innovation, 1810 Blanshard Street, Victoria, BC V8T 4J1, Canada
[e] (S&T) Squared Consultants Inc., Delta, British Columbia V4E 2Z2, Canada

ARTICLE INFO

ABSTRACT

The long-distance transport sector will be difficult to electrify and will likely require lower-carbon intensive, drop-in fuels if the sector is to effectively decarbonize. Policies such as the low carbon fuels standard (LCFS) have proven to be particularly effective in encouraging oil companies to produce lower carbon intensity (CI) fuels that the long-distance transport sector can use. One way to reduce the carbon intensity of the fuels is to co-process lower carbon intensive feedstock at various insertion points within a refinery (e.g. the hydrotreater or the fluid catalytic cracker (FCC)). However, to obtain "credits" from the appropriate regulator the carbon intensity of the final fuel and the renewable content must be determined. To date several processes, such as material balance and C14/C13-tracking, have been used to determine the renewable content of the final fuels, with each of these methods having their own strengths and weaknesses. As described here, challenges such as the lack of consistent terminology, through to variations in the "background noise" encountered in typical refinery operation, have complicated carbon intensity and renewable content determinations. However, when a co-processing approach is used in a routinely operating refinery, a multiple regression-based mass balance approach (based on observed yield) combined with C14 analysis is able to determine the renewable content of the final fuels.

1. Introduction

If the world is to successfully mitigate climate change we need to make significant changes to the way we consume energy. Although renewable energy (e.g. hydro, solar and wind) is increasingly contributing to the heat and power sectors, with falling costs over the last decade resulting in increased market share, the transportation sector has proven more difficult to decarbonize [1]. Although several groups have projected that "green" electricity will help decarbonize urban automobile transport [2–4], in 2018, renewable energy contributed about 3.7%

of the world's transport fuel demand, with biofuels representing 93% of this value [2,5]. Despite bioethanol and biodiesel's contribution to decarbonizing automobiles and light duty trucks, much of the long-distance transport sector (e.g. marine, aviation, rail and long-distance trucking) will require some sort of "drop-in" fuel, due to the limited potential of electricity and hydrogen options in the short-term and benefit of using already-established "oil refining" supply chains. Although policies such as California and British Columbia's Low Carbon Fuels Standard (LCFS) have encouraged the production and use of drop-in biofuels such as renewable diesel [6,7], production is relatively

---

limited compared to the amount of fossil transportation fuel that is consumed [2]. The refining sector has responded to these policy drivers by repurposing/reconfiguring older and smaller refineries into so-called, stand-alone, biorefineries. Several stand-alone refineries are already operating at a commercial level (e.g., Eni, World Energy, Marathon, Total, etc.) [8–11], with the use of oleochemical/lipid feedstocks significantly reducing the carbon intensity (CI) of the resulting fuels.

As well as establishing stand-alone facilities ongoing policy drivers such as the US's Renewable Fuel Standard (RFS2), Europe's Renewable Energy Directive (REDII) and Canada's Clean Fuels Standard (CFS) have encouraged the oil sector to continue to assess other ways to decarbonize [12,13]. For example, several national or regional mandates require fuel suppliers to either blend specific types of fuels (bioethanol and bio-diesel) or require fuel suppliers to reduce their fuels' carbon intensity on an annual basis [14,15]. Although, to date, most mandates have involved volumetric requirements (e.g. 10% ethanol, 2% biodiesel in Canada) polices such as the LCFS require evidence that the actual carbon intensity of the final fuels, as compared to fossil derived fuels, has been reduced. Determining the carbon intensity of a fuel is normally achieved via life cycle assessment (LCA) where a fuel's full life cycle emissions are calculated compared with the carbon intensities of fossil fuels such as gasoline/petrol, jet and diesel [16].

Biogenic feedstocks can be oleochemical feedstocks such as used cooking oil, canola, tallow, tall oil, etc., which are available and used commercially by the refining sector. Building standalone units, either co-located with oil refineries or by revamping existing oil refineries, are the dominant configurations which are currently used to process these biogenic feedstocks [17–19]. However, co-processing biogenic feedstocks at existing oil refineries provides another opportunity to utilize the existing infrastructure and to produce low carbon intensity drop-in fuels [20,21].

The vast majority of drop-in biofuels are currently produced using oleochemical/lipid feedstocks due to their availability, their relative homogenous structure, lower oxygen content and ease of conversion to Hydrotreated Esters and Fatty Acids (HEFA) and renewable diesel. In the longer term it is hoped that these oleochemical feedstocks will be supplemented with more abundant, cheaper and sustainably sourced biomass-derived-biocrudes [22]. However, even oleochemical feedstocks are quite different from what refiners typically process, with their oxygen content (~10 wt%) considerably higher than other oil associated impurities such as sulfur and nitrogen which are normally at the ppm level [23]. Despite differences in the composition of the low carbon intensive feedstock, it is likely that, if a co-processing strategy is adopted, they will be inserted at either the hydrotreater or their fluid catalytic cracker of a refinery [22,24]. Both insertion points have been successfully demonstrated [22,25,26]. Co-processing at the hydrotreater has been more commercialized and is similar to the process used to make renewable diesel in standalone units. However, hydrotreating biogenic feedstocks requires more hydrogen compared with hydrotreating hydrocarbon feedstocks, therefore, some refiners may be limited in hydrogen supply. Furthermore, catalysts are also need to be reformulated so they can handle the large exothermic reaction that will occur as a result of deoxygenating biogenic feedstocks, implying that a shorter turnaround might be needed to replace the catalysts more frequently. Thus, co-processing at the FCC may, in some ways, be less technically risky compared with co-processing at hydrotreater. As FCC's use a circulating fluidized bed reactor, the catalysts can be regenerated in-situ and do not need to be replaced offline. This robustness means that unconventional feeds, such as biocrudes, might be better co-processed at this location.

No matter where biogenic feedstocks might be co-processed within a refinery, determining the carbon intensities of the gasoline and diesel and tracking the "green molecules" is an on-going challenge, partly due to the complicated nature of refinery operations and particularly if it involves insertion at the FCC. As biogenic feedstocks are typically co-processed at a relatively low percentage compared to the oil stream,

any changes in processing the hydrocarbon component will contribute at background "noise" levels. This might mask any changes that might be detected after biogenic feedstock addition, making it difficult to quantify the "signal".

To date, two methods have been certified by the American Society for Testing and Materials, ASTM D6866 method B and C, where the renewable content of a co-processed derived fuel is physically measured by taking samples and performing carbon 14 analysis [27]. Earlier work has shown that method B, which uses accelerator mass spectrometry (AMS), is accurate and reliable and it is considered to be the "gold standard" for the industry [28,29]. Although method C, which uses liquid scintillation counting (LSC), is an alternative, cheaper option [30,31], the long sample preparation time and the lower precision compared with method B might limit its use at low blend ratios [29,32]. Currently, various groups are assessing alternative "tracking methods", such as the use of carbon 13 by the Los Alamos National Laboratory or the "no sample preparation LSC method" of Chevron [29,33], to reduce the cost and complexity of the existing ASTM methods.

Several other non-direct ways of tracking the green molecules have also been proposed including the carbon mass balance, mass balance based on observed yield and methods based on energy content of the various products. These methods do not require specific equipment and refiners are familiar with most of the methods. However, each method involves certain assumptions which detracts from their effectiveness as alternatives to the carbon 14 approach when used alone [32,34].

Currently, no commercial data has been reported regarding the carbon intensity of any fuels derived after FCC co-processing oleochemical feedstocks. To date, most studies have used lab scale (either using micro activity test (MAT) reactors, advanced cracking evaluation (ACE) [35,36], or pilot scale FCC facilities [37–39]. However, in subsequent work other researchers suggested that, using unconventional feeds a fixed fluidized bed reactor provides less reliable results [40], especially for coke estimation.

The work described here summarizes a refinery's experience in trying to track the green molecules used to determine the carbon intensity of final fuels when oleochemical feedstocks are co-processed within the FCC unit of the refinery. As will be described, a commercial FCC unit does not run as smoothly as a well-controlled lab scale/pilot scale unit, with heat balance playing a key role in maintaining the steady state of an FCC unit [41]. The benefit of having an advanced dynamic matrix control (DMC) system is that the unit will adjust to maintain its preset goal (likely maximizing feed rate) while ensuring it runs within its operational and safety limits [42].As will be described, a combination of a mass balance (based on observed yield) combined with C14 analysis will likely be needed to effectively determine the renewable content of the final fuels if biogenic feedstocks are inserted at the FCC unit of a refinery.

2. Materials and methods

2.1. Refinery and co-processing overview

The Parkland Burnaby refinery is located in Vancouver, British Columbia and has a capacity of 55,000 barrels/day [43]. The refinery currently supplies 25% of British Columbia's transportation fuels (25% of Vancouver airport's jet fuel and 30% of gasoline for metro Vancouver) [43]. It can be classified as a conversion refinery as it has a fluid catalytic cracker (FCC). The FCC was selected as the "model" insertion point because of its robust nature, which should make a technically less risky insertion point when compared to insertion at the hydrotreater [25].

2.2. The FCC role in the refinery

The FCC is an intermediate unit that processes the initial, heavy oil stream and "cracks" it into different products. It is connected to various hydrotreaters, liquid petroleum gas (LPG) units, alkylation and
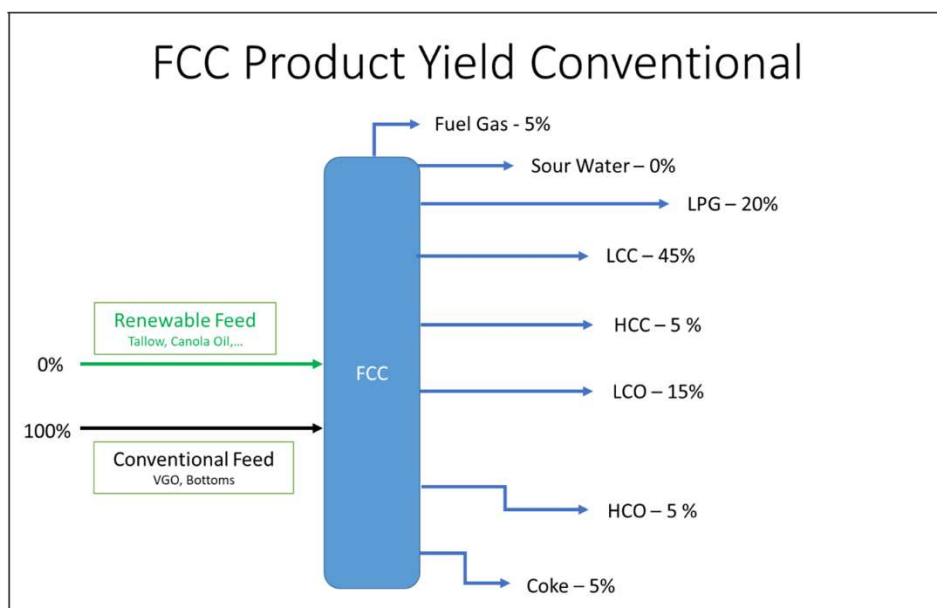
Fig. 1. FCC inputs and outputs. Lift gases from different units are not shown. As the yields vary, industrial average assumed yields are shown for illustrative purposes.

isomerization units and a reformer. In contrast with the diesel hydrotreater, where finished products are made, the FCC does not produce any final products but instead produces various intermediates that need to be further treated before blending into final products.

The Parkland FCC is similar to other FCC units globally, in that it converts less valuable gas oil feedstocks to more valuable lighter components, such as gasoline and LPG (a more recent trend to optimize the FCC in order to maximise diesel production) [41]. As summarized in Fig. 1, the various inputs and outputs of the FCC plus the typical yields obtained indicate the complexity of this unit's routine operation. As well as the liquid and solid streams, the gases streams in the feed (which are not shown) also needed to be considered when doing any mass balance assessments.

As will be described, the FCC produces a wide variety of different products that will be further processed before blending into the final products. The main output is the Light Catalytic Cracking (LCC) stream which is further processed in the gasoline hydrotreater before blending with gasoline. The Liquefied Petroleum gases go through several separation stages, such as removing the C1 and C2 components by combustion in the refinery and by using the C3 and C4 double bonds in the polymerization and isomerization unit to improve the octane rating of the gasoline. Although the butane stream can be blended with gasoline in winter, when the Reid Vapour Pressure (RVP) is high, it needs to be removed in the summer due to environmental regulations restricting over-vaporization. The fuel gas, together with the fractions derived from the LPG section are combusted for internal use. The Heavy Catalytic Cracking stream (HCC) (this is actually more commonly referred to as Heavy Cat Naphtha (HCN) can be either directed into either the gasoline or diesel fractions due to the overlap in the distillation range of gasoline and diesel [41]. The Light Cycle Oil (LCO) fraction can be sent to the diesel hydrotreater as a diesel blendstock. The Heavy Cycle Oil (HCO) can be sent for fuel oil purposes or marine fuel. Finally, coke is also generated which is burnt to provide all heat required for this process.

As background to the co-processing study, Parkland initiated commercial co-processing trials in 2017. The process data described was retrieved using TIBCO Spotfire® which was connected to the refinery's database. During the times identified, the oleochemical co-processing ratio varied from 0% to greater than 10%.

2.3. Mass balance definition and evaluation

Although the concept of mass balance might appear simple, i.e. the difference between the mass of the input and output, in fact, determining the mass balance of the various steams within a commercial FCC unit proved challenging. There are 10 inputs and 9 outputs for the Parkland FCC unit. Although each input and output unit usually has its own flow meter, (e.g. orifice plate, vortex flow meter, or Coriolis flow meter), some streams did not have a dedicated flow meter. Consequently, the downstream flow meters were used to calculate these streams. The flow meters also needed to be corrected for "standard conditions" which are designed for specific fluid to flow condition based on the fluid properties. For example, when correcting flow meters measuring liquids, density is required while for gases it also incorporates molecular compositions. However, as some streams, such as the recycle gases from other units, are sampled infrequently and other streams were never sampled, some assumptions have to be made. In general, although a 0% mass balance error is unlikely to be routinely achieved at a commercial unit, the goal is to have a mass balance error centered around 0 while considering random error that is irreducible and which fluctuates within an identified range. If the error is not close to 0%, one or more fractions need to be further evaluated. It should be noted that coke yield is typically determined by following the industrial standard of using the amount of dry air sent to the regenerator and analyzing the regenerator flue gases as the coke is being continuously regenerated [41].

2.4. Mass balance based on observed yield/step test

A "mass balance approach" or "mass balance based on observed yield" has been proposed as one method that refiners could apply when trying to determine the yield and carbon intensity of final fuels after co-processing biogenic feedstocks. In the refining industry this approach is often referred to as a "step test" and it is used to develop model predictive controls (MPC) where multivariable processes and interactions are significant [42]. An ideal step test moves one manipulated variables (MV) while simultaneously observing any changes in the controlled variable (CV). The recommended "signal" to "noise" level is at least 6:1, which means the move/ signal should be at least a 6:1 signal-to-noise ratio [42].

As described and reported here, the co-processed biogenic feedstock

Table 1
Mass balance comparison of the original mass balance, reconciled mass balance and updated mass balance.

Streams	Original mass balance baseline (default mass balance), klb/h	Reconciled mass balance difference from original, klb/h	Flow meter corrected mass balance difference from original, klb/h
Mass balance error	6.3%	0	2%
FCC liquid feed	0	+11	−2.2
Total feeds	0	+11	−6.6
Light catalytic cracked gasoline (LCC)	0	−3	−13.9
Total products	0	−4	−16.3

is the manipulated variable (MV), and the yield changes are the controlled variables (CV). However, the two major assumptions are, a) all of the other process variables remain constant and, b) changes resulting from co-processing (the signal) are big enough to be detected. Thus, by comparing the baseline and the co-processing data using basic statistical description and a *t*-test we were able to assess whether the average is different or not. The baseline and co-processing yields were first compared using the week-long co-processing trials. These trials helped establish a pattern and provided the data needed to form a baseline followed by "steady-state" co-processing operation.

The *t*-test was used to compare the yields of co-processing and baseline processing [44]. Due to variance and the unequal sample size between co-processing and baseline, the *t*-test had to be slightly modified to provide a comparison of the means (Welch's *t*-test).

2.5. Visualizing the process variables and yield changes for initial variable selections

Visualization is a powerful tool that is used to initially screen yield parameters, as commercial FCC operations involve many process variables which can impact yields. Several parameters versus yield were plotted using Seaborn (a statistical data visualization package in Python) with real refinery data [45].

2.6. Yield determination via statistical analysis based on single variable regression and multiple linear regression

Single variable correlation and multiple regression was assessed using Minitab (a statistical data analysis software) with the main evaluation metrics used for model estimations and parameters including the p value and the Adjusted R-squared value [46]. Minitab also provided an analysis of variance which included a calculation of the adjusted R-squared and p value to assess the importance of the variables. The main FCC products, which included the gasoline, diesel, LPG, gases and coke fractions, were evaluated separately and variable selection was based on initial visualization and process knowledge.
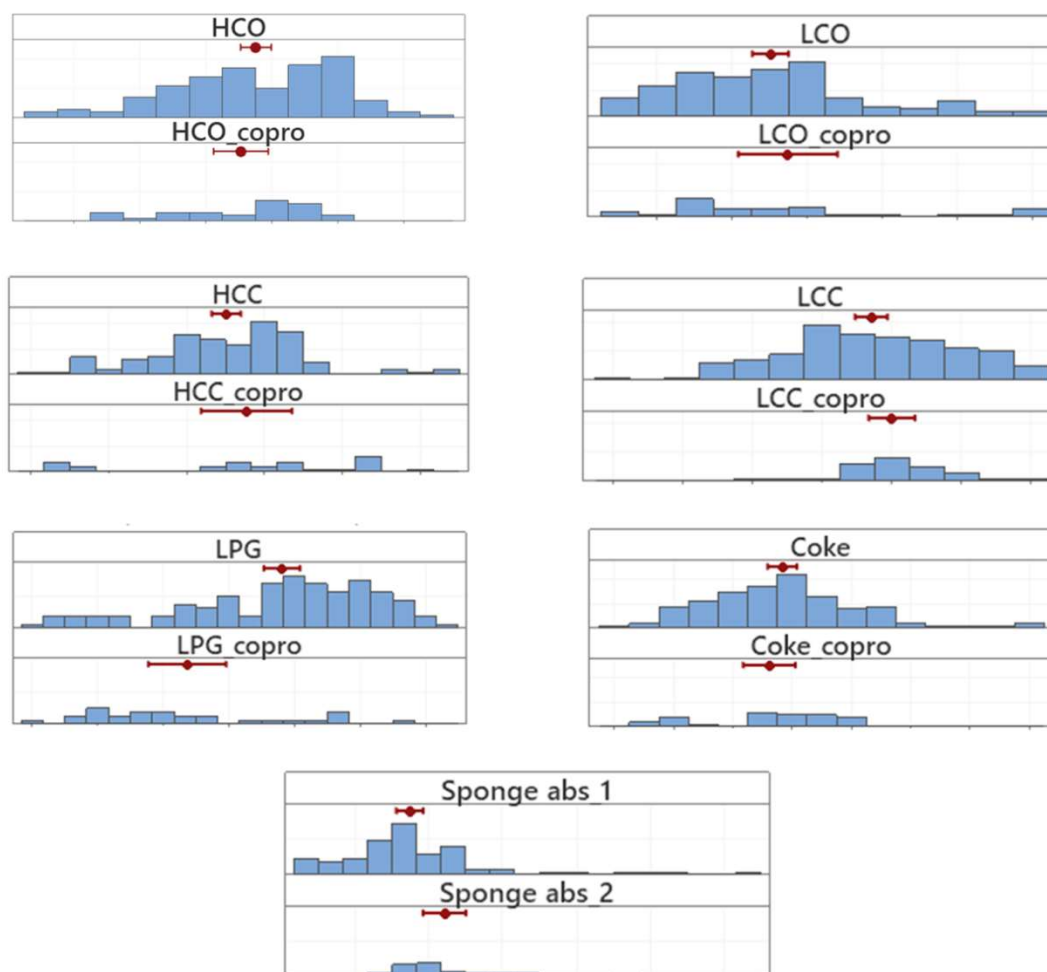

Fig. 2. Representation of Welch's *t*-test used to compare the mean of the regular baseline yield vs. co-processing yield. Other than the LPG and absorber off-gas, the averages of all the other streams indicated no real difference.
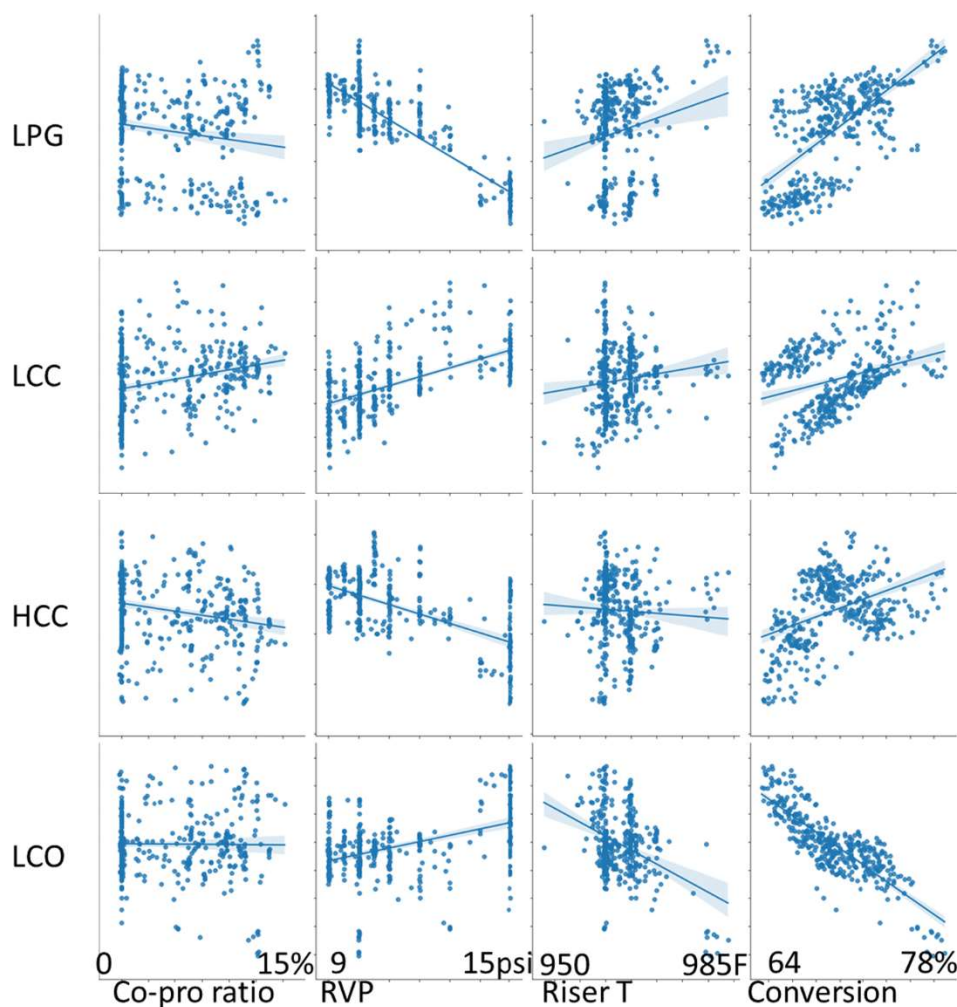
Fig. 3. The Major FCC products yields (LPG, gasoline, diesel) and their relationship with different process variables including co-processing, using single variable correlation and visualization. (Blue zones are 95 confidence interval of the correlation). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.7. Use of C14 to track the "renewable" content.

As previous work had used C14 to track the renewable content of co-processed fuels this method was further assessed for its accuracy and reproducibility in tracking the "green molecules" present in each fraction [47–49]. In this work co-processing was carried out over 3 days, with the feed rate held constant over the last 24 h to achieve "steady-state" operation. Numerous samples were taken and sent out for C14 analysis, including the gases streams. In the work reported here, although the C14 results are not discussed directly, some of the critical assumption behind their use, i.e. the basic mass balance of the FCC unit, are highlighted.

3. Results and discussions

3.1. Mass balance evaluation

As mentioned earlier, it is often challenging to obtain an ideal mass balance when routinely operating a commercial FCC unit within a refinery. Of the various methods used to obtain a mass balance, "forcing" the closure of the mass balance is often used. This is done by assuming any errors are attributed equally to all flow meters and subsequently correcting these errors to reconcile the overall mass balance.

The original mass balance was off by 6.3% during previous co-processing trials where C14 samples were taken (Table 1) and was

considered as baseline for comparison and are shown as "0". Although the reconciled mass balance can be used, it can, incorrectly, adjust the feed and the product to minimize the mass balance error comparing with the proper method to evaluate and correct each flow meter's flow. As discussed later, this mass balance error impacts the multiple regression and C14 analysis.

3.2. Step test/mass balance values based on observed yield

When the baseline during regular petroleum processing and the co-processing at a 6% oleochemical feedstocks blend are compared (Fig. 2), similar yields for the different streams were obtained other than the yields of the absorber sponge off gas and LPG. All of the yields from FCC co-processing were reported (Fig. 2) with the baseline yield at the top and co-processing yields at the bottom using histograms (frequency distributions). As the Minitab calculated a 95% confidence interval between the regular and co-processing baseline, there was a 95% chance that the two groups (other than the sponge off gas and LPG), show no differences (i.e. we cannot reject the null hypothesis that the mean of the two groups are different). This result implies that at this low 6% co-processing rate, the "signal" resulting from co-processing is not significant enough to be detected due to the "noise" of baseline hydrocarbon processing. The FCC yields obtained were not static but were dynamic, based on the season, market demand and operating conditions (Fig. 2).
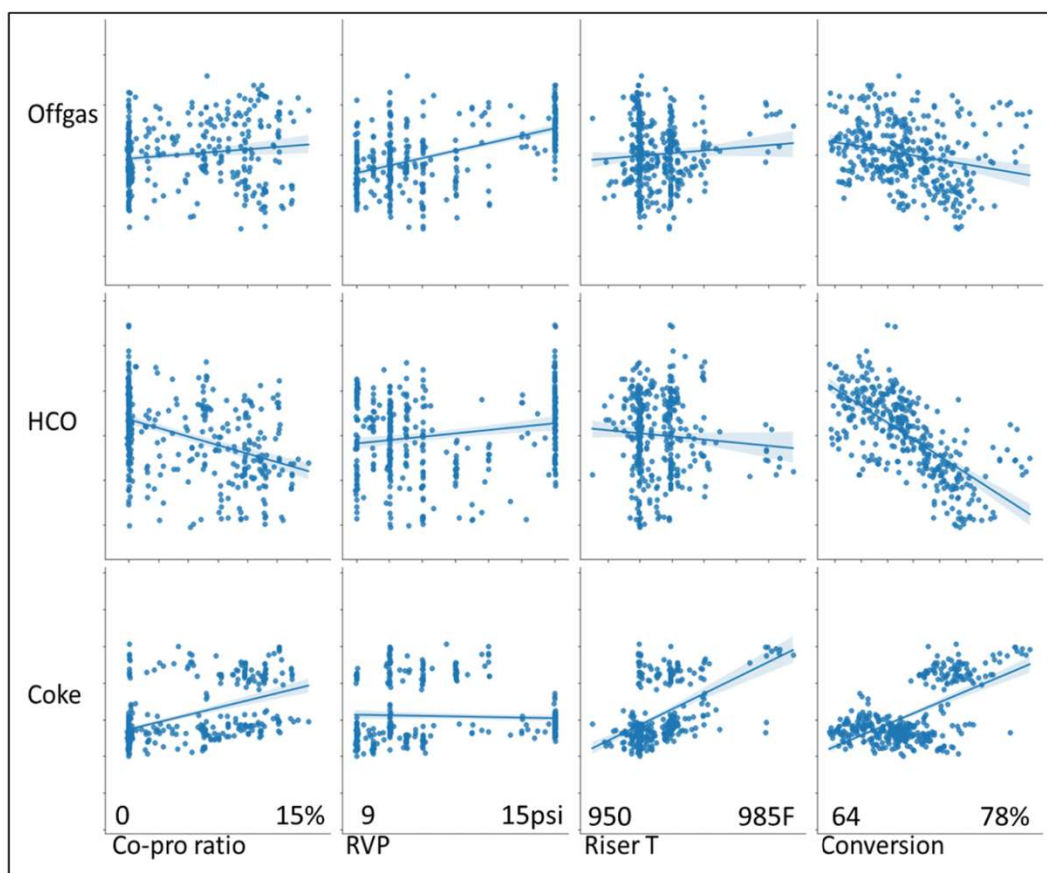
Fig. 4. Secondary products derived after FCC processing (Offgas burnt internally, coke burnt to maintain the heat balance, HCO used as marine fuel) vs. variables including co-processing. (Blue zones are the 95confidence interval for the single variable regression). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3. Single variable and multiple linear regression on co-processing

As mentioned earlier, the FCC product yield is a function of several variables such as the influence of the catalyst (catalyst activity, feed, metal contents, fresh to equilibrium catalyst ratio) or operating variables such as the catalyst-to-oil ratio, riser temperature, preheat temperature etc. As a 6% co-processing ratio had not resulted in any statistically significant changes we next aggregated the data generated during the 2019 and 2020 trials to assess whether product yield was related to specific factors (Figs. 3 and 4; each data point represents a daily average value).

As mentioned earlier, the fluid catalytic cracker is typically a "core" unit in a petroleum refinery [40] with the extent of conversion of the feedstock defined as the volume or weight percentage converted to gasoline and other lighter products (1-LCO%-HCO%). The apparent conversion is calculated using the customized refinery cut point while the true conversion that is used to compare different units needs to be calculated based on the fixed cut points of each fraction. Typically, the yield of each stream needs some adjustment [41]. Refiners can adjust the level of the cracking by also changing operating conditions such as lowering the riser temperature or decreasing the reaction severity.

It was apparent that changes in yield could not be explained by just the influence of co-processing but also by the impact of other variables such as overall unit conversion, Reid Vapour Pressure (RVP), co-processing ratio and the riser temperature. The conversion values have been shown to correlate well with yield (except for coke) while the RVP reflects how many light components are in the gasoline blendstock fraction [23].

As summarized in Figs. 3 and 4, with an increasing co-processing ratio, the lighter fractions (gases, gasoline) increased while the heavier fractions (LCO, HCO) decreased. This was likely due to the reactive triglycerides which seem to be heavier than the traditional FCC feed from the distillation curve [24]. However, the traditional petroleum distillation cannot be used to explain compounds with significant amount of oxygen [24].

Increasing the riser temperature can increase the reaction severity which promotes conversion/cracking. From the visualization (Figs. 3 and 4), it seems that all yields, with the exception of HCC trend similarly to the impact of conversion. The exact impact of different operating parameters will be quantified during multiple linear regression analysis later.

Another industrial practice is to convert the apparent conversion/ yield to true yield based on fixed cut points [41]. When we used past process data that had been collected regularly and while doing the correlation, the cut points were considered as variables. For example, the impact of changes in the RVP was considered as one variable instead of relating it to the fixed cut point based on limited lab samples.

As it was unlikely that a step test/ mass balance based on observed yield would allow adequate quantification of the changes resulting from co-processing, multiple linear regression was used to normalize the variables.

When the unit conversion, RVP and co-processing ratio were used as parameters to perform the multiple linear regression (Fig. 5), the co-efficients were shown to have a small p-value, indicating that they were statistically significant to predict the yields of LCC, LCO, LPG. However, it should be noted that correlation does not mean causation as good correlation only shows that the data correlated well. Thus, process knowledge has to be used and combined with the data to assess whether

Method

Test set fraction   29.9%

Regression Equation

LCC = -0.05 + X Co-pro_ratio + 0.008 RVP + 0.005 Conversion

Model Summary

S	R-sq	R-sq(adj)	Test S	Test R-sq
0.0058954	91.26%	91.13%	0.0057259	90.12%

Regression Equation

LCO = 0.35 - 0.006 Conversion + Y Co-pro_ratio + 0.0005 LGO90

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)	Test S	Test R-sq
0.0095860	77.31%	76.97%	76.39%	0.0078847	83.52%

Regression Equation

LPG = 0.097 + 0.002 Conversion + Z Co-pro_ratio - 0.008 RVP

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)	Test S	Test R-sq
0.0048703	96.27%	96.21%	96.12%	0.0058532	94.82%

Fig. 5. Multiple linear regression analysis of the yield of major FCC products during 2019 co-processing.

these variables are relevant.

It was hoped that the co-processing coefficient, derived from the co-processing ratio using multiple linear regression, could be used to quantify the impacts/changes and that these results could be used to validate the results obtained by visualization (Figs. 3 and 4). However, the multiple regression method did not perform well as the four streams (all streams in Fig. 4 and HCC in Fig. 3) had low adjusted R-squared values that varied from 0.3 to 0.6.

As summarized in Fig. 1, the average yield of the HCC, HCO, coke and flue gas was around 5 wt%. with the mass balance error fluctuating within $+/2$ wt% and occasionally around 3.5 wt%. Therefore, the mass balance error could be considered as "noise", similar to the concept of a step test where the yield is the signal. As a result, unless the signal is much larger than the noise, any changes will not be observed. This low signal to noise ratio is likely the reason why the correlation for these streams is relatively weaker.

3.4. Use of C14 tracking combined with multiple regression

As mentioned earlier, C14 tracking has the advantage of readily identifying the renewable content of a sample with this often reported as a percentage, as suggested by ASTM [27], and is often considered as the "gold standard" method [29]. However, if the FCC yields are to be determined, the flow of each stream and good mass balance values are needed in order to obtain any meaningful results. As coke yields cannot be readily measured, the industry standard is to use the amount of dry air sent to the regenerator followed by analysis of the flue gases to calculate the overall coke yield.

Another challenge with the C14 method is its practicality. Due to the expensive capital cost of setting up and operating an AMS certified facility, it is less likely to be used as an in-house method. Another challenge is that, as yields are not constant, one set of samples might not represent the standard yield over a longer term.

One way of determining the renewable content of fuels resulting from co-processing biogenic feedstock at an FCC is to combine multiple regression with C14 tracking. The benefit of multiple regression is that it normalizes several factors and quantifies the impact of co-processing based on the extended time during which co-processing was conducted, while the C14 method can be conducted less frequently.

4. Conclusions

Contrary to co-processing at a hydrotreater, FCC co-processing of oleochemical feedstocks resulted in a broad spectrum of products, ranging from light gases and coke (consumed internally) to LPG, gasoline, diesel and heavy cycle oil (sold as marine fuels). Consequently, as all of the fractions contained some renewable content, the carbon intensities of all of the fuels were reduced when compared to baseline petroleum products. A mass balance approach (termed "step-testing" by some refiners) proved to be problematic when trying to determine the carbon intensity of the fuels. This was due to a variety of issues such as the low blending rate (6%) making it difficult to differentiate the biogenic feedstock signal from the petroleum baseline assuming that other variables remained constant. Although a single variable approach proved unsatisfactory, the use of a multiple linear regression/correlation normalized most of the other factors. When the mass balance approach was supplemented with C14 assessment much greater accuracy can be obtained. However, the current, limited capacity to routinely carry out C14 monitoring is problematic plus the future use of C14 tracking will also rely on deriving an acceptable mass balance for the FCC unit. Thus, further work is still needed to quantify the variability of yield and the impact it will have on the credits awarded based on the low carbon fuel standard (LCFS).

CRediT authorship contribution statement

Jianping Su: Conceptualization, Methodology, Formal analysis. **Liang Cao:** Methodology, Formal analysis. **Gary Lee:** Resources, Writing - review & editing, Supervision. **Jonathan Tyler:** Resources. **Anna Ringsred:** Writing - review & editing. **Michael Rensing:** Resources, Writing - review & editing. **Susan van Dyk:** Methodology, Conceptualization, Supervision. **Don O'Connor:** Resources, Validation. **Robert Pinchuk:** Resources, Writing - review & editing, Supervision. **Jack (John) Saddler:** Conceptualization, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

References

[1] IEA (2020). Renewable energy market update, IEA, Paris. https://www.iea.org/reports/renewable-energy-market-update.

[2] REN21. Renewables 2020 Global Status Report. 2020.

[3] Global EV Outlook 2020. Glob EV Outlook 2020 2020. doi:10.1787/d394399e-en.

[4] IEA. Energy Technology Perspectives. Energy Technol Perspect 2020. doi:10.1787/9789264109834-en.

[5] IEA (2019). Renewables 2019, IEA, Paris. https://www.iea.org/reports/renewables-2019.

[6] Elam AR, Faulkner W, Laplante C, Chase P. California's LCFS : unlocking value in low- - carbon liquid fuels building equitable low- - carbon policy Part 2 : Projecting Value in California's LCFS Market 2017.

[7] Lepitzki J, Axsen J. The role of a low carbon fuel standard in achieving long-term GHG reduction targets. Energy Policy 2018;119:423–40. https://doi.org/10.1016/j.enpol.2018.03.067.

[8] The biorefineries of Venice and Gela | Eni n.d. https://www.eni.com/en_IT/operations/mid-downstream/refining-marketing/biorefineries.page [accessed December 4, 2018].

[9] World Energy acquires renewable jet fuel producer AltAir | Bioenergy International (2018). Available at: https://bioenergyinternational.com/biofuels-oils/world-energy-acquires-renewable-jet-fuel-producer-altair [accessed: 9 October 2020].

[10] Marathon. Marathon Dickinson Refinery 2019. https://www.marathonpetroleum.com/Operations/Refining/Dickinson-Refinery/ [accessed: 9 October 2020].

[11] La Mède: A Facility for the Energies of Tomorrow | Total.com n.d. https://www.total.com/energy-expertise/projects/bioenergies/la-mede-a-forward-looking-facility [accessed October 23, 2020].

[12] Renewable Fuel Standard (RFS2): Final Rule | Renewable Fuel Standard Program | US EPA n.d. https://www.epa.gov/renewable-fuel-standard-program/renewable-fuel-standard-rfs2-final-rule [accessed August 31, 2020].

[13] European Commission. Renewable Energy – Recast to 2030 (RED II) 2018. https://ec.europa.eu/jrc/en/jec/renewable-energy-recast-2030-red-ii.

[14] Yeh S, Witcover J, Lade GE, Sperling D. A review of low carbon fuel policies: principles, program status and future directions. Energy Policy 2016;97:220–34. https://doi.org/10.1016/j.enpol.2016.07.029.

[15] Taylor M. Assessing California's Climate Policies-Transportation; 2018.

[16] Chrysikou LP, Dagonikou V, Dimitriadis A, Bezergianni S. Waste cooking oils exploitation targeting EU 2020 diesel fuel production: Environmental and economic benefits. J Cleaner Prod 2019;219:566–75.

[17] Karatzos S, McMillan JD, Saddler JN. The potential and challenges of drop-in biofuels; 2014.

[18] Neste Corporation. Neste Renewable Diesel Handbook. Neste 2015:1–33.

[19] Delbianco SVP DOW AR, SpA E. Towards Sustainable Production of Biofuels: the Eni's Way Resource Efficiency e Sustainable Development Goals: il ruolo del Life Cycle Thinking Siena, 22-23 Giugno 2017, 2017, p. 22–3.

[20] Freeman C, Jones S, Padmaperuma A. Initial assessment of US refineries for purposes of potential bio-based oil insertions; 2013.

[21] Talmadge MS, Baldwin RM, Biddy MJ, McCormick RL, Beckham GT, Ferguson GA, et al. A perspective on oxygenated species in the refinery integration of pyrolysis oil. Green Chem 2014;16(2):407–53. https://doi.org/10.1039/C3GC41951G.

[22] Melero JA, Iglesias J, Garcia A. Biomass as renewable feedstock in standard refinery units. Feasibility, opportunities and challenges. Energy. Environ Sci 2012;5(6):7393. https://doi.org/10.1039/c2ee21231e.

[23] Gary JH, Handwerk GE, Kaiser MJ. Petroleum refining: technology and economics. CRC Press; 2007.

[24] Watkins B, Olsen C. New Opportunities for co-processing renewable feeds in refinery processes 2008:1–13.

[25] van Dyk S, Su J, Mcmillan JD, Saddler JJ. Potential synergies of drop-in biofuel production with further co-processing at oil refineries. Biofuels, Bioprod Biorefining 2019;13(3):760–75. https://doi.org/10.1002/bbb.2019.13.issue-310.1002/bbb.1974.

[26] Bezergianni S, Dimitriadis A, Kikhtyanin O, Kubicka D. Refinery co-processing of renewable feeds. Prog Energy Combust Sci 2018;68:29–64. https://doi.org/10.1016/j.pecs.2018.04.002.

[27] ASTM D6866-20. Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis, ASTM International, West Conshohocken, PA, 2020. www.astm.org.

[28] Haverly MR, Fenwick SR, Patterson FPK, Slade DA. Biobased carbon content quantification through AMS radiocarbon analysis of liquid fuels. Fuel 2019;237:1108–11. https://doi.org/10.1016/j.fuel.2018.10.081.

[29] Hurt M, Martinez J, Pradhan A, Young M, Moir ME. Liquid scintillation counting method for the refinery laboratory- based measurements of fuels to support refinery bio-feed co-processing 2020. doi:10.1021/acs.energyfuels.0c03445.

[30] Krištof R, Kožar Logar J. Liquid scintillation spectrometry as a tool of biofuel quantification. Front Bioenergy Biofuels 2017. doi:10.5772/65549.

[31] Bronić IK, Barešić J, Horvatinčić N, Sironić A. Determination of biogenic component in liquid fuels by the 14C direct LSC method by using quenching properties of modern liquids for calibration. Radiat Phys Chem 2017;137:248–53. https://doi.org/10.1016/j.radphyschem.2016.01.041.

[32] Schimmel M, Toop G, Alberici S, Koper M. ECOFYS-A Navigant Company Determining the renewability of co-processed fuels Final report. 2018.

[33] Li Z-H, Magrini-Bair K, Wang H, Maltsev OV, Geeza TJ, Mora CI, et al. Tracking renewable carbon in bio-oil / crude co-processing with VGO through 13 C / 12 C ratio analysis. Fuel 2020;275:117770. https://doi.org/10.1016/j.fuel.2020.117770.

[34] CARB. Co-processing of Low Carbon Feedstocks in Petroleum Refineries, Draft Discussion Paper. 2017.

[35] Al-Sabawi M, Chen J, Ng S. Fluid catalytic cracking of biomass-derived oils and their blends with petroleum feedstocks: a review. Energy Fuels 2012;26(9):5355–72. https://doi.org/10.1021/ef3006417.

[36] Melero JA, Clavero MM, Calleja G, García A, Miravalles Rubén, Galindo T. Production of biofuels via the catalytic cracking of mixtures of crude vegetable oils and nonedible animal fats with vacuum gas oil. Energy Fuels 2010;24(1):707–17. https://doi.org/10.1021/ef900914e.

[37] Bryden K, Weatherbee G, Habib ET. Flexible pilot plant technology for evaluation of unconventional feedstocks and processes. Grace Catal Technol 2013:32–60.

[38] Dupain X, Costa DJ, Schaverien CJ, Makkee M, Moulijn JA. Cracking of a rapeseed vegetable oil under realistic FCC conditions. Appl Catal B Environ 2007;72(1-2):44–61. https://doi.org/10.1016/j.apcatb.2006.10.005.

[39] Gilbert WR. Formation of thiophenic species in FCC gasoline from H2S generating sulfur sources in FCC conditions. Fuel 2014;121:65–71. https://doi.org/10.1016/j.fuel.2013.12.033.

[40] Corma A, Sauvanaud L. FCC testing at bench scale: new units, new processes, new feeds. Catal Today 2013;218–219:107–14. https://doi.org/10.1016/j.cattod.2013.03.038.

[41] Sadeghbeigi R. Fluid catalytic cracking handbook: an expert guide to the practical operation, design, and optimization of FCC units. Elsevier; 2012.

[42] Zelinka P. Multivariable Predictive Control. vol. 30. 2017. doi:10.1016/s1474-6670(17)41435-2.

[43] Parkland Fuel Corporation. Burnaby Refinery Operational Overview. 2018.

[44] Welch's t-test – Wikipedia n.d. https://en.wikipedia.org/wiki/Welch%27s_t-test [accessed August 28, 2020].

[45] Waskom M, Botvinnik O, Gelbart M, Ostblom J, Hobson P, Lukauskas S, et al. mwaskom/seaborn: v0.11.0 (Sepetmber 2020) 2020. doi:10.5281/ZENODO.4019146.

[46] Multiple Regression Analysis: Use Adjusted R-Squared and Predicted R-Squared to Include the Correct Number of Variables n.d. https://blog.minitab.com/blog/adventures-in-statistics-2/multiple-regession-analysis-use-adjusted-r-squared-and-predicted-r-squared-to-include-the-correct-number-of-variables [accessed August 28, 2020].

[47] Fogassy G, Thegarid N, Schuurman Y, Mirodatos C. The fate of bio-carbon in FCC co-processing products. Green Chem 2012;14:1367–71. https://doi.org/10.1039/c2gc35152h.

[48] Pinho ADR, De Almeida MBB, Mendes FL, Ximenes VL, Casavechia LC. Co-processing raw bio-oil and gasoil in an FCC Unit. Fuel Process Technol 2015;131:159–66. https://doi.org/10.1016/j.fuproc.2014.11.008.

[49] Wang C, Venderbosch R, Fang Y. Co-processing of crude and hydrotreated pyrolysis liquids and VGO in a pilot scale FCC riser setup. Fuel Process Technol 2018;181:157–65. https://doi.org/10.1016/j.fuproc.2018.09.023.