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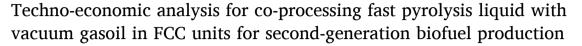
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ABSTRACT

National Renewable Energy Laboratory (NREL) and Petrobras have worked closely to develop process models and analysis approaches to assess the economic feasibility of co-processing bio-oils (pyrolysis oils) with fossil feedstocks in petroleum refinery unit operations. Petrobras conducted co-processing experiments with pine-derived bio-oils and Brazilian vacuum gasoil (VGO) at typical operating conditions on their 200 kg/h demonstration-scale fluid catalytic cracking (FCC) unit. NREL evaluated the experimental yield data and developed novel modeling approaches to simulate and optimize co-processing scenarios. Within the uncertainties of measurements and the simplified refinery models used, the process modeling and techno-economic analysis (TEA) results identify conditions in which co-processing bio-oils could be economically feasible for the case of refiners purchasing VGO, expanding prior work demonstrating technical feasibility.

TEA scenarios show a high potential for bio-oil co-processing to be economically attractive for petroleum refiners for benchmark crude oil prices at \$70 (U.S. dollars) per barrel using up to 5 wt% bio-oil produced with typical fast pyrolysis technology (\leq 400 t/d) fed with dried pine chips. For oil prices per barrel of \$55–\$60, up to 10 wt% bio-oil could be co-processed profitably if produced in pyrolysis plants performing at an "nth-plant" level, feeding 2,000 t/d with dried pine chip feedstocks producing bio-oil at \$48–\$56 per barrel from feedstock ranging from \$99-\$132 per t (\$90-\$120 per ton). Alternatively, low-price biomass feedstocks could make bio-oil co-processing viable at lower oil prices in both cases.

1. Introduction

Among the many pathways to couple renewable and fossil refineries, the refinery integration of raw, filtered bio-oils has been intensively studied over the past three decades to leverage the successful research, development, demonstration, and commercialization of these bio-oils (pyrolysis oils) occurring around the world (Fig. 1).

Government-funded efforts and multilateral collaborations, such as through the International Energy Agency (IEA) Bioenergy Task 34, part of the Technology Collaboration Programme, have focused on biomass pyrolysis. IEA Bioenergy and national programs, in collaboration with industry, have spurred the establishment of standard analytical methodologies and bio-oil product specifications as technologies mature [1]. Suppliers are offering commercial quantities of bio-oils for heating oil, natural gas replacements, heat, and power, and for three decades have

provided bio-oil fractions for specialty chemicals and flavorings [2]. In addition, the commercial scale associated with the current state of fast pyrolysis technology is approaching 400 t/d [3–5], benefitting from economies of increased scale.

The direct conversion of biomass using existing facilities in petroleum refineries has been discussed in recent years, because it allows traditional fossil-energy companies to incorporate low-carbon fuels in the energy matrix. The co-processing of bio-oils (from fast pyrolysis or direct liquefaction) with regular fossil streams has been studied as a feasible low-investment route to curb CO_2 emissions [7–12].

One of the main conversion processes in many refineries is fluid catalytic cracking (FCC). FCC is primarily used to produce high-quality gasoline by using zeolite catalysts to convert larger molecules into smaller ones. Over the years, FCC technology has evolved into a very flexible process that can handle a wide range of feeds from vacuum

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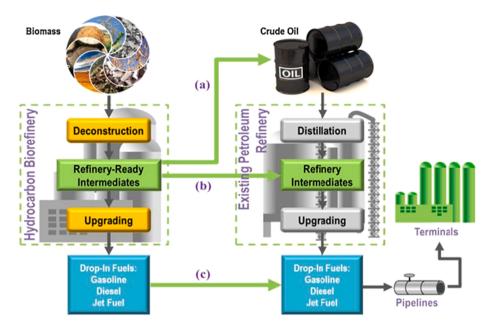


Fig. 1. Renewable products/intermediates that may enter petroleum refineries through (a) crude oil distillation, (b) petroleum refinery conversion units, or (c) finished product blending (reproduced with permission from Elsevier) [6].

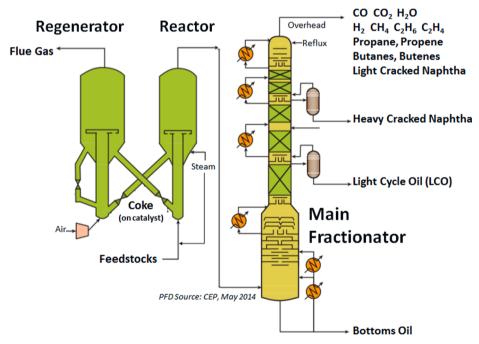


Fig. 2. Simplified process flow diagram of typical FCC unit (reproduced with permission from AIChE) [15].

gasoil (VGO) to atmospheric residues, including highly impure and heavy-refinery streams. Moreover, operating conditions can be manipulated to optimize yields of light olefins such as propylene or gasoline- or diesel-range products. The FCC riser reactor may be designed with different sets of feed nozzles positioned at different heights to take advantage of local internal conditions inside the reactor. FCC is widely practiced in petroleum refining worldwide and is present in most U.S. and Brazilian refineries. Fig. 2 shows a simplified process flow diagram for a typical FCC unit configuration.

The major pieces of processing equipment associated with the FCC are the reactor, regenerator, and main fractionator. The reactor is where the endothermic, catalytic cracking of larger molecules takes place via entrained flow of catalyst and feedstocks at temperatures ranging from

510 °C to 565 °C and at a residence time around 2 s [12]. The regenerator is where the spent FCC catalyst, deactivated by accumulation of coke, is reactivated by burning the coke from the surface of active sites of the catalyst. The main fractionator serves to remove heat and separate the products from the FCC reactor into appropriate cuts for downstream processing to finished fuels or other products.

Previous experimental studies demonstrated that bio-oils from pine woodchips in a biomass pyrolysis pilot-scale unit could be co-processed along with Brazilian VGOs with drastically reduced impacts on coke yield, even when 20 wt% bio-oil was used; the impacts of coke on catalyst with 10 wt% bio-oil were found to be negligible. In addition, feed nozzle or feed line plugging were not observed at demonstration scale (200 kg/h) [13,14].

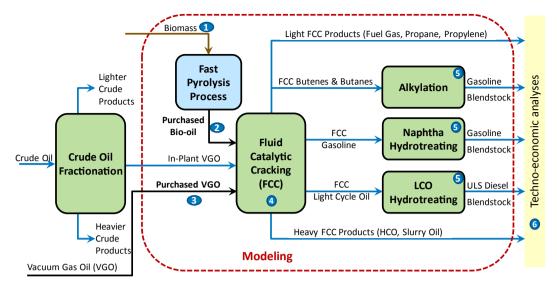


Fig. 3. Renewable bio-oils supply chain (Steps 1 and 2) is compared to purchased VGO (Step 3) fed into the FCC unit (Step 4) of a petroleum refinery. Additional steps (Step 5) produce finished co-processed fuel blendstocks. The techno-economic analysis (Step 6) uses Steps 1–5 to establish the breakeven price of bio-oil with the price of VGO, or the refinery purchasing cost.

1.1. Paper context

We address the coupling of a biorefinery, producing minimally treated fast pyrolysis oils containing 50 wt% oxygen, with petroleum refinery FCC units processing VGO, a commodity intermediate produced by fractionation of crude oil in refineries. VGO is sold on the market by refiners with excess crude fractionation capacity and often purchased by refiners that have excess FCC capacity but insufficient crude processing capacity. In addition to refineries with excess FCC capacity, refiners may also consider operating changes like changing refinery crude mix, reducing crude processing rate or rerouting portions of existing FCC feedstocks to other processing units like hydrocrackers and cokers to enable co-processing if positive economic incentives exist. Fig. 3 describes the groups of petroleum-refining unit operations and biomass-processing systems that are included in the scope of modeling and analysis. We will refer to these step numbers in subsequent sections of the paper.

Step 1 represents the wood pyrolysis process generating bio-oils. We perform a techno-economic analysis (TEA) to establish a cost basis for refiners to purchase bio-oils; bio-oil cost is primarily a function of the pyrolysis plant size and price of the biomass feedstock. We addressed the widely different sizes of biorefineries and petroleum-processing plants, including minor capital cost modifications required for the FCC to accept this new renewable stock (Step 2). In Step 3, the simplified cost basis used was spot VGO pricing as a function of the West Texas Intermediate (WTI) spot crude oil prices. We will use "prices" to refer to "spot prices" of petroleum commodities in this paper. Step 4 develops the new coprocessing FCC model of bio-oils with VGO, which is the core of this paper. The FCC model co-processes 0-20 wt% bio-oil and 80-100 wt% VGO based on data from experimental results [13,14]. In Step 5, literature data served as the basis for expanding the modeling to finished, coprocessed fuel blendstocks. Along with the process models and pricing data, other key inputs and assumptions required to complete the analysis include the operational basis for the FCC, costs for materials and utilities consumed or produced by the FCC, values for feedstock and product densities, and heating values for fuel gas components from the FCC. The combination of these models establishes the product yields and processing costs as functions of the FCC cracking severity and bio-oil content with subsequent processing steps to produce finished fuel blendstocks. We then report the simplified refinery TEA (Step 6) in terms of the delta gross profit margin (\$/bbl) between VGO-only processing and VGO/bio-oil co-processing (United States dollars used throughout).

Table 1TEA parameters applied for calculating MSP of raw filtered bio-oils (costs on a 2014 constant U.S. dollar [USD] basis) [18].

| Description of Parameter | Value Assumed for TEA |
|--|-------------------------------------|
| Internal rate of return (IRR) | 10% |
| Plant financing debt-to-equity ratio | 60%:40% of fixed capital investment |
| Plant life | 30 years |
| Income tax rate | 35% |
| Interest rate of debt financing | 8% annually |
| Term for debt financing | 10 years |
| Working capital cost basis | 5% of fixed capital investment |
| | (excluding land) |
| Depreciation schedule | 7-year MACRS ^a [17] |
| Construction period and capital spend plan | 3 years (8% in 1st, 60% in 2nd, 32% |
| | in 3rd) |
| Plant salvage value | No value |
| Startup time | 6 months |
| Revenue and costs during startup (% of | Revenue = 50% |
| normal operation) | Variable operating costs = 75% |
| | Fixed operating costs = 100% |
| On-stream factor (%) | 90 (7,884 operating hours per year) |

^a Modified Accelerated Cost Recovery System.

In addition to the analysis focused on gross profit margin, another methodology commonly used in refinery operations is applied to estimate the breakeven value of bio-oil, which represents the maximum price a refiner would pay for a feedstock. The analysis presented here uses scenarios to uncover conditions where there are favorable economics for the development of supply chain biomass and bio-oil suppliers that are also favorable to petroleum refiners that would otherwise purchase VGO to fill spare FCC processing capacity. All modeling data are provided so users can analyze the process with their own data. We conducted uncertainty analyses for Step 1 and for the combined Steps 1–5 to generate the overall results of the analyses (Step 6). Additionally, we show that the rationale for the co-processing TEA conducted in this effort is contextually relevant to the markets and refineries in Brazil, the United States, and likely other countries.

2. Methods

2.1. Techno-economic analysis for raw filtered bio-oils from pine wood

We used a standard reference basis common to these studies, known

Table 2Comparisons of pine-derived bio-oil properties from sources at various processing capacities.

| Bio-oil property | Commercial 2,500–4,200 kg/h $^{\rm d}$ [13] | Demonstration 25 kg/h [14] | Pilot 5–25 kg/h [19] | Fast pyrolysis design report [18] |
|---|---|----------------------------|----------------------|-----------------------------------|
| Density (g/cm ³ , 20 °C) | 1.20 | 1.21 | 1.19 | 1.20 |
| Elemental analysis (wt % wet) | | | | |
| Carbon ^a | 41.8 | 42.4 | 41.6 | 42.4 |
| Hydrogen ^a | 7.5 | 6.5 | 7.9 | 7.7 |
| Sulfur ^a | < 0.3 | < 0.1 | 0.1 | 0.0 |
| Oxygen ^a | 50.7 | 51.1 | 50.5 | 49.8 |
| Water content (wt %) | 31.9 | 25.5 | 21.9 | n.a. ^c |
| Ash content (wt %) | 0.17 | 0.017 | < 0.05 | n.a. |
| Acidity (mg KOH/g) b | 128 | 70.3 | 67.2 | n.a. |
| Viscosity at 60 °C (mm ² /s) | 6.7 | 48.4 | n.a. | n.a. |
| Raw bio-oil organic yield (wt %) | n.a. | n.a. | 60 | 62 |

^a Elemental analyses corrected for consistent water content of 25 wt% in all fast pyrolysis liquids.

as the "nth-plant" design [16], to calculate the minimum selling price (MSP) of the bio-oils. The assumptions did not account for additional first-of-a-kind plant costs, including special financing, equipment redundancies, large contingencies, and longer startup times necessary for the first few plants. We assume that the costs of the nth plant reflect a future time when the technology is mature, with several plants already built and operating. The specific financing and operating assumptions applied for the nth-plant TEA listed in Table 1 can be easily modified by users.

We analyzed two capacities of wood fast pyrolysis plants: 400 t/d, which is consistent with currently operating commercial fast pyrolysis plants, and the typical 2,000 t/d envisioned biorefinery scenarios employed by the U.S. Department of Energy Bioenergy Technologies Office (BETO) program. These parameters represent conditions employed by BETO for design report methodology to guide technology development, using comparable economic conditions for future n^{th} plants. The design reports for this technology were jointly developed in 2013 by the National Renewable Energy Laboratory, Pacific Northwest National Laboratory, and Idaho National Laboratory [18].

The purpose-grown pine is harvested, collected, debarked, and chipped at the landing. Harvest is costed as a custom operation with a fixed cost per dry mass, consisting of feller buncher, skidder, chipper, and chip van. Logistics include costs from the gate of the landing to the biorefinery. Storage and handling occur within the gates of the biorefinery (Appendix [18]). The dispersed nature of the renewable feedstock increases the collection cost over an increased area for the 2,000 t/ $\,$ d, and thus offset part of the advantages of economies of scale introduced by the larger biorefinery processing capacity. Table 2 presents a comparison of properties for raw bio-oils from several different sources used, showing the consistent quality of bio-oils from different suppliers operating commercial [13] and demonstration [14] pyrolysis plants compared to a more recent pilot verification [19] and those of the design report [18]. The two commercial/demonstration liquid bio-oils used in the demonstration-scale FCC unit had one phase only, the organics-rich phase. Typically, the liquid yield is about 60 wt% to 75 wt% containing 25 wt% of water. The other two components are volatile gases and char at ~ 15 wt% each, closing the mass balance. The pilot plant bio-oils were collected in continuously recycled dodecane [19], which separated into two phases. The reference presents the three main components from the pine pyrolysis process obtained in three pilot plant runs to provide the mass balance repeatability and uncertainties as follows 74% liquid, 11% char and ash, and 15% light volatile gases, for a mass balance of 100% \pm 10%. The consistency of the data at these conditions increases the confidence in the TEA results for the supply chain of biomass to bio-oils, and of potential refinery purchasers.

2.2. Linking biorefineries to petroleum refining

2.2.1. Rationale for sizing the biorefineries

The scales of petroleum refining and biomass pyrolysis operations are generally mismatched because of the lower energy per mass density of the solid renewable feedstock and costly logistics with increasing feedstock supply radius. Relationships between capacities of commercial FCC operations and fast pyrolysis biomass conversion facilities are summarized in Fig. 4. The average United States FCC plants or 50,000-barrel-per-day unit was chosen to serve as the base capacity for developing co-processing scenarios. For a single FCC unit processing 50,000 barrels per day (bbl/d) (1 bbl = 0.159 m³ of crude oil), the output of a biomass refinery using 400 t/d of feedstock would provide a fresh feed (FF rate required for co-processing roughly 5/95 wt% bio-oil/VGO. A 2,000 t/d bio-oil facility would provide feedstock sufficient for roughly 20/80 wt% pyrolysis oil/VGO co-processing.

Current biomass pyrolysis facilities processing 400 t/dcould use today's infrastructure supplying pine wood chips to pulp mills or solid forest products mills. A fivefold capacity increase to 2,000 t/d may require scale-up, multiple pyrolysis facilities, and/or appropriate lowcost feedstocks [20].

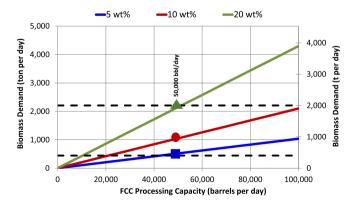


Fig. 4. Biomass demand to generate bio-oils (fast pyrolysis biorefinery capacity) as a function of FCC processing capacity for 5 wt% (blue), 10 wt% (red), and 20 wt% (green) of bio-oil in the FCC feed. The bottom black line represents a 400 t/d dried biomass facility currently operating commercial fast pyrolysis plants; the upper line projects a five-fold capacity increased operation in biorefinery scenarios employed by the U.S. Department of Energy Bioenergy Technologies Office to measure progress and compare technologies. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

^b Acidity measured by the total acid number method.

c not available.

^d 60-100 ton/d (dry).

Table 3Capital cost basis and co-processing scenario results for bio-oil storage and feeding system.

| Compo | Unit | Basis | 5 wt% bio-oil | 10 wt% bio-oil | 20 wt %bio-oil | |
|------------------------------|-------------------------|-------------------|---------------|----------------|----------------|-----------|
| Capital scalin | ig exponent | | 0.7 | 0.7 | 0.7 | 0.7 |
| Bio-oil feed tank | | | | | | |
| | Storage capacity basis | d | 14 | 14 | 14 | 14 |
| | Storage volume | m^3 | 4,382 | 4,382 | 8,862 | 18,135 |
| | Installed cost | \$ | 1,303,300 | 1,303,296 | 2,133,953 | 3,522,612 |
| Bio-oil feed pumps | | | | | | |
| | Liquid flow rate | m ³ /h | 26.1 | 12.9 | 26.3 | 54.1 |
| | Installed cost per pump | \$ | 44,500 | 27,365 | 44,806 | 73,963 |
| | Number of pumps | | 2 | 2 | 2 | 2 |
| Total installed capital cost | | \$ | | 1,358,026 | 2,223,565 | 3,670,537 |

2.2.2. Capital costs for bio-oil storage at the refinery site and delivery to the FCC unit

We used the Aspen Capital Cost Estimator to estimate the costs of additional capital equipment necessary for bio-oil co-processing, including storage tanks, pumps, and piping from storage tanks to FCC unit. Based on the feeding strategy for bio-oil co-processing in the FCC described elsewhere [13,14] and using materials compatible with bio-oil properties [1,2,12], the 14-day bio-oil storage was linked to the FCC reactor site by a feeding line maintained at 25 °C to 30 °C. The basis for capital cost calculations and results are provided in Table 3. Other capital requirements specific to the refining plant relate to likely downstream requirements with increasing pyrolysis oil content in FCC feed such as for wastewater treatment with the added phenolics from biomass compared to VGO alone [14], carbonate formation from ${\rm CO_2}$ in fractionators, and amine and sulfur plant capacity from CO₂ for in-plant reuse of gases or environmental releases. To estimate such requirements, significant additional co-processing operating time and analytical data would be needed, not available from the references used [13,14].

2.3. FCC feedstock and product pricing basis

To assess bio-oil co-processing opportunities, the variable and often volatile nature of fossil fuel markets needs to be addressed. Co-processing economic scenarios were assessed with a simplified pricing structure that varies fossil feedstock, intermediate, and product prices as a function of a benchmark crude oil price. Data from the Oil Price Information Service (OPIS) International Feedstocks Intelligence Reports [21] for WTI—one of the crude oils used as a benchmark in oil pricing—ranges from \$40-\$100/bbl; the prices of the specific year served as the basis for the analysis product pricing structure. The data points used to develop the pricing equations represent snapshots derived from the open literature. Examples of the simplified pricing models applied for the co-processing TEA are shown in Fig. 5.

Three grades of VGO commodities are purchased by refiners—low, medium-, and high-sulfur VGOs, with decreasing prices. Although biooils derived from pine have low sulfur content, the presence of alkali and alkaline earth metals could present issues for catalyst deactivation downstream and possibly decrease their value (Table 2). Deactivation issues were considered by assuming a higher percentage of catalyst makeup for bio-oil processing relative to VGO. The scenarios developed in this paper were based on comparing VGO prices in the market with the costs of bio-oils produced under various conditions to show levels of profitability that could justify petroleum industry investment. The amount of additional capital costs estimated for enabling co-processing at a refinery (see Table 3) represents a small capital addition compared to the billion-dollar investment in the refinery.

The FCC profit margin on typical petroleum-derived feedstock (VGO in this case) was estimated based on the pricing models and confirmed by comparison with the the "3-2-1 crack spread" trends for both WTI and VGO. The 3-2-1 crack spread metric is an operational guide for refiners and was used to provide a simplified route to compare and confirm refining profit margins calculated in the co-processing analysis based on

market prices and cost of products to feed the refinery unit operations. The 3-2-1 crack spread was calculated using Eq. (1):

$$3-2-1$$
 Crack Spread = $2 \times Regular$ Gasoline Price + ULSD Price
 $-3 \times WTI$ (or VGO) Price

(1)

Based on the calculated profit margins derived from refinery process/pricing models and consistent comparisons with correlations for 3-2-1 crack spreads versus WTI prices, we judged the economic basis for the co-processing scenarios as credible, absent proprietary data. The 0% bio-oil (100% VGO) case was taken as the base case for the FCC operation to facilitate comparisons and interpretations of the TEA results.

2.4. FCC co-processing data and models for the techno-economic analysis

The experimental data, FCC yield models, and TEA frameworks were used to explore the economic feasibility of bio-oil co-processing in the FCC unit, Step 4 of Fig. 3. Economic results are presented based on two primary economic metrics: (1) FCC gross profit margin (\$/bbl of total fresh feed to the FCC) and (2) bio-oil breakeven value (\$/bbl of bio-oil), which represents the maximum price a refiner would pay for the feedstock to make a profit from processing (breakeven). TEA calculations used constant 2014 U.S.dollars.

2.4.1. FCC co-processing data

To build the FCC co-processing model, we used experimental data from a previous publication using commercial bio-oils [13], which confirmed and expanded prior data using the same demonstration-scale FCC unit to co-process bio-oils produced at a pilot-scale biomass pyrolysis unit [14]. Combining both data sets, we analyzed 54 experiments that had mass balances ranging from 96% to 100%. Table 2 compares capacities of the bio-oil processing plants and values of some analytical properties of these two oils and other well-characterized bio-oils. References [13] and [14] include more details on metal content, which—with the exception of iron—were higher in reference [13] than in [14] for the common set of metals. The experimental data were obtained in Petrobras's demonstration-scale (200-kg/h) FCC unit and serve as the fundamental basis for this study. Results from [13] and [14] show that co-processing of raw bio-oil in the FCC was technically feasible. Renewable carbon content of the crude liquid products from coprocessing tests were measured by ¹⁴C isotopic analysis [13,14]. Coprocessing 5 wt%, 10 wt% and 20 wt% results in liquid products containing 1 wt%, 2 wt% and 5 wt% of renewable carbon respectively, which corresponds to about 30% of the renewable carbon from the crude bio-oil. FCC product yields were determined as a function of (i) bio-oil content in the FCC feed, (ii) VGO feed temperature to the FCC, and (iii) FCC riser/reactor temperature. The segregation between the bio-oil and the fossil VGO stream and their injection into different axial reactor positions into the FCC riser reactor made it possible for these two feeds to take advantage of different local reactor conditions, such as reaction temperatures and catalyst-to-oil ratios, and obtain an optimum feed dispersion through the nozzles for both feeds [14]. Properties of the

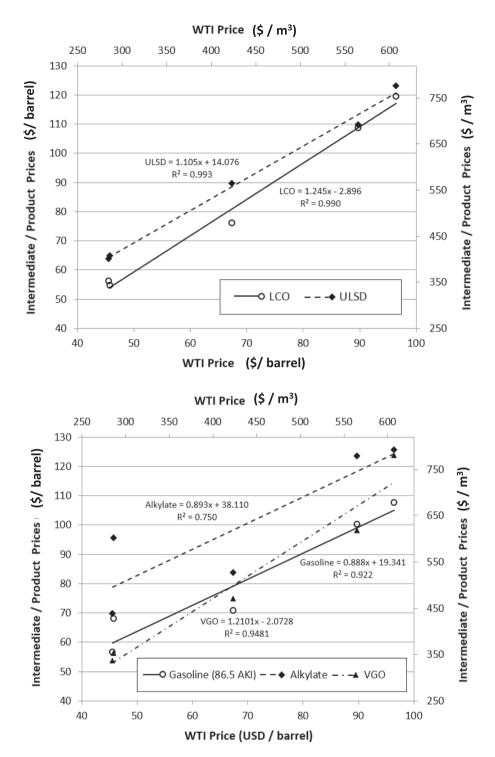


Fig. 5. Examples of how product pricing values were determined based on an assumed WTI price.

Brazilian VGOs used to generate the data are shown in Table 4.

The FCC conversion is a metric of the unit operating severity and is calculated by Eq. (2). Feed and riser/reactor temperatures are typically the primary drivers for FCC conversion. Therefore, FCC conversion was used as the primary independent variable, in addition to bio-oil content in the feed, for statistical model development and plotting yield/economic data. Throughout the remainder of this paper, percent feed represents the weight percent of incoming fresh feed (FF) to the FCC unit.

Examples of the yield data from the demonstration-scale FCC unit for liquefied petroleum gas (LPG) (including propane, propylene, butanes, and butenes), cracked naphtha, LCO, and bottoms oil are shown in Fig. 6. The FCC-intermediates yields are presented as functions of FCC conversion; additional experimental data are from previous studies [13,14].

Table 4Reference feedstock (VGO) properties.

| Reference | 2017 [13] | 2015 [14] |
|--|---------------|-----------|
| Density (g/cm ³ , 20 °C) | 0.9362-0.9374 | 0.9470 |
| Sulfur, wt % | 0.59-0.67 | 0.46 |
| Total nitrogen, wt % | 0.33-0.34 | 0.24 |
| Basic nitrogen, mg/kg | 1,194-1,260 | 1,187 |
| Aniline point, °C | 74.7-76.0 | 81.9 |
| Ramsbottom carbon residue, wt % | 1.19-1.49 | 1.73 |
| Simulated distillation per mass recovery, °C | | |
| Initial | 199.0-206.4 | 130.8 |
| 10% | 331.2-330.2 | 350.0 |
| 30% | 402.0-403.0 | 426.8 |
| 50% | 443.4-444.4 | 477.0 |
| 70% | 486.2-490.4 | 539.4 |
| 90% | 563.8-567.6 | 642.6 |
| Final | 715.0–737.8 | 741.0 |

2.4.2. FCC process model development

The next major aspect of the analysis approach is the development of optimizable FCC yield models based on the experimental data. Two unique process yield models were developed: Method 1, based on JMP statistical software from the SAS Institute [22], a correlation-based yield model; and Method 2, based on the FCC Aspen HYSYS model [23].

2.4.2.1. Method 1 correlations. Method 1 is an empirical correlation-based FCC yield model developed directly from the experimental data produced from the demonstration-scale FCC unit [13,14]. The two independent variables for the model are (1) "Bio-oil," the bio-oil content (wt %) in the total FCC feed, and (2) "Conv," representing the "FCC Conversion," previously defined in Eq. (2). Eq. (3) shows the format for the statistical correlations of Method 1.

FCC Intermediate Yield (wt % of Total FCC Feed)

$$= A + B \times Bio-oil + C \times Conv + D \times (Bio-oil - X)^{2} + E$$
$$\times (Conv - Y)^{2} + F \times (Bio-oil - X) \times (Conv - Y)$$
(3)

Where: A, B, C, D, E, and F are specific to each FCC intermediate product yield correlation and Bio-Oil and Conv are independent variables: X = 6.03333 and Y = 68.08930.

Table 5 shows the estimated coefficients (parameters) for the product yields determined using the JMP statistical analysis software. Applying the coefficients generates the various equations for specific products from the empirical correlation-based FCC yield model, which was developed directly from the experimental data produced from the demonstration-scale FCC unit.

2.4.2.2. Method 2 approach and calibration cases. Method 2 used the FCC Aspen HYSYS simulation refinery integration model, which predicts

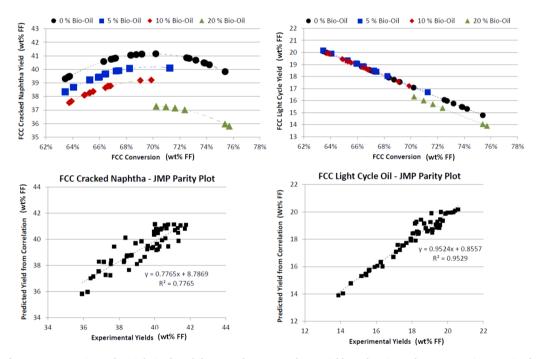


Fig. 6. Examples of composite experimental FCC-derived naphtha, LCO, bottoms, and LPG yields as functions of FCC conversion severity from the two studies [13,14] considered in this analysis (FF = fresh feed).

Table 5Correlation coefficients for Eq. (3).

| | A | В | С | D | E | F |
|------------------------------|---------|---------|---------|---------|---------|---------|
| Dry Gas | -3.6903 | -0.1281 | 0.1092 | 0.0063 | 0.0159 | -0.0070 |
| Propylene | -8.3547 | -0.1359 | 0.2144 | | | 0.0026 |
| LPG (Excl. C ₃ =) | -8.9404 | -0.1860 | 0.2799 | -0.0074 | 0.0145 | 0.0071 |
| Naphtha | 30.0393 | -0.1938 | 0.1611 | | -0.0440 | |
| LCO | 48.4176 | -0.0086 | -0.4445 | -0.0036 | | |
| Bottoms Oil | 51.5581 | 0.0090 | -0.5552 | 0.0036 | | |
| Coke | -3.8930 | -0.0417 | 0.1540 | 0.0177 | 0.0067 | -0.0166 |
| Water | 0.4645 | 0.3126 | -0.0101 | 0.0074 | 0.0003 | 0.0006 |
| CO | -1.1506 | 0.2255 | 0.0211 | -0.0102 | 0.0044 | 0.0038 |
| CO_2 | -0.8287 | 0.0547 | 0.0137 | -0.0028 | 0.0003 | 0.0024 |

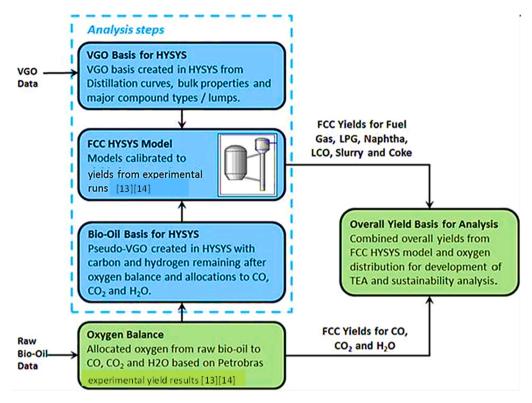


Fig. 7. Logic flow used in Method 2 to address the new oxygenated feedstock in the FCC Aspen HYSYS model based on experimental results [13,14].

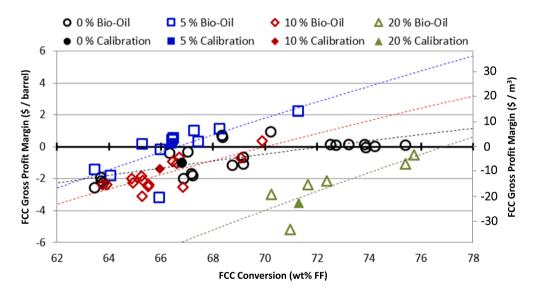


Fig. 8. FCC gross profit margin as a function of FCC conversion (wt %) using Method 2 at WTI crude benchmark price of \$100/bbl. Calibration cases for coprocessing TEA are averages of data under compatible conditions and are represented by full symbols, while the open symbols represent experimental points.

FCC yields and qualities of products based on calibration cases, which were tuned to match the experimental data from the FCC unit [13,14] from VGO-only experiments. However, the FCC HYSYS model was created to process conventional feeds that do not contain oxygenated compounds. Therefore, a pseudo-VGO model was created based on bio-oil/VGO data and fed into the FCC model. Fig. 7 details the logic flow diagram for the development of the model capable of representing oxygenated feeds co-fed with petroleum VGO. The four model calibration cases, derived from averaging multiple compatible experimental data points from the demonstration-scale FCC unit, are shown in Fig. 8 as full points, while open data points are experimental. The figure shows the FCC gross profit margin derived from TEA for each experimental

data point at a WTI crude price of \$100/bbl.

The calibration case for the 0% bio-oil (VGO only) Method 2 model represents an average of 15 experimental data points. The 5/95 wt% and 10/90 wt% bio-oil/VGO calibration cases used 11 and 15 data points, respectively, from experimental data from references [13] and [14], and the 20/80 wt% bio-oil/VGO calibration case had only 4 data points from reference [14].

2.5. Model development for product finishing operations to blendstocks

In Step 5 of Fig. 3, the FCC process yield models were integrated with spreadsheet-based product finishing models for (1) FCC cracked

Table 6Groupings applied to experimental data set for pooled standard deviation analysis.

| Experimental Variable | Values for Data Groupings ^a |
|--|--|
| Raw filtered bio-oil in FCC feed, wt % | 0, 5, 10, 20 |
| FCC riser reactor outlet temperature, °C | 540, 560 |
| FCC feed temperature, °C | 220, 280, 320 |

^a Experimental values were rounded for grouping as needed.

Table 7
Pooled standard deviation analyses on experimental data from the FCC demonstration-scale unit.

| | Range of Ex Results | rperimental | Pooled Analysis Results | | |
|--------------------------|------------------------|-------------|------------------------------|---------------------------|--|
| FCC Product, wt % | Minimum | Maximum | Pooled Standard Deviation | Pooled 95% Uncertainty | |
| Dry Gas | 2.19 | 5.96 | 0.26 | 0.52 | |
| Propylene | 3.43 | 7.96 | 0.46 | 0.89 | |
| LPG (Excl. Propylene) | 5.21 | 12.88 | 0.54 | 1.05 | |
| Naphtha | 35.91 | 41.76 | 0.78 | 1.53 | |
| Light Cycle Oil | 13.88 | 20.60 | 0.69 | 1.35 | |
| Bottoms Oil | 10.03 | 16.85 | 0.63 | 1.23 | |
| Water | _ | 9.32 | 0.59 | 1.16 | |
| CO | - | 4.46 | 0.66 | 1.29 | |
| CO_2 | _ | 1.06 | 0.04 | 0.08 | |
| Coke | 5.64 | 9.82 | 0.32 | 0.63 | |

naphtha hydrotreating to finished gasoline blendstock, (2) FCC LCO hydrotreating to finished ULSD blendstock, and (3) conversion of C_4 olefins from FCC and purchased *iso*-butane to gasoline blendstock via alkylation.

Operational bases for FCC product hydrotreater were required for the analysis to model the processing of cracked naphtha to produce a gasoline blendstock and processing LCO to ULSD blendstock. These refinery operations were modeled by first predicting the feed-to-product yields, properties, and hydrogen consumption using data from the experiments and various literature sources. Using the hydrogen consumption estimate as an indication of the hydrotreater operational severity, raw material and utility consumption estimates were determined using published data from Gary, Handwerk, and Kaiser [24] and others on petroleum refinery operations and economics [25].

In addition to the modeled hydrotreater operations, a sulfuric acid alkylation process was also modeled to convert C_4 olefins from FCC and produced/purchased *iso*-butane to a high-octane gasoline blendstock called alkylate. Published data from [24] serves as the basis for estimating the operational performance of the C_4 alkylation process and estimates for raw materials, utility consumption, and operating costs.

2.6. Uncertainty analysis

In Fig. 3 Step 6, the TEA and complex coupling of data have uncertainties in data groupings and in the models used. A pooled standard deviation analysis was used to derive a standard deviation that represents these sources. Each group of points has an average spread of data points about the mean of data obtained under consistent experimental conditions. Groups have different numbers of data points and thus different standard deviations. The pooled standard deviation is the weighted average of each group's standard deviation. The weighting gives larger groups a proportionally greater effect on the overall estimate. Table 6 summarizes the groupings of experimental data applied for calculating the pooled standard deviation and Table 7 shows the results of the analysis using the R software package [26].

Another approach to the uncertainty analysis performed were uncertainties associated with the experimental data sets using the TEA

Table 8Results of uncertainty analysis on experimental data [13,14] from FCC. Bold numbers represent maximum uncertainties.

| Feedstock processing scenario and WTI price (\$/bbl) | Data points (#) | Uncerta gross pr margin WTI 100 | • | Uncertai bio-oil b value WTI 100 | nty on reakeven WTI 50 |
|--|--------------------|---|-----------|--|---------------------------------|
| 0% bio-oil (VGO only) | 5 | ±1.9 | ± 1.4 | n.a. a | n.a. |
| 0% bio-oil (VGO only) | 8 | ± 2.2 | ± 2.1 | n.a. | n.a. |
| 5% bio-oil | 5 | ± 0.7 | ± 0.6 | ± 17.5 | ± 16.7 |
| 10% bio-oil | 7 | ± 1.5 | ± 1.1 | ± 19.3 | ± 14.3 |

^a n.a. = not applicable.

results from groups of data points derived at the same operating conditions. Specifically, those conditions included data points from the same bio-oil content in the FCC feed, FCC riser/reactor temperature, and VGO feed temperature to the riser/reactor. Using four sets of data points with at least five data points per set, the uncertainties of the two economic metrics were calculated through TEA of each data point for (1) FCC gross profit margin \$/bbl of FCC feed) and (2) bio-oil breakeven value (\$/bbl). There were not five consistent data points for 20% bio-oil co-processing to conduct such uncertainty analyses. The 20% bio-oil points were investigated in fewer conditions [14] and not repeated in the subsequent work [13]. These figures are shown for completeness of information but with the caveat that they were preliminary. The results of the assessment are presented in Table 8; the bold values estimate maximum uncertainties for each of the two economic metrics. These maximum uncertainty values apply to both the experimental data and the Method 1 correlation model, which was developed directly from the experimental data.

The uncertainties for the bio-oil breakeven value are much more significant relative to the FCC gross profit margin. This is a result of how each economic metric allocates the uncertainty. In the case of FCC gross profit margin, the uncertainty is allocated to the entire FCC feedstock, both VGO and bio-oil feeds. However, for the bio-oil breakeven value, the uncertainty is in the experimental yields that were allocated only to the bio-oil portion of the feedstock, making the apparent uncertainties for these calculated values much more significant.

3. Results and discussion

3.1. Geographic context

Although the present work was conducted using Brazilian VGO, the following information suggests that it applies to a much broader geographic context. According to the U.S. Energy Information Administration, petroleum refineries in the United States imported and processed, on average, more than 200,000 barrels of Brazilian crude oil per day in 2015 [27]. To further validate the contextual relevance for the U.S. refining industry, we compared properties of several Brazilian crude oils with their assays from countries like Canada, Venezuela, Iraq, Nigeria, and Angola, which also export crude oil to the United States, as shown in Table 9. Moreover, VGO fractions of the various crude oils (abbreviated as gasoils), which are typically fed to the FCC unit in a refinery, were also included.

The overall crude property data show that the Brazilian crudes—Marlim and Albacora Leste—have comparable properties relative to crudes produced in the United States (Alaskan North Slope) and crudes imported from other countries for processing in U.S. refineries. The overall crude comparison indicates that the Brazilian crude oils are low in sulfur content, high in nitrogen content, high in density, and high in total acid number. In general, the Brazilian crude oils most closely compare to the properties of Ebok crude produced in Nigeria. Brazilian crudes are relatively low in carbon residue (an indicator for the propensity to produce coke) and metal content (nickel and vanadium),

Table 9
Comparison of crude oil properties used in the United States, either self-produced or imported from Brazil and other countries [28].

| Crude oil name | Alaskan | Kearl | Sokol | Hamaca | Basrah Heavy | Ebok | Hungo Blend | Marlim | Albacora Leste | Min. | Max. |
|--|---------|--------|--------|-----------|-----------------|---------|----------------|--------|-------------------|-------|-------|
| Origin | USA | Canada | Russia | Venezuela | Iraq | Nigeria | Angola | Brazil | Brazil | | |
| Whole crude oil properties | | | | | | | | | | | |
| API gravity | 31.4 | 22.6 | 34.8 | 26.0 | 24.0 | 19.0 | 28.3 | 19.4 | 19.0 | 19.0 | 34.8 |
| Specific gravity | 0.869 | 0.918 | 0.851 | 0.898 | 0.910 | 0.940 | 0.885 | 0.938 | 0.940 | 0.850 | 0.940 |
| Sulfur, wt % | 1.0 | 3.4 | 0.29 | 1.6 | 3.8 | 0.4 | 0.6 | 0.8 | 0.6 | 0.3 | 3.8 |
| Total nitrogen, ppm wt | 1,800 | 3,212 | 1,192 | 2,474 | 1,845 | 4,328 | 2,640 | 4,900 | 4,500 | 1,200 | 4,900 |
| Carbon residue, wt % | 4.9 | 8.9 | 1.0 | 7.3 | 10.1 | 4.3 | 5.6 | 8 | 6.8 | 1 | 10.1 |
| Total acid number, mg/g | 0.2 | 2 | 0.19 | 0.7 | 0.2 | 2.9 | 0.5 | 1.3 | 2.4 | 0.2 | 2.9 |
| Nickel, ppm wt | 11 | 41 | 3.3 | 42 | 21 | 32 | 18 | 19 | 11 | 3.3 | 42 |
| Vanadium, ppm wt | 25 | 113 | 1.3 | 152 | 80 | 5 | 15 | 28 | 18 | 1.3 | 152 |
| Crude oil volumes (vol. % whole crude) | | | | | | | | | | | |
| Butane & Lighter (-200°F to 60°F) | 2.5 | 0.8 | 1.6 | 1.9 | 1.6 | 0.4 | 1.3 | 0.6 | 0.6 | 0.4 | 2.5 |
| Naphtha (60°F to 330°F) | 22.1 | 22.5 | 27.1 | 13.0 | 15.9 | 5.6 | 16.5 | 7.9 | 6.8 | 5.6 | 27.1 |
| Kerosene (130°F to 480°F) | 14.1 | 3.9 | 20.0 | 13.1 | 11.4 | 12.9 | 13.1 | 9.6 | 8.2 | 3.9 | 20.0 |
| Diesel (480°F to 650°F) | 16.0 | 9.7 | 20.3 | 19.8 | 14.2 | 23.9 | 16.0 | 14.2 | 13.5 | 9.7 | 23.9 |
| Gas oil (650°F to 1,000°F) | 27.1 | 31.1 | 23.9 | 29.1 | 29.3 | 37.6 | 31.2 | 33.8 | 37.2 | 27.1 | 37.6 |
| Residue (+1,000°F) | 18.3 | 32.0 | 7.0 | 23.1 | 27.5 | 19.7 | 21.8 | 33.9 | 33.6 | 7.0 | 34.0 |
| Gas oil (650°F to 1,000°F) Properties | | | | | | | | | | | |
| API gravity | 21.2 | 14.1 | 22.3 | 21.9 | 18.7 | 14.0 | 21.2 | 17.8 | 17.7 | 14.0 | 21.9 |
| Specific gravity | 0.926 | 0.972 | 0.920 | 0.922 | 0.942 | 0.973 | 0.927 | 0.948 | 0.949 | 0.920 | 0.970 |
| Sulfur, wt % | 1.2 | 3.3 | 0.5 | 1.2 | 4.1 | 0.4 | 0.8 | 0.8 | 0.6 | 0.4 | 4.1 |
| Total nitrogen, ppm wt | 1,307 | 1,895 | 1,539 | 687 | 1,037 | 2,989 | 1,439 | 3,609 | 3,046 | 687 | 3,609 |
| Carbon residue, wt % | 0.5 | 1.0 | 0.30 | | 0.6 | 0.4 | 0.5 | 0.3 | 0.4 | 0.3 | 1.0 |
| Total acid number, mg/g | 0.3 | 3.4 | 0.4 | 1.1 | 0.3 | 4.4 | 0.7 | 1.5 | 3.3 | 0.3 | 4.4 |

Table 10Summary of simplified TEA results for raw filtered bio-oils considering that, on average, each dry ton of biomass produces 159.4 gallons of bio-oil^a [18].

| | · r | |
|--|-------------------------------|----------------------------|
| Description of Parameter | Near-Term Commercial Plant | Mature Commercial Plant |
| Biomass processing capacity dry pine, t/d | 400 | 2,000 |
| Biomass feedstock cost [29,30], \$/t (\$/ton) | 94-110 (85–100) | 99-132 (90–120) |
| Fixed capital investment [18], million \$ | 91 | 334 |
| Total operating costs, million USD/a [18] | 17.2 | 18.2 |
| MSP for bio-oils, \$/bbl | 78–82 | 48-56 |

^a Raw bio-oils from biomass contain 25 wt% water.

which typically contribute to catalyst poisoning and deactivation in petroleum refineries. The similarities in Brazilian whole crude and gasoil properties relative to other crude oils processed in U.S. petroleum refineries support our conclusion that the present study results and models are applicable to U.S. petroleum refining operations.

3.2. Bio-oils minimum selling price

MSP is the minimum price at which the bio-oil can be sold while covering all production costs. MSP serves as the basis for the refinery purchase cost and as a benchmark value for comparing TEA results. MSP was calculated from the methodology described in Section 2.1. Table 10 presents the results of the two scenarios for raw bio-oil production from a "near-term commercial plant" at a 400 t/d biomass processing capacity and a future "mature commercial plant" at a 2,000 t/d scale.

The average benchmark value for a 400 t/d biorefinery facility is \$80/bbl bio-oil and \$52/bbl for a 2,000 t/d facility.

Applicable data for capital, fixed operating, and variable operating costs were derived from prior work [18] up to the production of the raw filtered bio-oil, but the reference further evaluated subsequent standalone processing options. The fast pyrolysis yields were independently demonstrated by Wilcox, Gaston, and Dunning [19].

The associated uncertainties in the bio-oils MSP were derived using the sensitivity analysis completed by Jones et al. [18] and by applying

Table 11
Uncertainty analysis for raw, filtered bio-oil relative to base MSP of \$60 USD/bbl

| Source | Basis | Source Range of Uncertainty (% relative to base) | | Uncertainty (% relative Uncerta | | | |
|-------------------------|---|--|---------|---------------------------------|----------------|--|--|
| | | Minimum | Maximum | Minimum | Maximum | | |
| Jones et al. [18] | Range of uncertainty from sensitivity analysis applied to raw bio-oil MSP, \$/bbl (%) | -14.9 | +17.8 | 51 (-4.9) | 71 (+17.8%) | | |
| AACE [16] | Fixed capital investment uncertainty range applied to raw bio-oil MSP calculation, \$/bbl (%) | -11.0 | +18.3 | 53 (-11) | 71 (+18) | | |

uncertainty ranges for fixed capital investment (FCI) from the Association for the Advancement of Cost Engineering (AACE); results from both approaches are shown in Table 11 and were consistent. The range of uncertainty applied to the FCI uncertainty analysis is consistent with the AACE Class 4 cost estimates for feasibility studies [16].

3.3. Co-processing models

The co-processing models refer to Fig. 3, Step 4 and their methodology was described in Section 2.4.2. Method 1 statistical correlation-based FCC yield models were developed to assess the value of filtered, non-upgraded bio-oils that contain about 50 wt% oxygen as a feedstock to a typical commercial FCC unit. The following discussions describe how the process models were used to (1) establish a base case scenario to represent optimized FCC operations on VGO feedstocks and (2) model co-processing scenarios and identify economic incentives for co-processing relative to the base VGO scenarios.

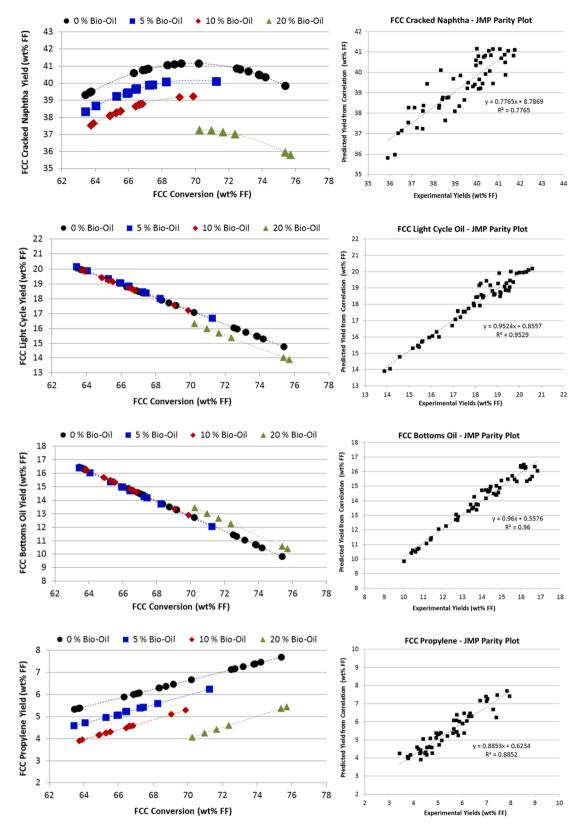


Fig. 9. Effect of the feed at different conversion severity levels on naphtha, LCO, bottoms, and propylene using Method 1 correlations (on the left). Experimental yields shown as symbols for various proportions and calculated yields are shown as dotted lines. On the right are the corresponding parity plots.

3.3.1. Method 1

To generate Fig. 9, the raw experimental data, as shown in Fig. 6, were analyzed by Method 1 statistical correlation of calculated yields as a function of (1) FCC conversion severity and (2) wt % of bio-oils in the

FCC. Fig. 9 exemplifies sets generated by the comprehensive yield model for various products and parity plots comparing calculated versus experimental data to easily assess the goodness of the fit. Fig. 9 shows the experimental and modeled yield data as a function of FCC

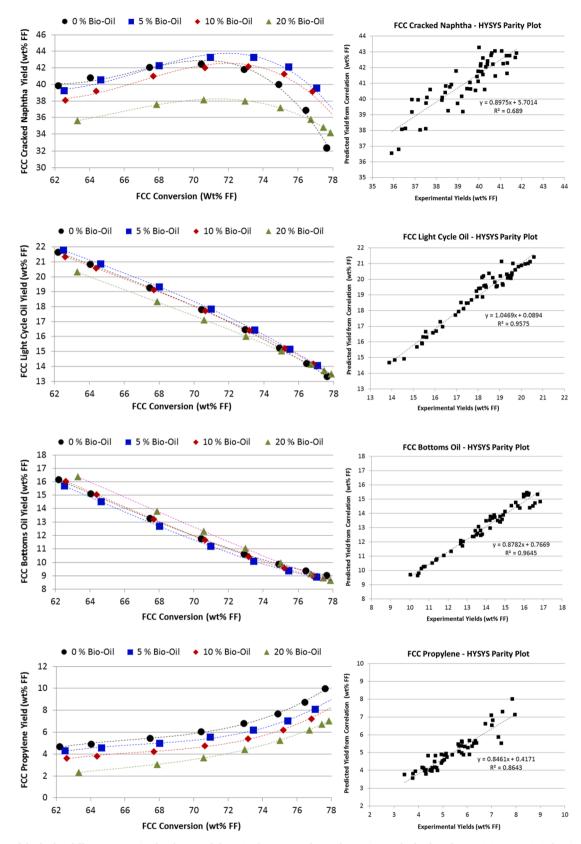
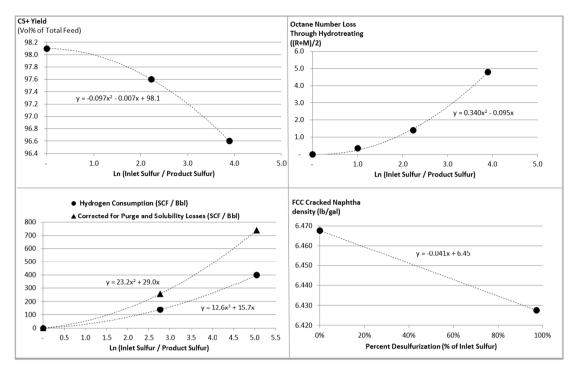


Fig. 10. Effect of the feed at different conversion levels on naphtha, LCO, bottoms, and propylene using Method 2, based on FCC Aspen HYSYS showing experimental yields (symbols for various proportions) and calculated yields as dotted lines (on the left). On the right are the corresponding parity plots.



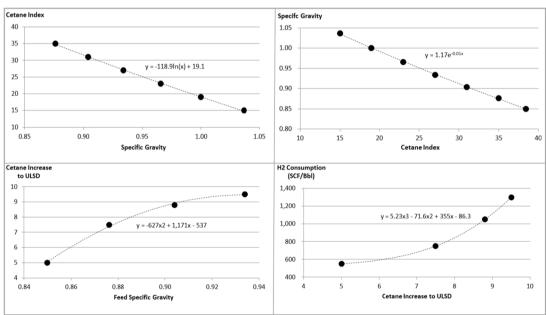


Fig. 11. Composite of FCC cracked naphtha hydrotreater correlations (top) and composite of FCC LCO to ULSD hydrotreater correlations (bottom).

conversion for cracked naphtha, light cycle oil, and bottoms oil with their corresponding parity plots. Fitted data explained 78% of the variance for naphtha and 95% for LCO and bottoms. In addition, the figure also shows an example of correlation for a single valuable product, propylene, where 96% of the fitted data variance was explained. In modeled correlations for products generated primarily by bio-oils, such as water, CO, and $\rm CO_2$, the fitted data represented 90%, 81%, and 98% of the variance, respectively. Fitted data for common products such as dry gas, LPG, and coke (excluding oxygen) had about 93% of the variance explained by the model. Some of these measurements, such as water, had higher uncertainties.

3.3.2. Method 2

Method 2, based on FCC Aspen HYSYS model results (see Section

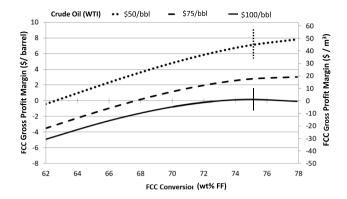
2.4.2) had similar suitability for liquid products and propylene, as observed for JMP; the data are shown in Fig. 10.

3.4. Models for product finishing operations to blendstocks

Step 5 is necessary to complete the scope of Fig. 3, as described and referenced in Section 2.5. The performance basis for the hydrotreaters of cracked naphtha and LCO are shown in Fig. 11.

3.5. Co-processing bio-oils and VGO techno-economic analysis metrics

One of the metrics used in this work was the profitability—in terms of the gross profit margin expressed in dollars per barrel of feed, as presented in Fig. 8—for refineries that purchase VGO. In Fig. 12 (top),



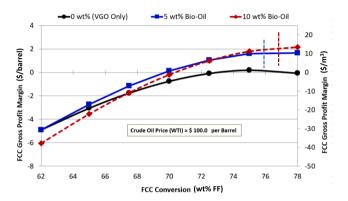


Fig. 12. (Top) FCC gross profit margins in \$/bbl for VGO processing as a function of the FCC conversion for WTI in \$/bbl: 50, 75, and 100. (Bottom) FCC gross profit margins (\$/bbl) as a function of the FCC conversion (wt %) at a fixed WTI price of \$100/bbl for VGO only, 5/95 bio-oil/VGO, and 10/90 bio-oil/VGO, illustrating statistically significant profit margin opportunities in the optimized performance region (78%).

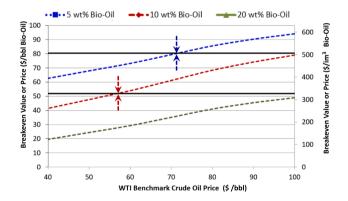


Fig. 13. Bio-oil breakeven analysis as a function of WTI price (\$/bbl). Solid black lines represent the cost or minimum selling price (MSP) of bio-oil produced at current facilities (upper) and projected 2,000 t/d facilities (lower). Sloped colored, dotted lines present the modeled breakeven values of bio-oil as FCC feedstock at various contents as a function of WTI benchmark price. The crossing points indicated by arrows show when the value to the refiner is equivalent to that of the bio-oil price the biorefiner must obtain (MSP).

FCC gross profit margins of the refinery operating with VGO only as a function of the conversion severity are shown for three benchmark crude oil prices in \$/bbl —50, 75, and 100. The modeled gross profit margins in \$/bbl are 7.0, 2.7 and 0.2, respectively, and their uncertainties are indicated in Table 8. These margins are achieved in the 75% to 78% conversion region where the FCC performance is optimized based on the experimental VGO processing data set. On the bottom of Fig. 12, the

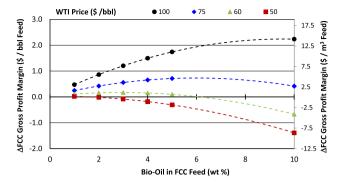


Fig. 14. FCC operating/economics curves for co-processing scenarios with biooil compared to the optimized VGO operation, or the delta of the respective gross profit margins as a function of bio-oil content in the FCC feed for four crude oil prices.

effect of bio-oil/VGO 5/95 and 10/90 wt% are shown on the low FCC gross profit margin for the \$100 \$/bbl WTI crude price scenario. The TEA results show that FCC gross profit margin increases to \$1.8–\$2.2 with bio-oil co-processing relative to VGO only profit margin of \$0.2, in the 75% to 78% optimized conversion severity region. The uncertainty analysis presented in Section 2.6 shows that at 5 wt% bio-oil the uncertainty is \pm 0.7 \$/bbl and double for twice the bio-oil content. Therefore, statistically significant economic incentives for the petroleum refinery to purchase bio-oil instead of VGO exist at \$100 \$/bbl WTI.

The breakeven price for the bio-oil as a function of the crude oil price and of the size of the pyrolysis facility capacity is another economic metric of this study (Table 10). Fig. 13 shows the impact of these variables in terms of pine chip pyrolysis processing capacity and as a function of the content of bio-oil fed with the fossil feed. The blue, red and green dotted lines represent the bio-oil breakeven values determined from TEA at 5/95, 10/90 and 20/80 bio-oil/VGO blends, respectively. The black solid lines represent the minimum selling prices (MSPs) for bio-oil production at 400 t/d (top line) and 2,000 t/d (bottom line) scales. If a point on a dotted line, defined by bio-oil percent in FCC feed and FCC conversion, is greater than the corresponding point on a solid line at constant WTI price, defined by pyrolysis production scale, then there is potential economic incentive for the refinery to co-process biooil in the FCC. The blue arrows at \$72/bbl, the intersection of the black line for the near-term commercial biomass processing to bio-oil with the blue dashed line for 5/95 bio-oil/VGO co-processing, is the breakeven price for the supplier of bio-oil or the value for the refiner compared to purchasing VGO in the spot market. Therefore, above crude prices of \$72 bbl, there are likely positive economics for bio-oil co-processing at 5/95 bio-oil/ VGO. Similarly, for 10/90 bio-oil/VGO we show the modeled projection of a developing fivefold increased size would put the breakeven value at \$55/bbl, as indicated by the red arrows at the intersection of the figure. Therefore, increasing pyrolysis scale to 2,000 t/d would enable positive co-processing economics for all 5/95 bio-oil/ VGO scenarios and 10/90 scenarios above \$55/bbl WTI crude prices. In all cases, lower biomass feedstock prices could lower the breakeven point by lowering the solid black lines in the figure.

The results from Fig. 13 showed that bio-oil co-processing may be economically attractive without policy considerations and crude oil prices above \$55/bbl (WTI) if pyrolysis liquids are produced by a mature biorefinery with a scale of 2,000 t/d and sold to petroleum refiners at approximately \$55/bbl for 10/90 bio-oil/VGO content. At this scale, TEA figures for bio-oil MSP range from \$48 to \$56/bbl. A smaller-scale biorefinery of 400 t/d, producing bio-oils for FCC units at approximately \$80/bbl, can be economically attractive with crude oil prices above \$70/bbl (WTI) with a co-processing ratio of 5/95 bio-oil/VGO. As the figure shows, there are no 20/80 bio-oil/VGO scenarios identified in the current data sets and models that are likely to provide positive co-

processing economics. However, technology improvements in pyrolysis oil production, co-processing catalysis and equipment design, and feedstock cost reduction can contribute to increasing the potential economic value of bio-oil co-processing.

The final example of analysis results in Fig. 14 shows the modeled coprocessing economics curves as a function of the bio-oil content in the FCC feed for several crude oil prices. Petroleum refiners can use economics curves like these to assess the economic incentives of coprocessing when fossil markets fluctuate. The curves identify ranges of profitability potential for different market scenarios. For example, when crude prices are high at around \$100/bbl, the petroleum refiner has incentive to increase bio-oil purchases to approximately 10 wt% of the FCC processing capacity. However, when crude prices are at around \$75/bbl, the petroleum refiner should target 5-6 wt% bio-oil in FCC feed to maximize profit. At \$60/bbl, there is an indication of small profitability potential in the 2/98 to 5/95 bio-oil/VGO range, which coincides within the uncertainties of the analysis with the breakeven value for bio-oil of Fig. 13.

4. Conclusions

Based on extensive published data that established the technical feasibility of co-processing oxygen-rich, minimally processed wood biooils with VGO, this work provides new modeling tools for co-processing fluid catalytic cracking unit operations for the case of refineries with spare FCC capacity or the means to re-optimize refinery processing strategy to enable FCC co-processing opportunities. We created an analysis approach to calibrate AspenTech's FCC HYSYS simulation tools with experimental data and utilize the models to estimate bio-oil coprocessing yield shifts with the introduction of oxygenated feedstocks and provide a significant data set to facilitate continued studies ongoing worldwide (see Appendix). In addition, we developed a statistical model (JMP) using only experimental data, which enabled the assessment of uncertainties through a pooled standard deviation analysis and validate the results of the HYSYS yield model. We generated a simplified model of the refinery based on public data of spot prices of crude oil, VGO, and major refinery products so as not to rely on unpublished, proprietary data, which cannot be published in open literature. Combined with the techno-economic analysis of bio-oils production and their uncertainties, we demonstrated statistically significant economic feasibility of pine bio-oils co-processing in commercial FCC unit operations. Based on the integration of TEA and experimental co-processing data from Petrobras, we have demonstrated that bio-oils/VGO co-processing may be economically attractive for petroleum refiners at benchmark (WTI) crude prices of \$70/bbl for co-processing up to 5/95 wt% bio-oil/VGO if the bio-oil is produced from a near-term commercial 400 t/d wood facility and dry wood costs \$99/t (\$90/ton). We modeled larger facility at 2,000 t/d scale processing wood at a cost of \$116/t (\$105/ton) and found the breakeven value for 10 wt% bio-oil at benchmark WTI of \$55/ bbl. No policy considerations were analyzed.

The study provides analysis tools that indicate economic potential and opportunities for optimizing FCC operations for bio-oil co-processing. Although conducted with Brazilian VGO, the study's results are applicable to U.S. and other crude oils.

The results obtained indicate that a few percent-level penetration of bio-oils in FCCs could be achieved with feedstocks that have lower prices than pine wood chips in the United States, as the wood cost contributes significantly to the bio-oil price to refiners.

The co-processing experiments and analyses completed herein have only begun to explore the possibilities of establishing a supply chain for transportation fuels from both fossil and renewable sources. Continued research and development in bio-oil production technologies at 400 t/d or higher scales coupled with simultaneous efforts in petroleum corefining technology development will serve to improve the economic incentives for co-processing across the entire supply chain from biomass to finished, co-produced fossil and renewable fuels.

CRediT authorship contribution statement

Michael Talmadge: Conceptualization, Methodology, Formal analysis, Writing - original draft, Writing - review & editing. Christopher Kinchin: Methodology, Formal analysis. Helena Li Chum: Conceptualization, Formal analysis, Writing - original draft, Writing - review & editing. Andrea Rezende Pinho: Conceptualization, Investigation, Writing - review & editing. Mary Biddy: Investigation, Writing - review & editing. Marlon B.B. Almeida: Conceptualization, Investigation, Writing - review & editing. Luiz Carlos Casavechia: Investigation.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2020.119960.

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