# Executive Summary Report

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from the submitted manuscript to publication in Fuel (peer review phase)

**"Techno-economic analysis for co-processing fast pyrolysis liquid with vacuum gasoil in FCC units for second-generation biofuel production"**

- NREL conducted a techno-economic analysis and provided new modeling tools for co-processing in fluid catalytic cracking (FCC) unit operations using the case of refineries with spare FCC capacity that purchase vacuum gas oils (VGO) (or gasoil) to establish a value for bio-oil

- One of the models used an Aspen HYSYS FCC simulation to predict FCC yields and qualities of products based on calibration cases. The calibration cases were tuned to match experimental data and then used to extrapolate to different operating scenarios to estimate an economically optimal point for co-processing (often >76% conversion severity)

- NREL generated a pseudo-VGO HYSYS model with the carbon and hydrogen remaining after oxygen balance and allocations to CO, $CO_2$ and $H_2O$ added to the mostly hydrocarbon model. This information will facilitate bio-oils and VGO simulations, process design, performance modelling, and optimization necessary for commercial predictability of performance. Refinements in the methodology continue at NREL

- The model data from 54 demonstration trials with high quality data produced by Petrobras during the FCC co-processing of Ensyn and BTG products at biocrude substitutions of 5, 10 and 20% (weight)

- The experimental data were obtained at the Petrobras's SIX demonstration-scale 200 kg/h fluid catalytic cracking unit (FCC) in São Mateus do Sul, Brazil. Mass balance closures of 96% to 100% and high-quality analytical data for fractions and main products enabled model development

- Brazilian VGO feedstocks were used in the study and the similarities in Brazilian whole crude and gasoil properties, relative to other crude oils and gasoils used in U.S. petroleum refineries support our conclusion that the present study results and models are applicable to U.S. petroleum refining operations

- The segregation between the bio-oil and VGO streams and their separate injection into different axial FCC reactor positions, made it possible for these two feeds to take advantage of different reactor conditions and obtain an optimum feed dispersion through the nozzles

- A summary of the Aspen HYSYS simulation in terms of yields of the major products of FCC bio-oil co-processing as a function of conversion severity conducted by the National Renewable Energy Laboratory (NREL) and Petrobras. Figure 1 shows data (as points) and simulation (as dashed lines) for (a) naphtha (gasoline precursor), (b) light cycle oil (diesel precursor), and (c) coke on the left and goodness data fit to the model on the right

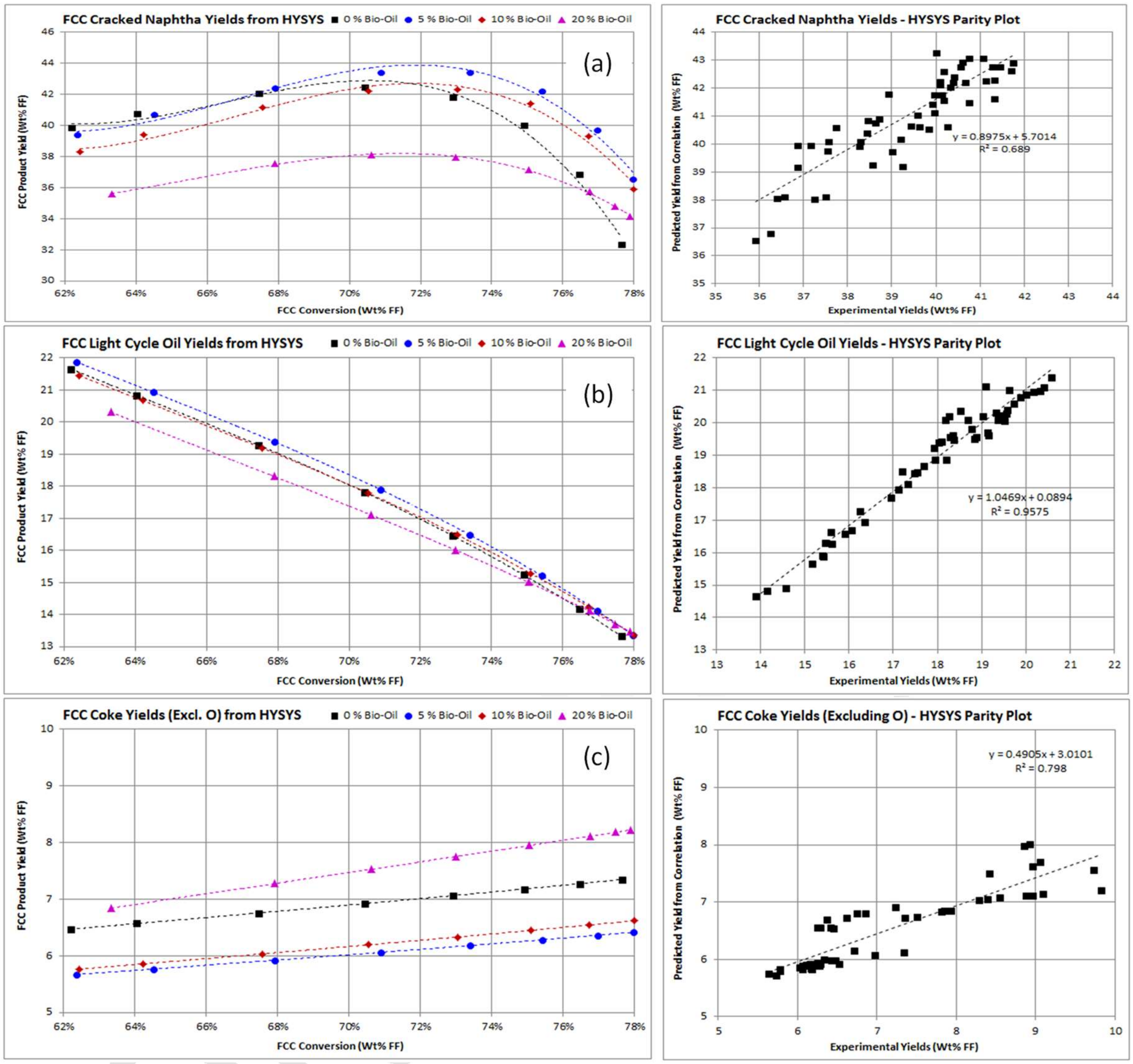



Figure 1. FCC Product Yields (wt%) as a function of conversion severity (wt%) using fresh feed (FF) of co-fed VGO and Bio-oil (wt%) for (a) naphtha (gasoline precursor), (b) light cycle oil (diesel precursor), and (c) coke. [FF does not include recycle of gas/catalyst]

- Naphtha yields, at conversions higher than 70%, were higher for the 5/95 and 10/95 bio-oil/VGO wt% than VGO 100 wt%. *(note: naphtha is the gasoline cut from the FCC)*
- For light cycle oil yields, the 5/95 bio-oil/VGO wt% are higher than just VGO, which was very similar to the 10/90 bio-oil wt%, possibly within the uncertainties of the data and model.
- The coke yields (which exclude oxygen) are lower for 5/95 and 10/90 bio-oil/VGO wt% throughout the conversion severities analyzed. The 20/80 bio-oil/VGO wt% exhibited higher coke yields than the VGO alone curves.

- The results summarized used the first published paper by NREL and Petrobras with Ensyn bio-oils [1 (2017)], and the Petrobras published data [2 (2015)] with BTG bio-oil produced in a small pilot plant conducted without the now presented modeling efforts [3].
- The lower coke results at low contents of bio-oil, as demonstrated in the Petrobras trials (i.e., in the large FCC that was used to test the performance of the catalysts at Petrobras' operating facilities) have not been apparent in bench-scale experimentation using small laboratory catalytic crackers. This is largely due to plugging of the feed system by coked biomass in bench-scale systems [4].

## Supplemental 1 information:

### 1. Bio-oils used in the FCC co-processing trials

In this report, we used experimental FCC co-processing trial data from a previous publication, using Ensyn commercial bio-oils [1], which confirmed and expanded prior data using the same demonstration-scale FCC unit to co-process bio-oils produced at a BTG pilot-scale biomass pyrolysis unit [2]. Combining both data sets, we analyzed 54 experiments that had mass balances ranging from 96% to 100%. The following Table compares capacities of the bio-oil processing plants and values of some analytical properties of these two whole un-enriched fast pyrolysis oils and other well-characterized bio-oils.

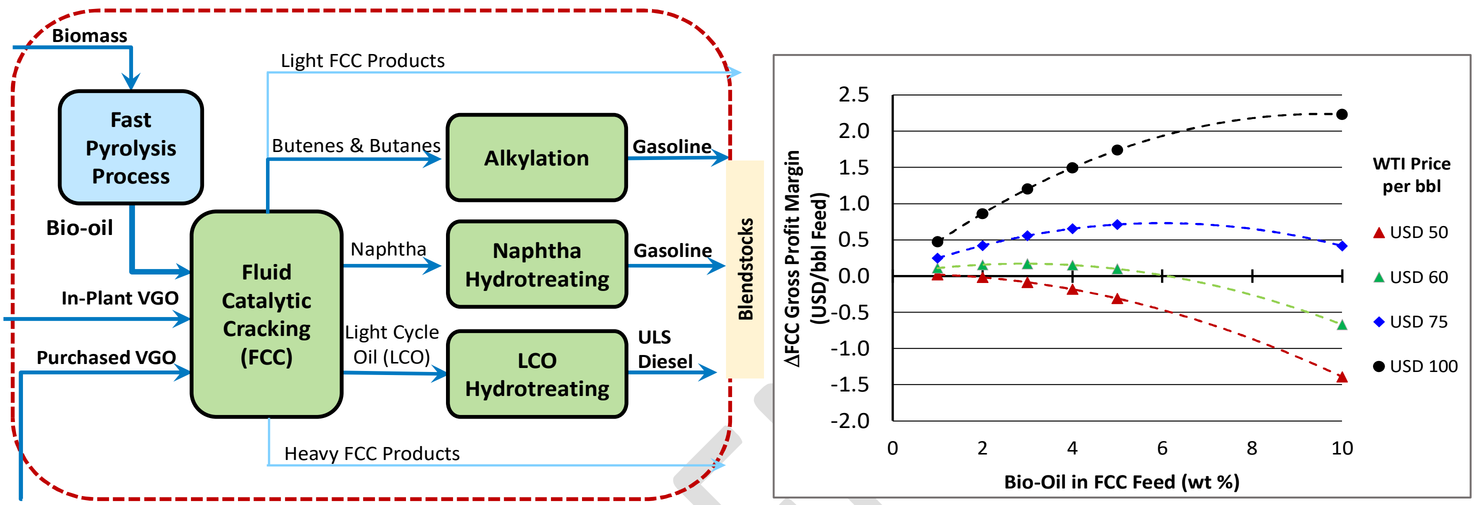
Comparison of pine-derived bio-oil properties at various processing capacities

| Bio-oil property | Commercial (2500-4200 kg/h)[d] | Demonstration (25 kg/h)[e] | Pilot 5-25kg/h (5-25 kg/h) | Fast Pyrolysis Design Report (avge properties used for techno-economic study |
|---|---|---|---|---|
| Density (g/cm3, 20C) | 1.20 | 1.21 | 1.19 | 1.20 |
| Elemental Analysis[a] (wt % wet) | | | | |
| Carbon | 41.8 | 42.4 | 41.6 | 42.4 |
| Hydrogen | 7.5 | 6.5 | 7.9 | 7.7 |
| Sulfur | <0.3 | <0.1 | <0.1 | 0.0 |
| Oxygen | 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 | 0.17 | 0.17 | 0.17 |
| Acidity (mg KOH/g)[b] | 128 | 128 | 128 | 128 |
| Viscosity | 6.7 | 6.7 | 6.7 | 6.7 |
| Raw bio-oil yield(wt %) | n.a. | n.a. | n.a. | n.a. |

a. Elemental analyses corrected for consistent water content of 25 %
b. Acidity measured by the total acid number method.
c. not available
d. 60–100 ton/d (dry) Ensyn
e. 0.6 ton/day – BTG

**2. Graphical summary of the submitted paper below [3].**

**Graphical Summary**




**VGO – Vacuum Gas Oil**

## Highlights:

- Bio-oil co-processing in existing FCC units is a potential low-cost pathway to increase renewable carbon content in transportation fuels.
- Statistical FCC yield models developed with JMP and technoeconomic tools used to estimate fuel blendstock costs and uncertainties.
- New Aspen HYSYS FCC model for co-processing scenarios with bio-oil oxygenated compounds and VGO.
- Conditions identified to match bio-oil supply chain with US average FCC capacity to provide up to 5-wt% bio-oil to refiners near-term.
- Co-processing at 10-wt% may be economically attractive with pyrolysis process scaled-up or multiple pyrolysis plants.

**Supplemental information (attached) 2: Detailed yields of additional products**

Heavy FCC oils, gases (CO, CO2, H2O) and light hydrocarbons including propylene.

## References:

[1] de Rezende Pinho, A., de Almeida, M. B., Mendes, F. L., Casavechia, L. C., Talmadge, M. S., Kinchin, C. M., & Chum, H. L. (2017). Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production. *Fuel*, *188*, 462–473.

[2] Pinho AR, 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.

[3] Submitted to publication in Fuel (and published in March 2021):
"Techno-economic analysis for co-processing fast pyrolysis liquid with vacuum gasoil in FCC units for second-generation biofuel production"
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[4] 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;16:407–53

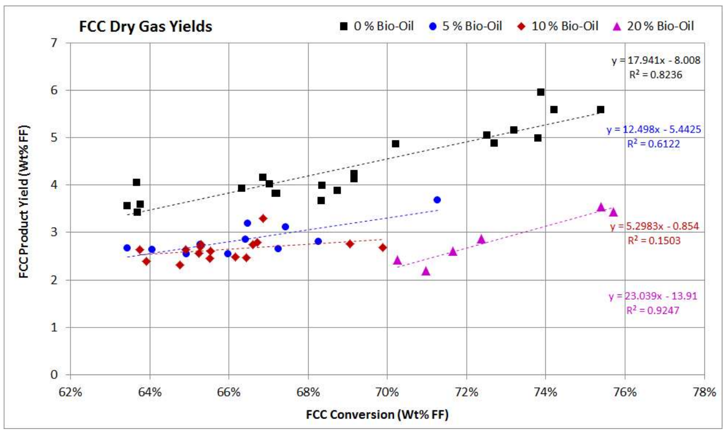
## Supplemental 2 information:

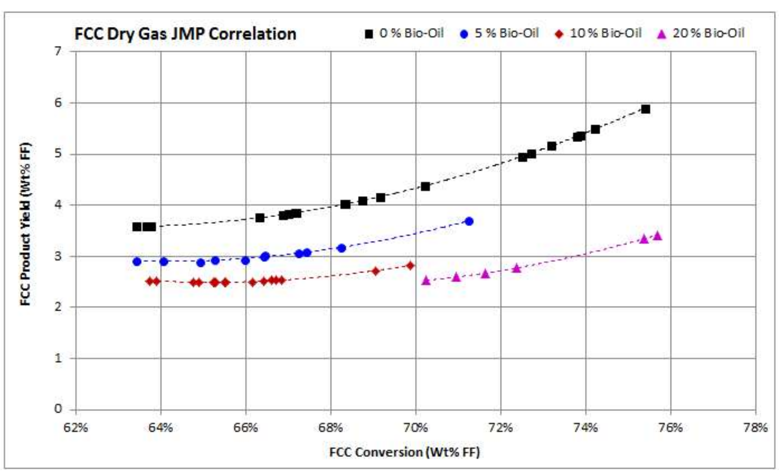
## Experimental and Modeled Yields for Additional Products Measured

Experimental data comparisons for FCC component yields with those obtained using JMP and HYSYS model predictions are presented as composites of groups of five figures each of Figures A-1x where x corresponds to the specific group of FCC intermediates as follows: (a) dry gases; (b) propylene; (c) liquefied petroleum gas C3/C4 excluding propylene); (d) bottoms oil; (e) water; (f) CO; and (g) $CO_2$.

### Figure A-1a

***FCC Dry Gas ($C_2$-) Yields***



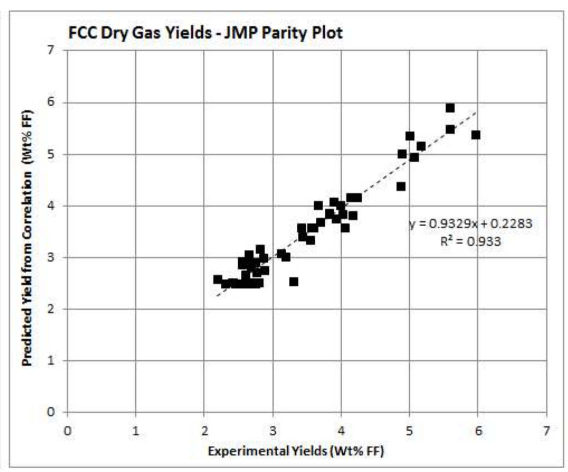
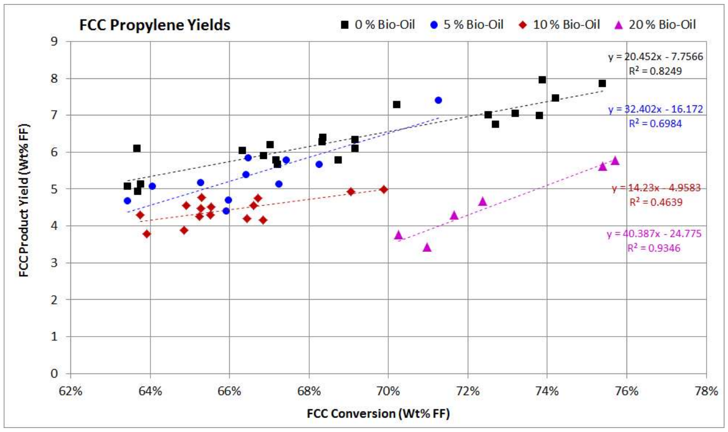
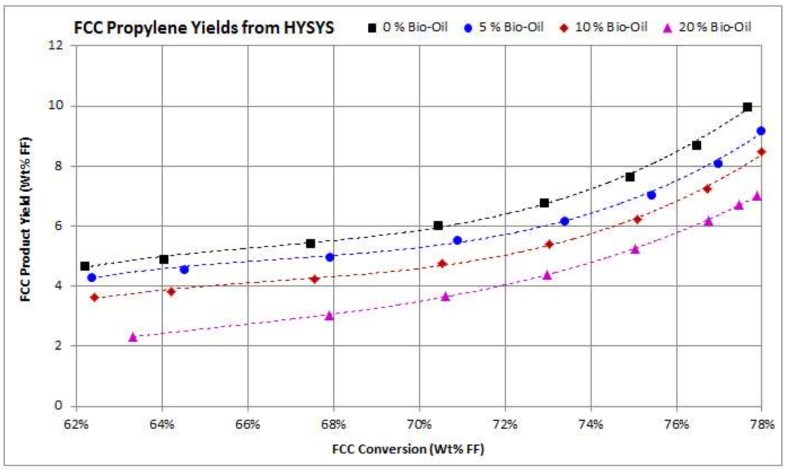



**Figure A-1b**

***FCC Propylene Yields***



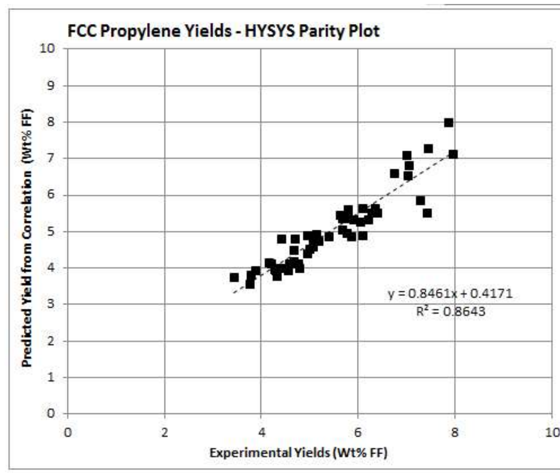
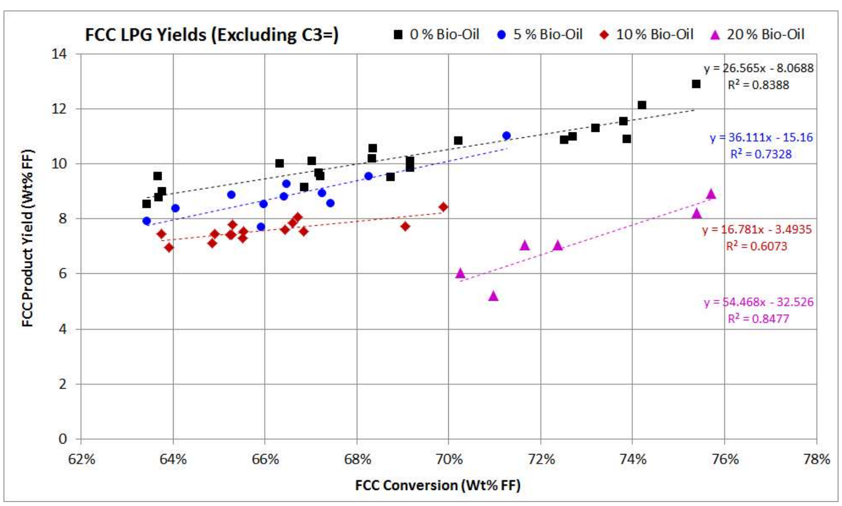
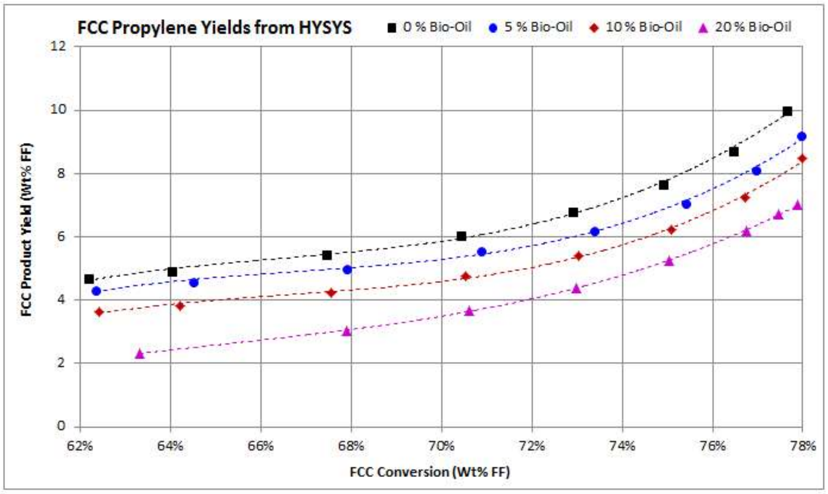
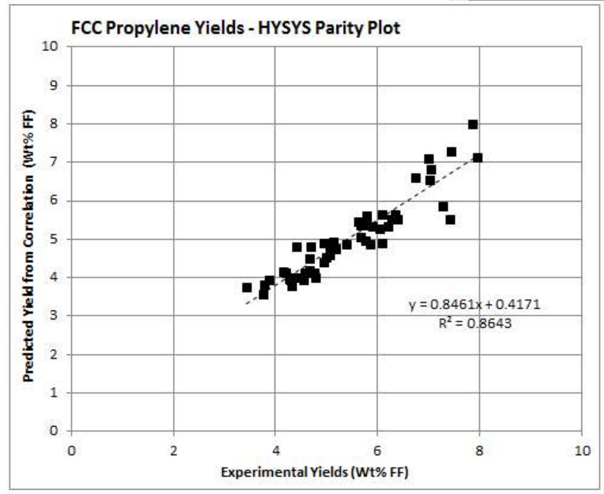




**Figure A-1c**

***FCC Liquefied Petroleum Gas ($C_3$/$C_4$ Excluding Propylene) Yields***

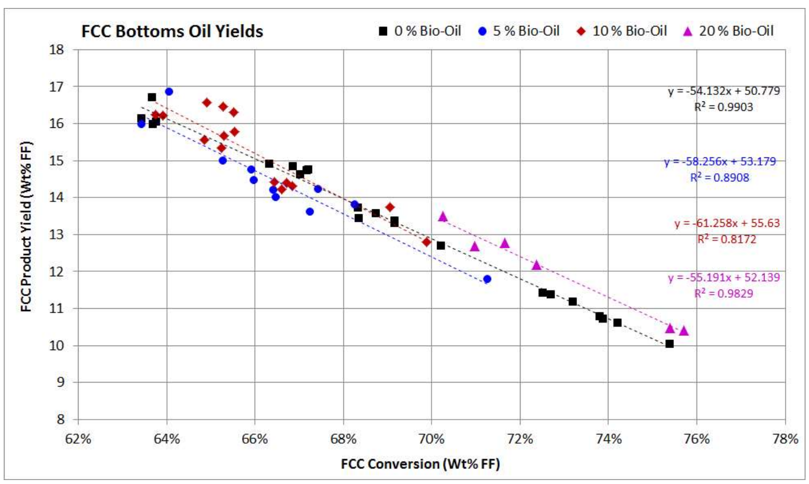


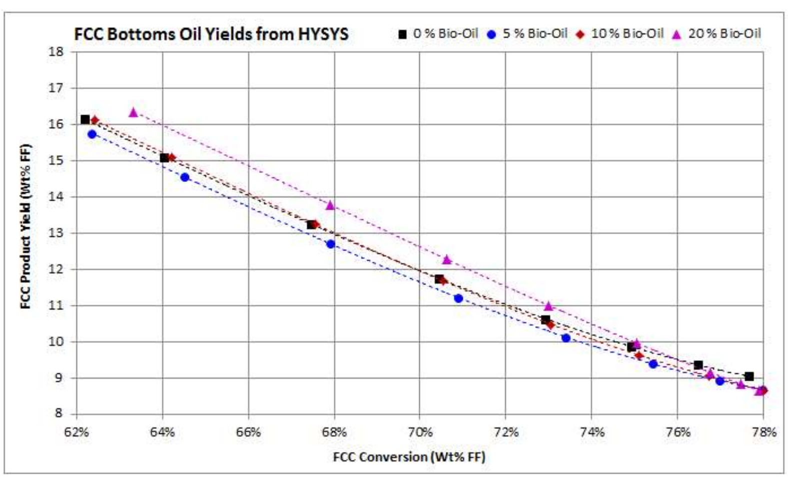


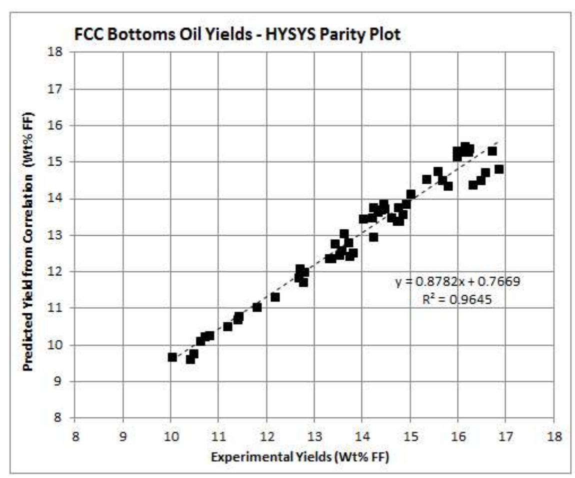




## Figure A-1d

## *FCC Bottoms Oil Yields*

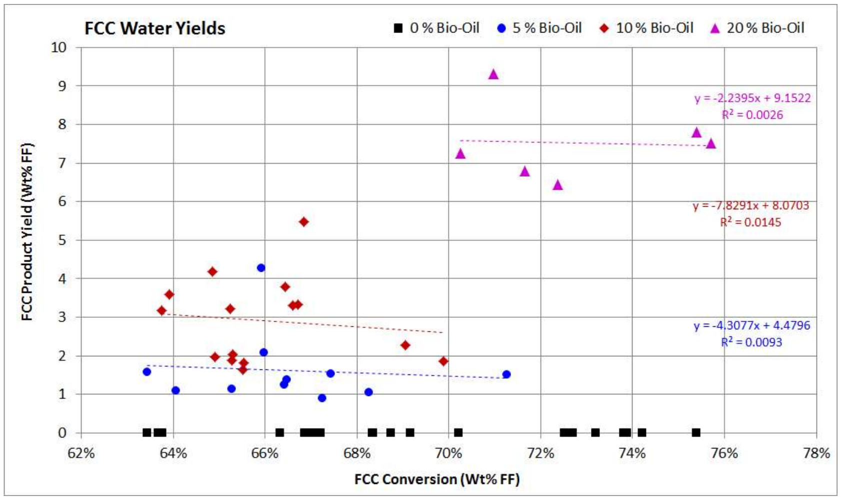


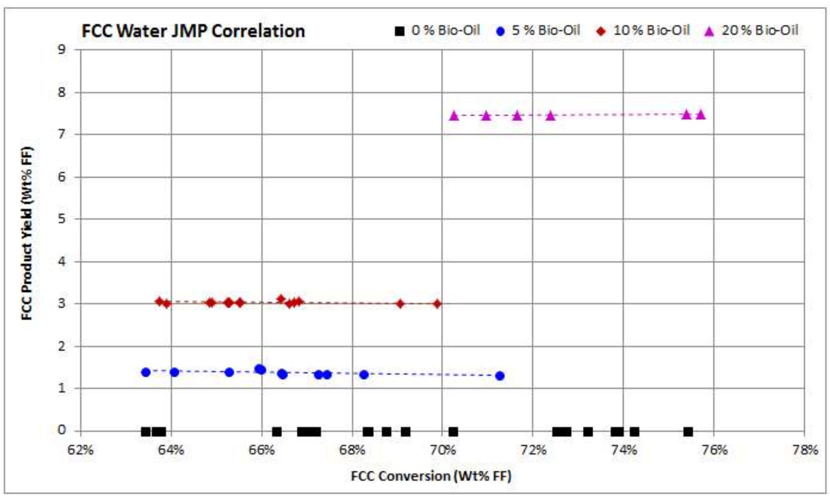



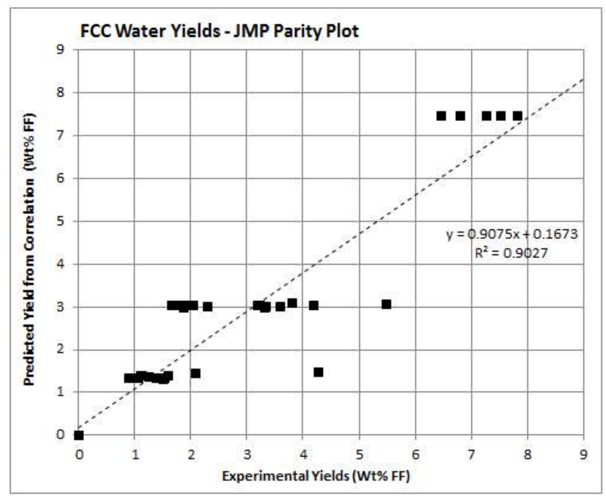



## Figure A-1e

### *FCC Water Yields*



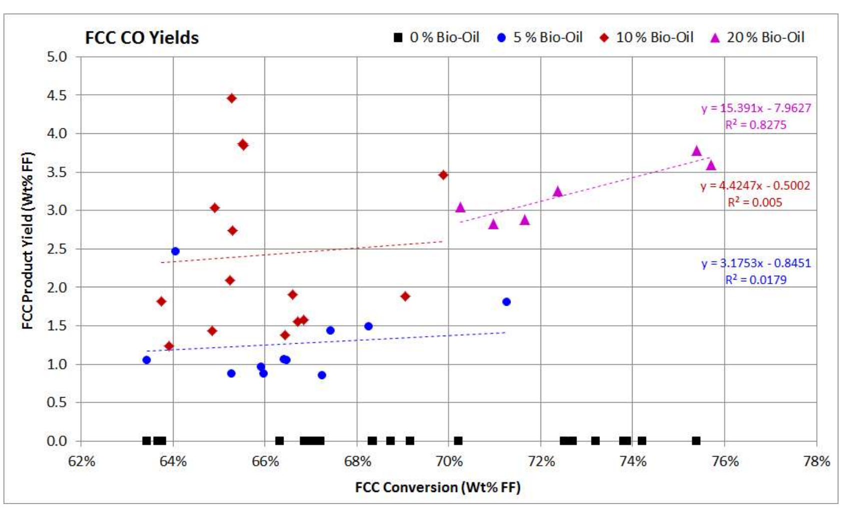



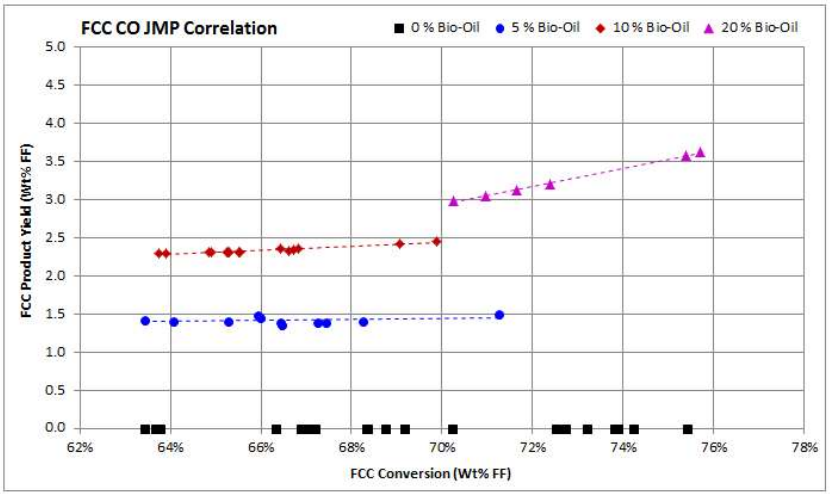



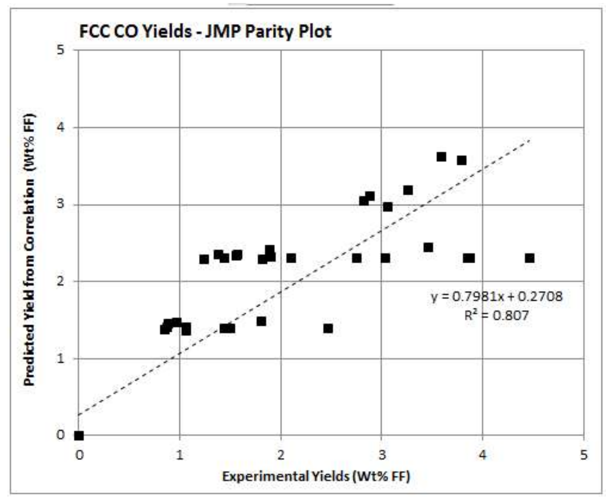

*Note: The correlations developed from the JMP software for water, CO, and $CO_2$ yields from the FCC reactor were applied to the mass balance calculations for the modeling approach with Aspen HYSYS FCC.*

## Figure A-1f

### *FCC CO Yields*



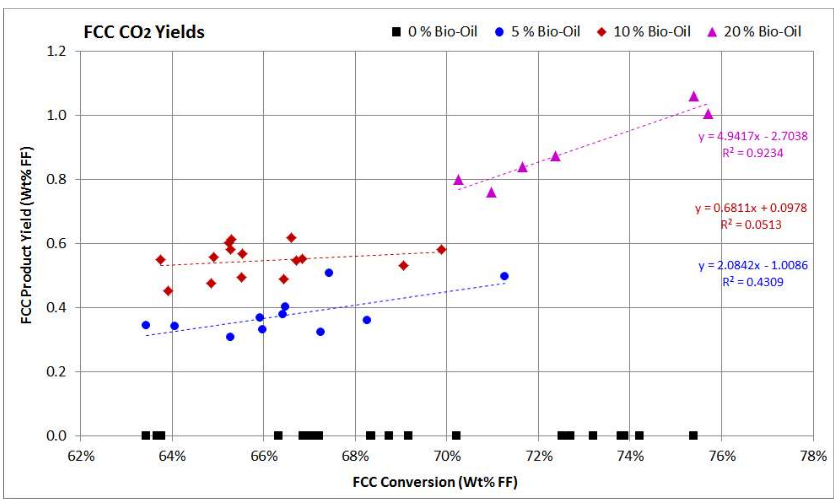


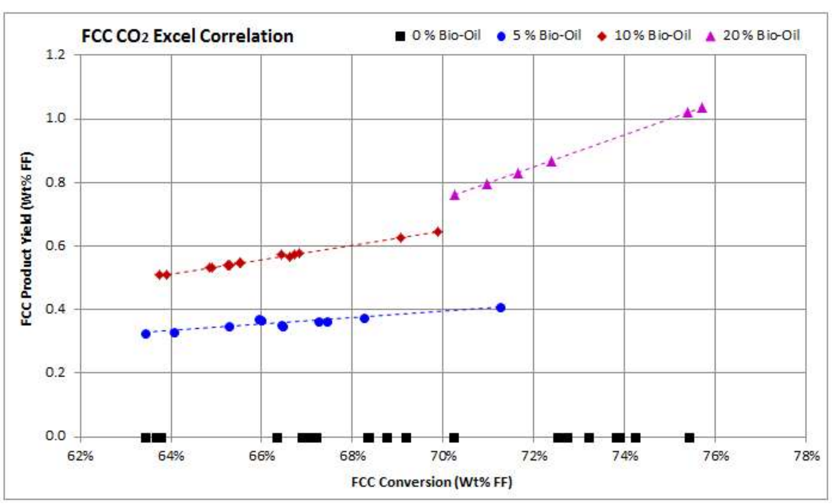



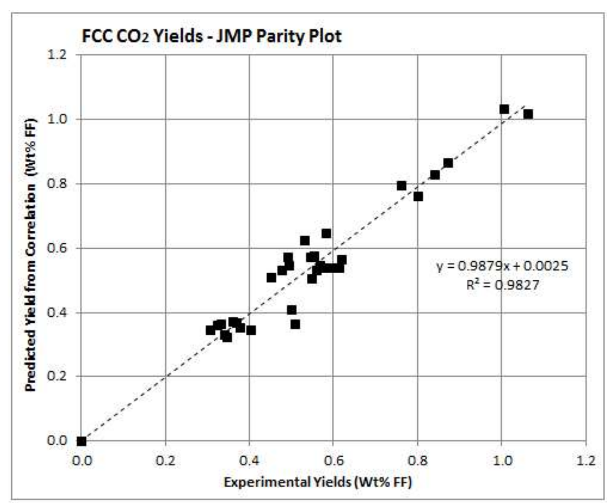

*Note: The correlations developed from the JMP software for water, CO, and $CO_2$ yields from the FCC reactor were applied to the mass balance calculations for the modeling approach with Aspen HYSYS FCC.*

## Figure A-1g

### *FCC $CO_2$ Yields*




*Note: The correlations developed from the JMP software for water, CO, and $CO_2$ yields from the FCC reactor were applied to the mass balance calculations for the modeling approach with Aspen HYSYS FCC.*

## References:


[5] de Rezende Pinho, A., de Almeida, M. B., Mendes, F. L., Casavechia, L. C., Talmadge, M. S., Kinchin, C. M., & Chum, H. L. (2017). Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production. *Fuel*, *188*, 462–473.

[6] Talmadge, M., Chum, H., Kinchin, C., Zhang, Y., Biddy, M., de Rezende Pinho, A., de Almeida, M. B. B., Mendes, F. L., Casavechia, L. C., & Freel, B. (2016). Analysis for co-processing fast pyrolysis oil with VGO in FCC units for second generation fuel production. *TCS—Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products, Chapel Hill, NC*.