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Renewable product allocation methods assessed for FCC co-processing of pyrolysis oil

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Overview of Analysis Scope

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Petrobras "SIX" data for co-processing bio-oil with VGO from crude oil

Feedstock, intermediate and product pricing basis as a function of crude benchmark price

OPIS an IHS Markit company

Capital and operating cost basis for FCC co-processing

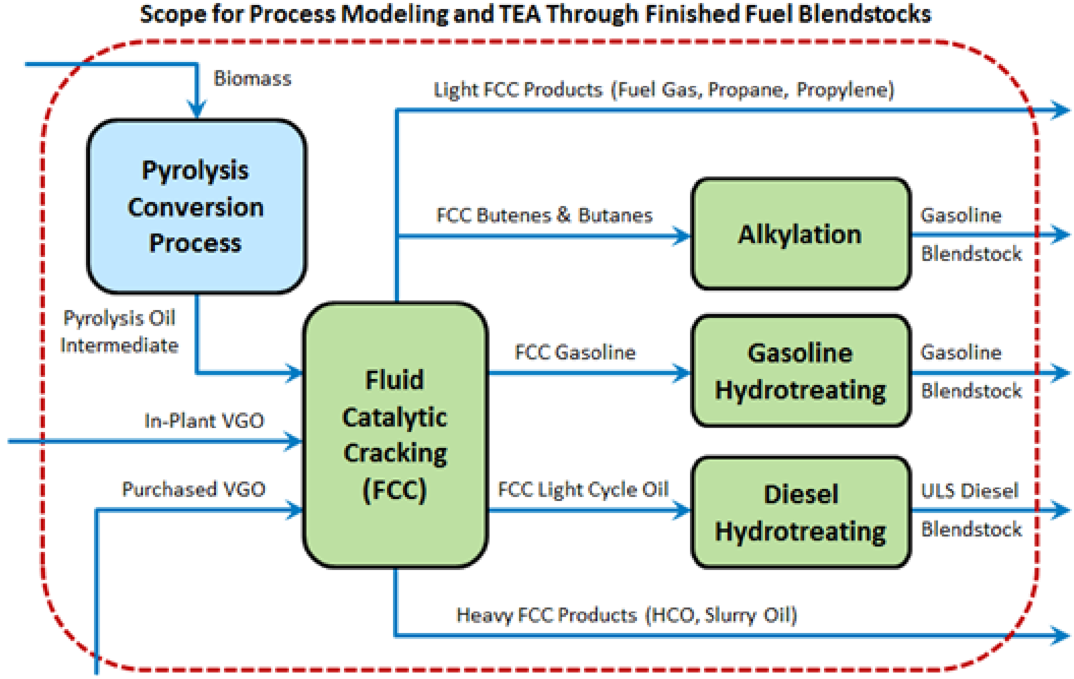
Models developed from Petrobras "SIX" data for FCC operations

aspentech Aspen HYSYS

jmp

Models for hydrotreating and alkylation based on literature

Modeling and TEA for Pyrolysis Oil Co-Processing Scenarios



Overview of Fluid Catalytic Cracking (FCC)

PFD Source: CEP, May 2014

FCC Conversion = 100 – LCO – Bottoms

U.S. FCC Capacity

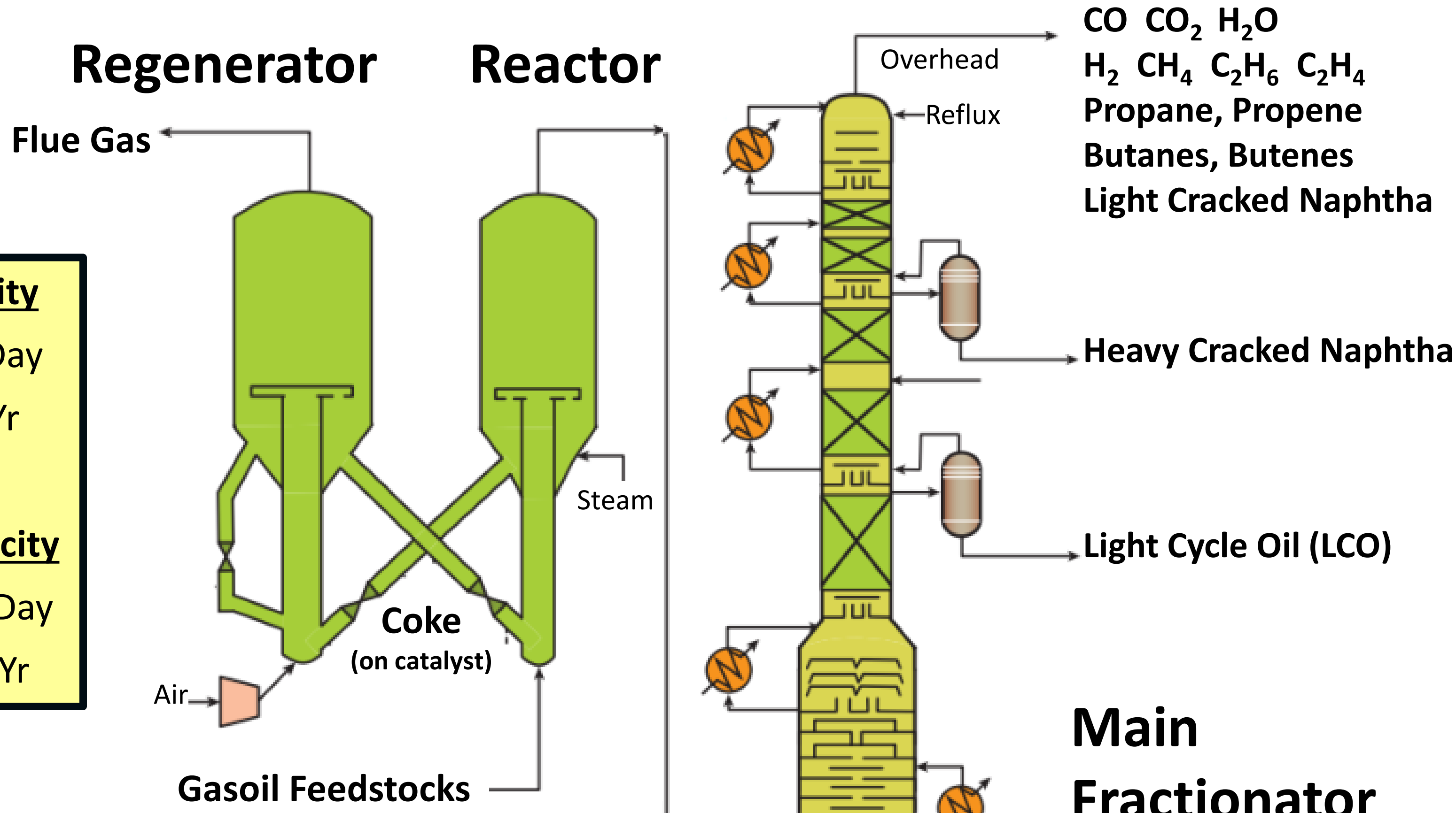
6 MM Barrels/Day

92 B Gallons/Yr

Global FCC Capacity

15 MM Barrels/Day

220 B Gallons/Yr



Petrobras Vacuum Gas Oil (VGO)	
Specific Gravity	0.94
SimDist 10% Boiling Pt.	630 F
SimDist 90% Boiling Pt.	1,050 F

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Assessed Renewable Product Allocation Methods

Carbon-14 Analysis by ASTM D6866-16

Based on C-14 results from NREL-Petrobras CRADA and additional data points from Petrobras literature using test method ASTM D6866-16 (B). This method allocates mass of renewable carbon percent over total carbon (fossil and bio).

% Bio-Products = Bio-C by ASTM D6866 -16

Carbon Balance Based on CO and CO_2 Yields

Based on subtracting the carbon losses to CO and CO2 from the total renewable carbon in pyrolysis oil and allocating the difference across the distribution of carbon in FCC products.

$$\%\ \text{Bio-Products} = \frac{\text{Bio-C in Feed} - \text{C in CO/CO}_2}{\text{Total C in FCC Products}} * 100$$

Mass Balance Based on Observed FCC Liquid Products Yields

Based on observed yields from the experimental data assuming that yields from VGO remain constant. In addition to the product-carbon from the pyrolysis oil, this method allocates VGO-carbon in products that were not present in VGO processing.

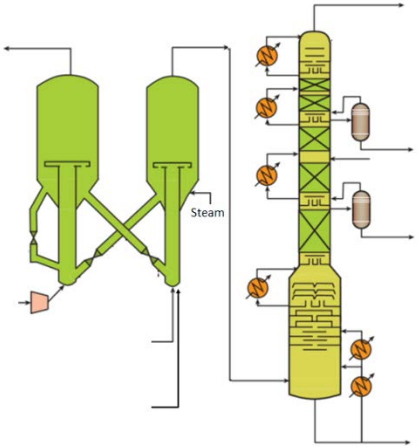
Py-Oil Liquid Product Yield = Overall Yield – (VGO-Only Yield * VGO%)

$$\%\ \text{Bio-Products} = \frac{\text{Py-Oil Liquid Product Yield}}{\text{Overall Liquid Product Yield}} * 100$$

Carbon-14 and FCC Mass Balance Examples

Note: Carbon balance examples represent rounded yield approximations from experiments and models from the NREL-Petrobras CRADA for illustrative purposes. Full analysis details are presented in in-progress manuscript.

Feed Carbon		
	VGO Only	5-wt% Py-Oil
Fossil	1000	960
Bio		25
Total	1000	985



- Carbon-14 does not tell the "whole story" and does not properly account for full GHG reduction benefit
- FCCs are equipped to perform mass and elemental balances to continuously track "renewable products" at minimal cost
- In absence of policy credits, refiners will assess co-processing opportunities and economics per mass balance

PFD Source: CEP, May 2014

Carbon-14 per ASTM D6866-16

Gases + Coke		
	VGO Only	5-wt% Py-Oil
Fossil	145	128
Bio		17
Total	145	145

Liquid Products		
	VGO Only	5-wt% Py-Oil
Fossil	855	832
Bio		8
Total	855	840

C-Efficiency		
Fossil	85.5%	86.7%
Bio		32.0%

C-Balance Based on $CO + CO_2$ Yields

Gases + Coke		
	VGO Only	5-wt% Py-Oil
Fossil	145	136
Bio		9
Total	145	145

Liquid Products		
	VGO Only	5-wt% Py-Oil
Fossil	855	824
Bio		16
Total	855	840

C-Efficiency		
Fossil	85.5%	85.8%
Bio		64.0%

FCC Yields Relative to VGO-Only

Gases + Coke		
	VGO Only	5-wt% Py-Oil
Fossil	145	139
Bio		6
Total	145	145

Liquid Products		
	VGO Only	5-wt% Py-Oil
Fossil	855	821
Bio		19
Total	855	840

C-Efficiency		
Fossil	85.5%	85.5%
Bio		78.0%

Uncertainty in Carbon-14 ASTM Method

"ASTM D6866 cites an uncertainty of ±3% (absolute) on each % biogenic carbon result."

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BETA

Biobased and Biogenic Carbon Testing Laboratory

ISO/IEC 17025:2005 Accredited

Report of % Biogenic Carbon Content Analysis: ASTM D6866-16 Method B(AMS)

Explanation of Results

ASTM D6866-16 cites the definition of biogenic as containing carbon (organic and inorganic) of renewable origin like agricultural, plant, animal, fungi, microorganisms, macro-organisms, marine, or forestry materials. "Renewable" is defined as being readily replaced and of non-fossil origin, specifically not of petroleum origin. Therefore, % biogenic carbon testing results most commonly indicate the amount of non fossil derived carbon present. It is calculated and reported as the percentage renewable carbon present relative to total carbon (TC) present.

Two methods of analysis are described in ASTM D6866-16 - Method B (AMS) and Method C (Liquid Scintillation Counting (LSC). Method B is the most accurate and precise and was used to produce this result. The methods determine % biogenic carbon content using radiocarbon (aka C14, carbon-14, 14C). The C14 signature is obtained relative to modern references. If the signature is the same as CO2 in the air today, the material is 100 % biogenic carbon, indicating all the carbon is from renewable sources and no petrochemical or other fossil carbon is present. If the signature is zero, the product is 0 % biogenic carbon and contains only petrochemical or other fossil carbon. Values between 0% and 100% indicate a mixture of renewable and fossil carbon.

The analytical term for the C14 signature is percent modern carbon (pMC) and will typically have a cited error of 0.1 – 0.4 pMC (1 RSD) using Method B. Percent modern carbon is the direct measure of the product's C14 signature to the C14 signature of modern references. The modern reference used was NIST-4990C with a C14 signature approximating CO2 in the air in AD 1950. AD 1950 is chosen due to the "BOMB CARBON EFFECT". This effect is a consequence of atmospheric thermonuclear weapons testing between 1952 and 1963. During this period, the 14CO2 content in the air increased by 90%. This means that a plant living in 1963 would measure about 190 pMC. Since the signing of a test ban treaty in 1963, this signature declined to about 140 pMC by 1975, 120 pMC by 1985, and 102 pMC by 2015. For example, to obtain the % biogenic carbon content of a product relative to living biomass in 2015, the pMC value needs to be divided by 1.02. ASTM D6866-16 cites a constant decline in this value of 0.5 pMC per year and provides requisite values to be used according to the year of measurement. The adjustment factor is termed "REF".

The consequence of bomb carbon is that the accuracy of the % biogenic carbon content will depend on how well REF relates to when the biogenic material in the product was last part of a respiring or metabolizing system. The most accurate results will be derived using biogenic material from short-lived material of very recent death such as corn stover, switch grass, sugar cane bagasse, coconut husks, flowers, bushes, branches, leaves, etc. Accuracy is reduced in materials made from wood contained within tree rings. The rings within trees each represent the previous growth season with the previous year's 14CO2 signature. The center most ring of a tree living today but planted in 1963 would be about 190 pMC whereas the outermost ring/bark would be the present-day air pMC (e.g. 102 in 2015). If this tree is harvested and used in manufacturing a biogenic product, the % biogenic carbon of the product will depend on where the carbon came from within the tree. ASTM D6866-16 cites to use average values of past carbon pMC for REF when values greater than 100 pMC are measured. For more details, the Standard can be purchased from the ASTM International website (www.astm.org).

ASTM D6866-16 also cites requirements for materials of known aquatic origin and options for analyzing materials for which a single C14 measurement cannot produce a % biogenic carbon content value (complex products). Also, reporting requirements are cited.

The result provided in this report is unique to the analyzed material and is reported using the labeling provided with the sample. Although analytical precision is typically 0.1 to 0.4 pMC, ASTM D6866 cites an uncertainty of +/- 3 % (absolute) on each % biogenic carbon result. The reported % biogenic carbon only relates to carbon source, not mass source.

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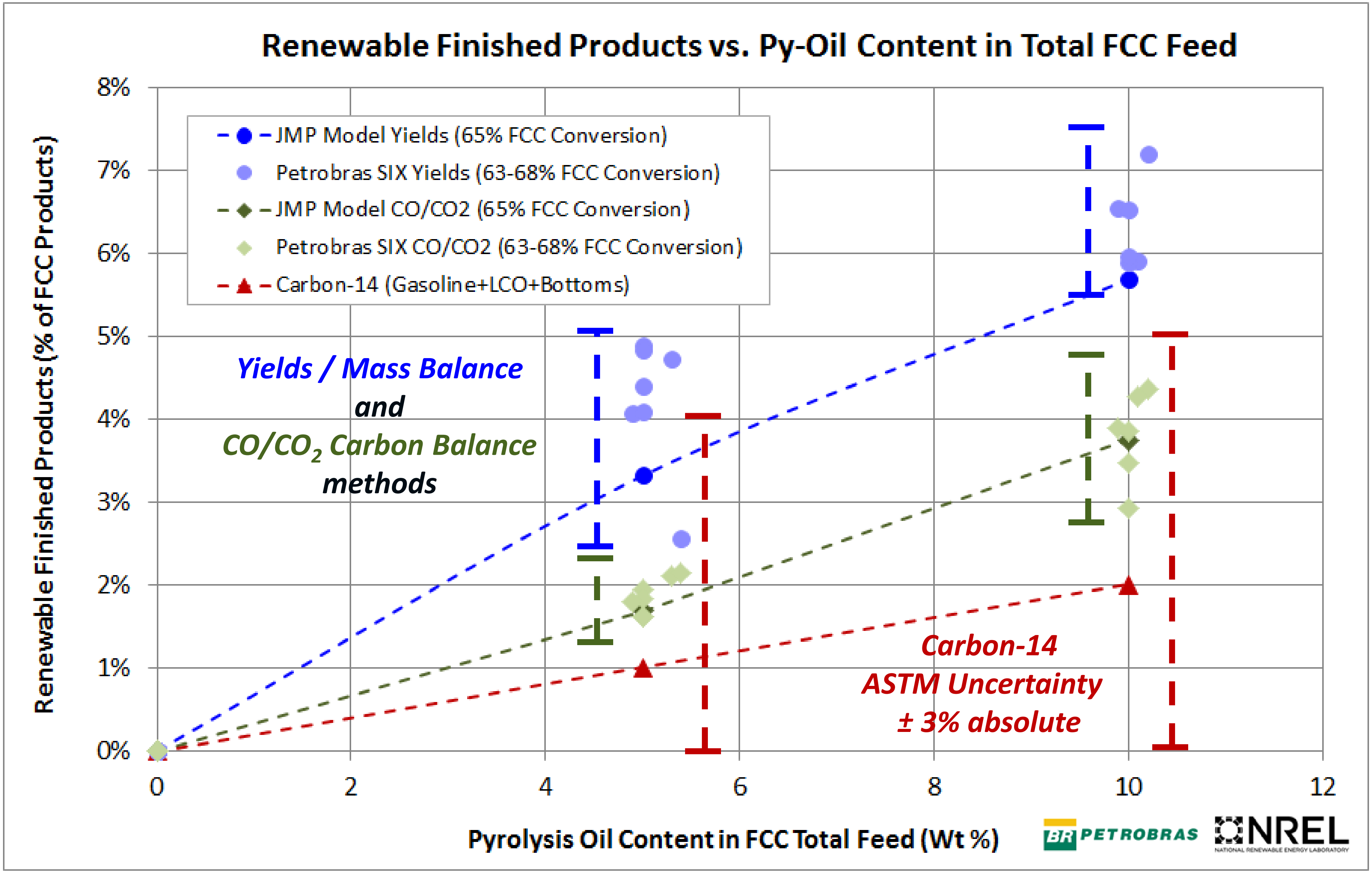
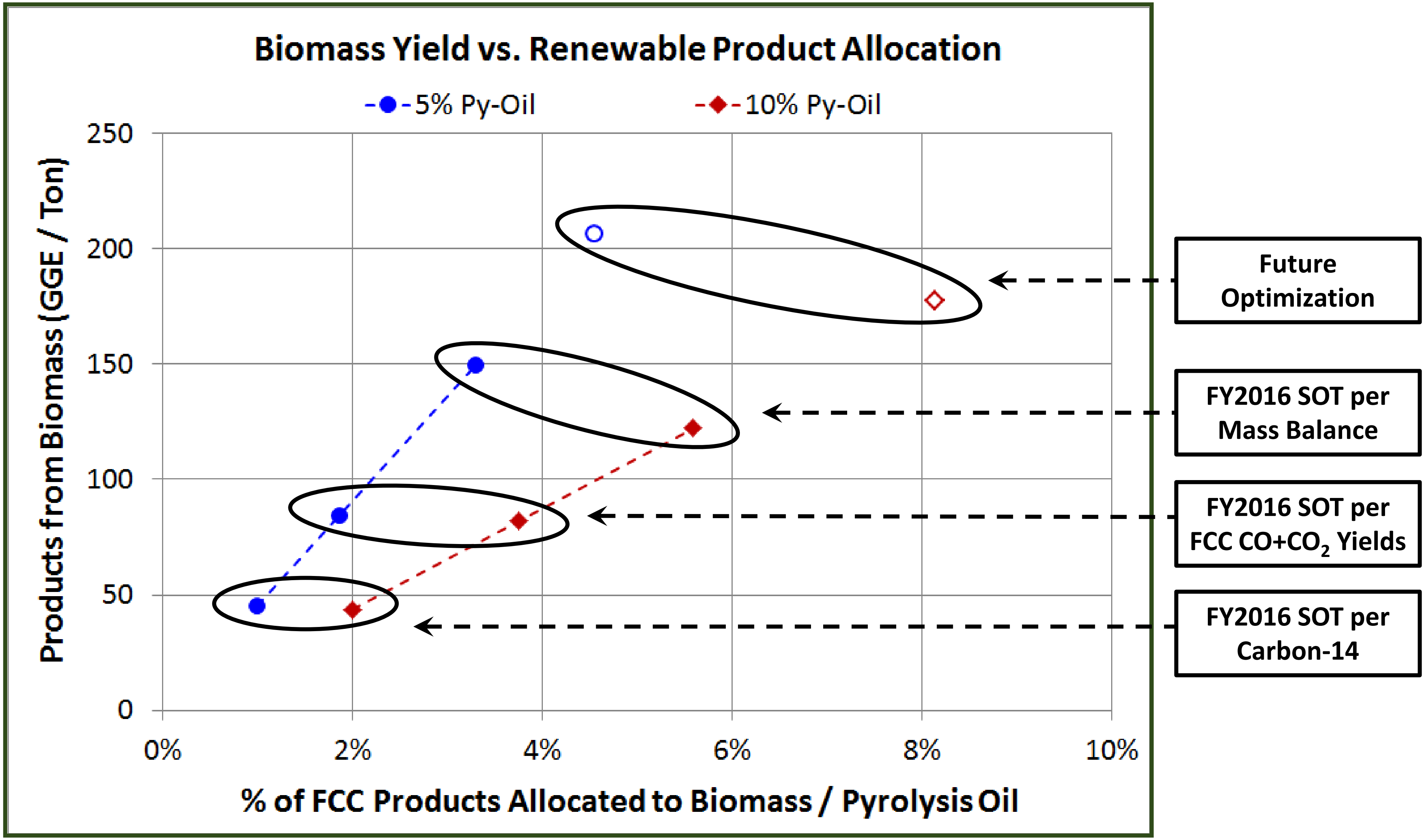
Method Results and Uncertainties

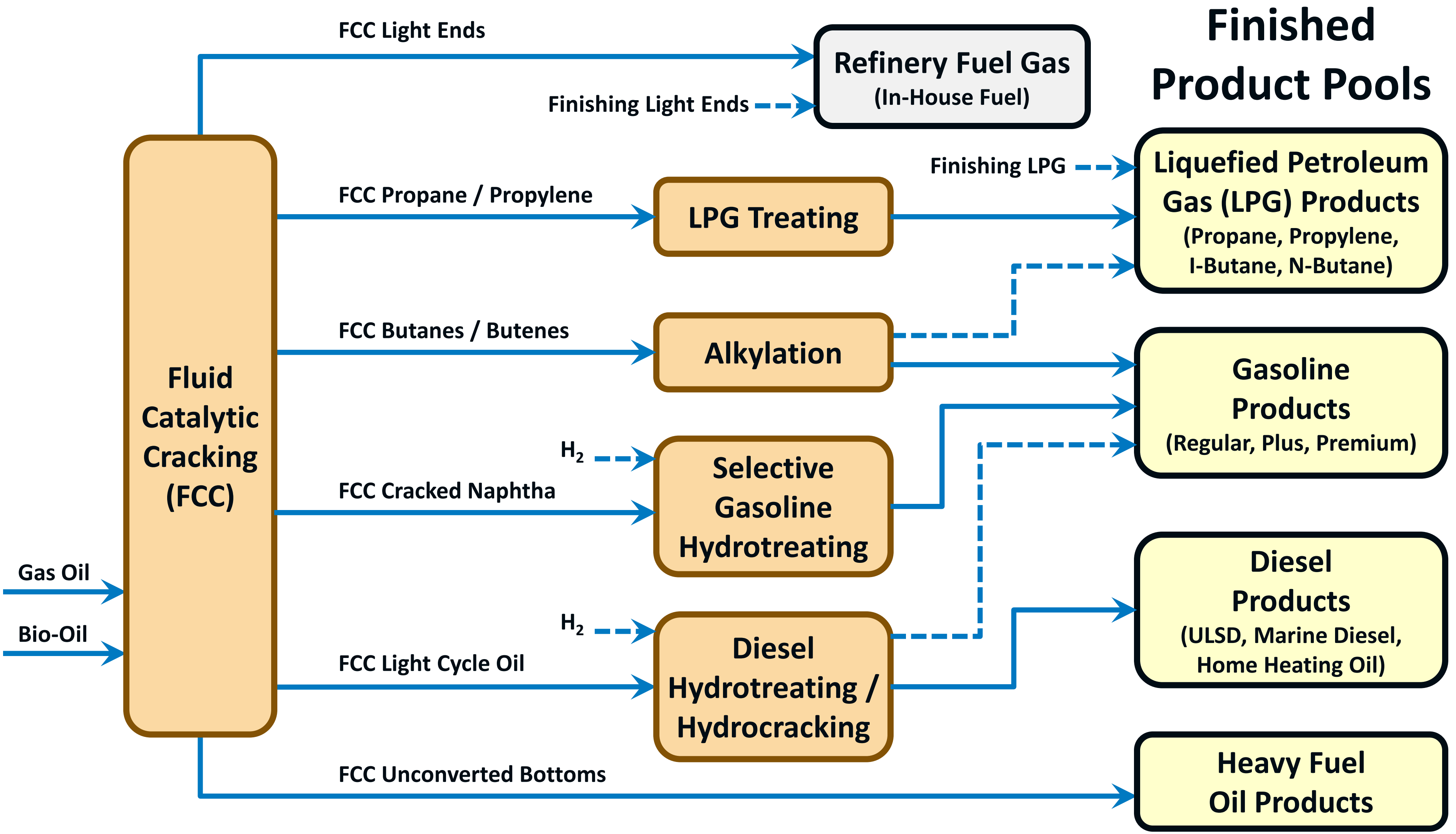


Product Yield vs. Renewable Product Allocation



FCC Instrumentation and Sampling

- What are the appropriate locations to assess product allocation?
- How do we account for H_2 and other process inputs?



Acknowledgements

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