NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Brazil Bilateral (2.4.2.303): Petrobras–NREL CRADA

BETO Thermochemical Conversion | NREL Industry and Refinery Integration

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In collaboration with **Barry Freel** of Ensyn Corp. ENSYN

U.S. Department of Energy's Bioenergy Technologies Office 2017 Project Peer Review

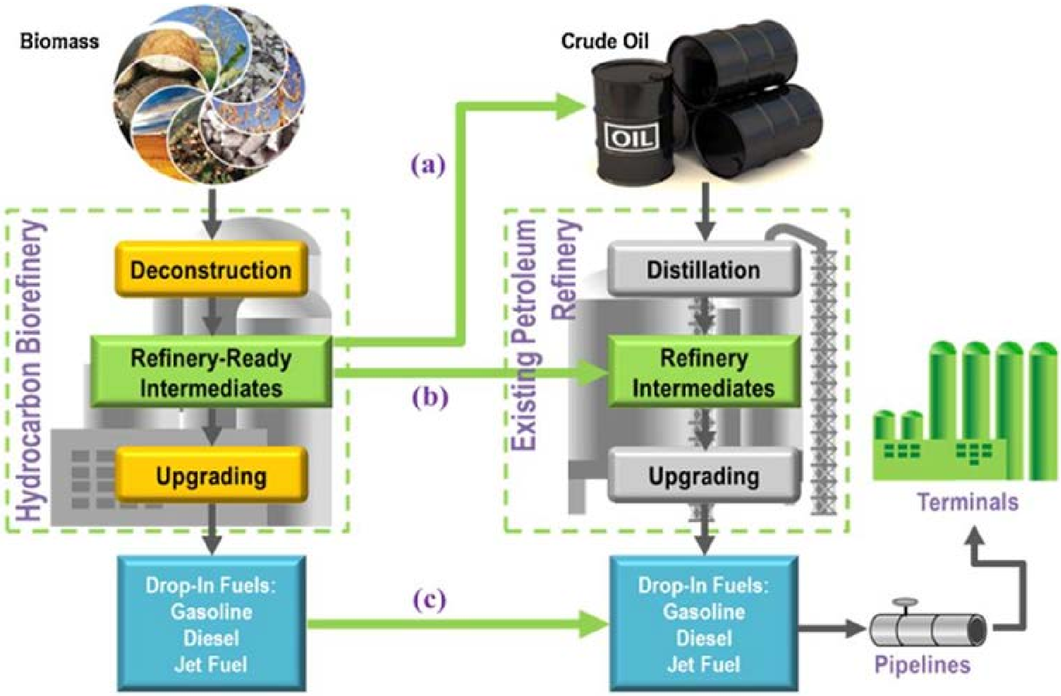
Sheraton Denver Downtown, Denver, CO

March 8, 2017

Goal Statement

Demonstrate technical and economic feasibility of co-processing raw, pine-derived pyrolysis oil with fossil feedstocks in FCC operation to produce renewable hydrocarbon fuels.

- Generate co-processing data at industrially-relevant scale.
- Enable industrial partners to produce finished fuels for testing.
- Disseminate results broadly in the scientific and regulatory communities



Outcome: Linking Refinery FCC with minimally treated raw biomass pyrolysis oils as a renewable complement to Vacuum Gas Oil (VGO) commercial intermediate

Relevance: Py-oil co-processing is a near-term commercially-viable route to biofuels

Quad Chart Overview

Project Timeline

Start Date	February, 2013
End Date	March, 2017 (per no-cost extension for publications through peer review)
% Complete	Overall: >90%; NREL: 80%; Petrobras: 100%

Budget (WBS 2.1.0.302)

Funding Source	FY2012 – FY2014 Costs	FY2015 Costs	FY2016 Costs	Planned FY2017- End Date
DOE BETO	$22.8K	$177K	$148K	*$57K*
EERE Intl.	$133K	$ 41.2	$44K	*$6K*
Cost Share	Petrobras: $1,976K Ensyn Corp: $100K			

Barriers Addressed by Demonstrating Near-Term Commercial Feasibility of Co-Processing Pyrolysis Oil in FCC

- Ct-K. Petroleum Refinery Integration of Intermediates (raw, filtered pyrolysis oil)
- Ct-J. Process Integration
- Ct-I. Product Finishing Acceptability and Performance
- Commercial Suppliers of Bio-oils
- Direct Bio-Oil Coprocessing in FCC previously deemed infeasible (coke formation)

Partners

- Petrobras R&D, CENPES, Rio de Janeiro, RJ
- Petrobras SIX facility, Sao Matheus do Campo, PR, Brazil
- Ensyn Corp. and partners, Fibria Celulose, BR
- NREL TCPDU (demonstrated bio-oil yields)
- INL(feedstock) subcontract; scenarios
- PNNL (TEA basis for raw FP bio-oil)

Overview: Key Objectives

1. ***Demonstrate feasibility of co-processing*** raw, pyrolysis oils with VGO to acceptable hydrocarbon products and acceptable low coke formation.
2. ***Partner with commercial pyrolysis oil supplier*** with shipping capabilities to deliver large pyrolysis oil quantities for co-processing experiments.
3. Use NREL and Petrobras chemical analytical facilities and capabilities to ***characterize intermediates and fuel products***.
4. Based on experimental data, develop yield models, ***techno-economic analysis and lifecycle analyses*** for VGO and coprocessing scenarios.
5. ***Leverage synergy with Ensyn***, the commercial bio-oil supplier who needed bio-oils for regulatory fuel testing. Petrobras modified its facility to enable continuous operation and set up the distillation facility.
    a. SOW of the CRADA was altered to center on these objectives.

Management Approach: Overview

- Establish collaborations with commercial pyrolysis oil supplier and petroleum refiner
  - Ensyn Corp. selected as supplier of commercial pyrolysis oil
  - Petrobras selected as petroleum refiner
  - NREL enabled through the CRADA a Materials Transfer Agreement with ENSYN and Petrobras for bilateral shipping of samples. ENSYN Corp. partnership with Fibria, a Brazilian company, eliminated timing uncertainties.
- Active management style by milestones/deliverables
  - Unpredictable shipping times between the two countries by 9/2013 implied the project would not deliver pyrolysis oils to Petrobras on 12/2013
  - Early decision made on performing much more 200 kg/hour coprocessing runs at Petrobras SIX instead of kg/hour with NREL oils at Petrobras CENPES

Go/No-Go

- Management by quarterly milestones, active communications with partners -- monthly group phone calls, frequent POCs phone calls, with frequent emails, reciprocal site visits
- Data exchanged by the partners using spreadsheets with process data enabled reaching the milestone of 12/2014 with the preliminary technoeconomic analysis on time and continuation to the final results, included in publication #1.
- Similarly TEA models were exchanged for verification in spreadsheets.

Management Approach: Petrobras Collaboration

Petrobras SIX Facility

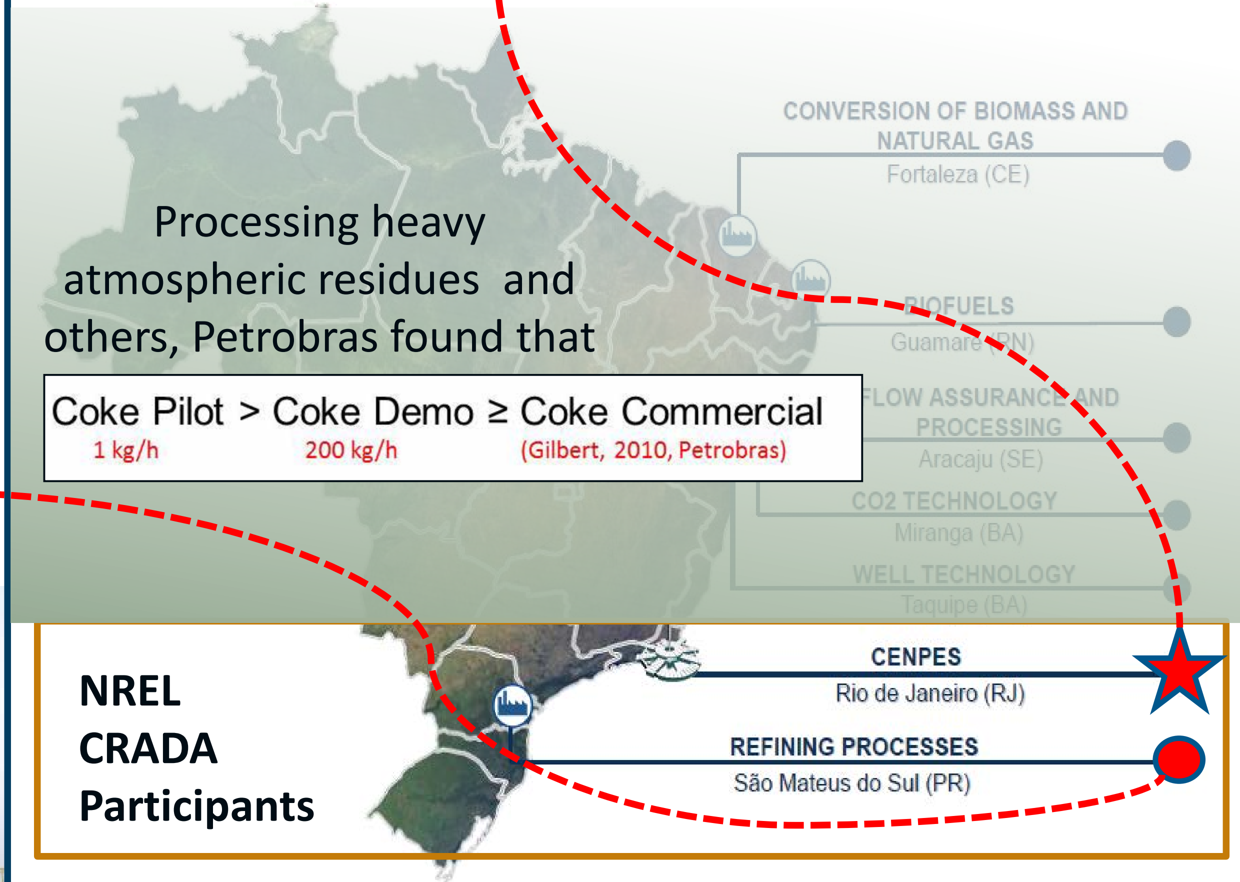
São Mateus do Sul, Parana

Infrastructure

Petrobras R&D Facilities

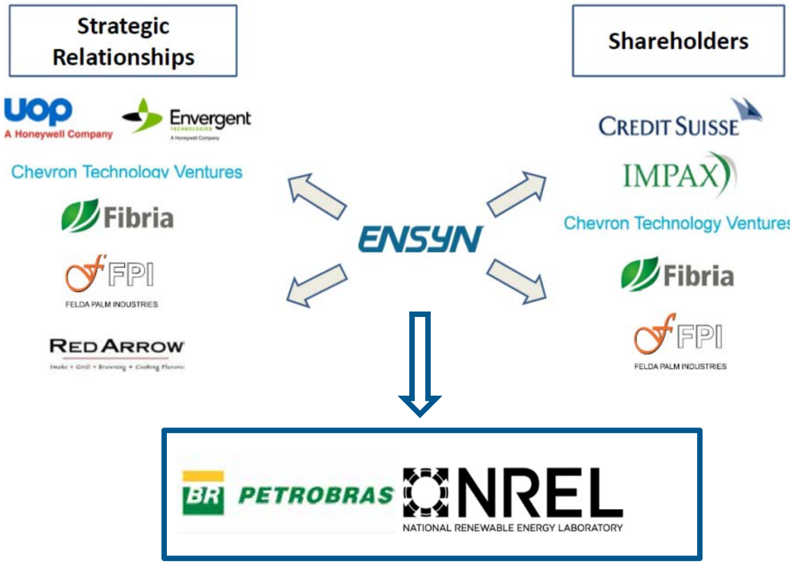
Petrobras Research Center

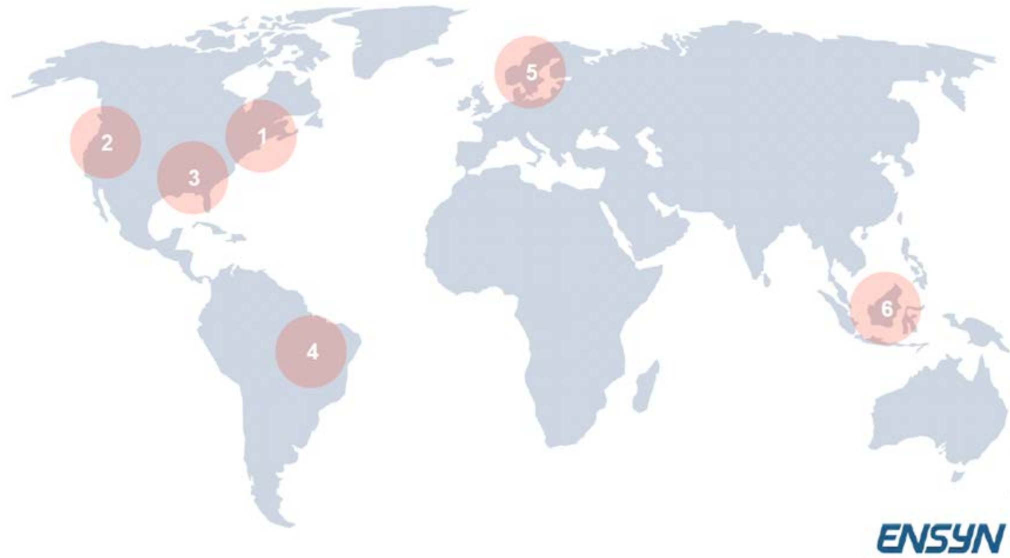
CENPES, Rio de Janeiro, Andrea Pinho



Petrobras, Supply Journal, Year 7, Number 67, 14-17, October 2014
http://asp-br.secure-zone.net/v2/index.jsp?id=2225/6153/6434

Management Approach: Ensyn/Fibria Partnership





Fibria Celulose, 2.5 million ton/yr pulp mill in Aracruz, Espirito Santo, Brazil where Ensyn and Fibria are developing a 20 million gallon/year RFO^{TM} plant

http://www.datamark.com.br/en/news/2016/8/fibria-plans-advance-in-bio-oil-213889/

Technical Approach: Experimental

Petrobras "SIX" demo unit has same hardware as a commercial FCC

- Feed nozzles
- Riser cyclone
- Packed stripper
- Heat balanced
- Mass flowrate: 200 kg/h
- Riser: L=18 m, d= 2"

Co-Processing Experiments

- Two pine-derived pyrolysis oils with consistent physical properties
- Mass balance range of 96 – 100%
- 3-hour test runs
- Cumulative time w/ py-oil > 400 hours
- Up to 20 wt% pyrolysis oil in FCC feed
- 54 experimental data points

This experimental protocol provided:

- Evaluation of process stability and operability
- Data to generate yield models and perform TEA analyses
- Large quantities of fractionated product streams for upgrading to finished fuels

Technical Approach: Analysis

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

Models developed from Petrobras "SIX" data for FCC operations

aspentech

Aspen HYSYS

jmp

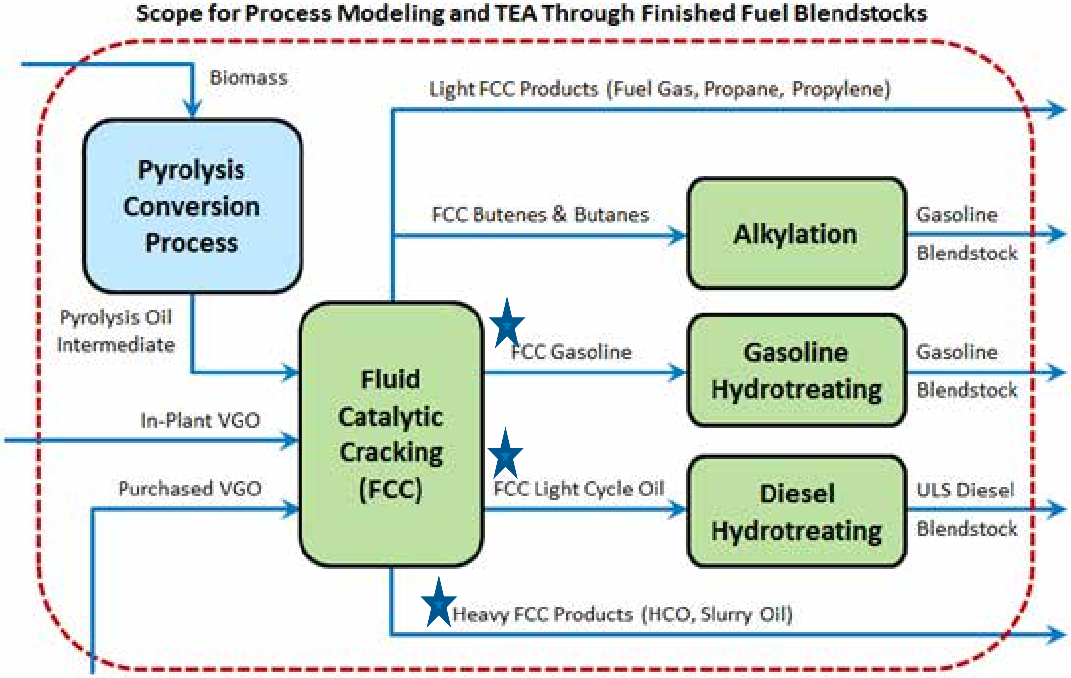
Models for hydrotreating and alkylation based on literature

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

OPIS an IHS Markit company

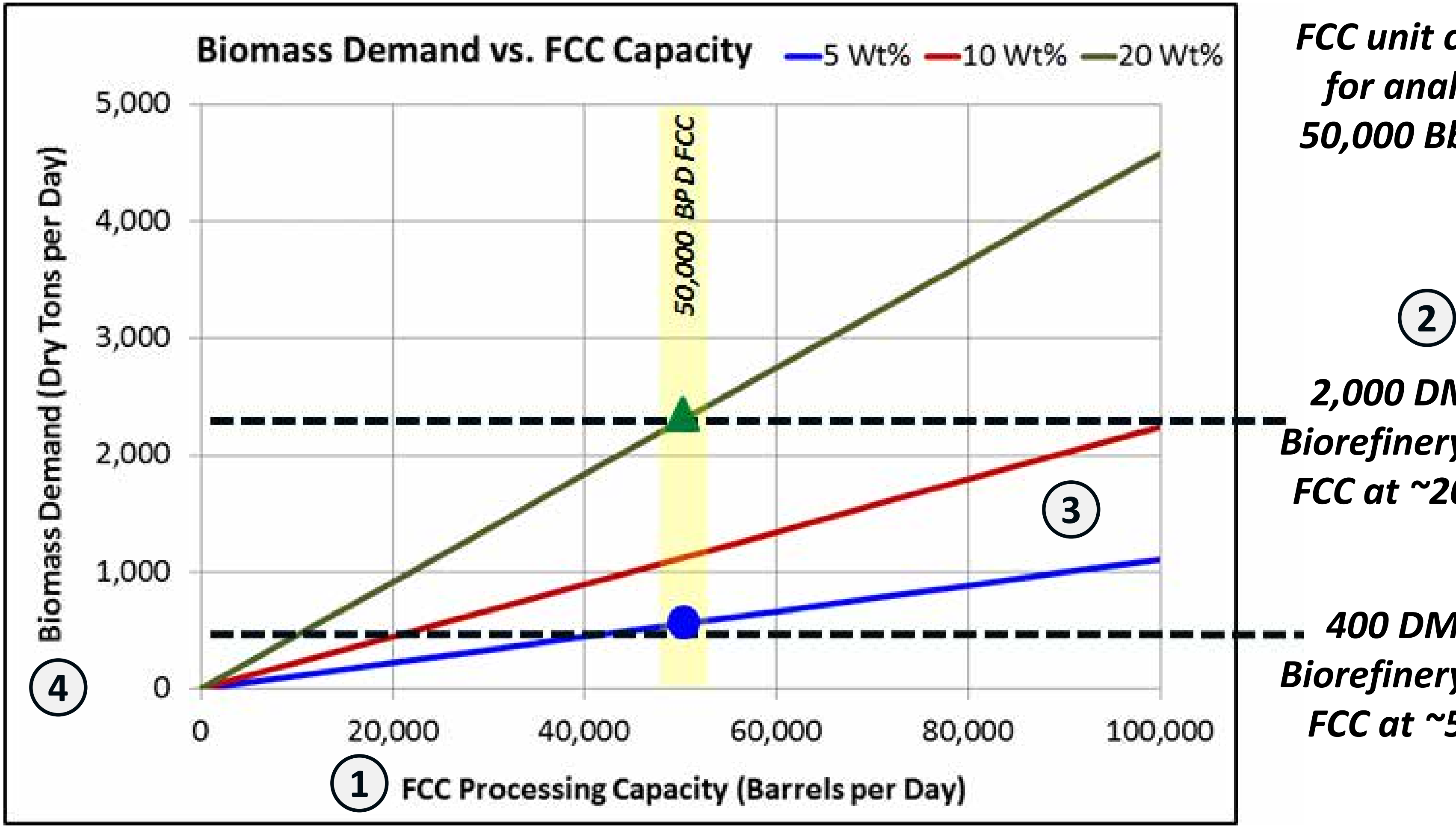
Capital and operating cost basis for FCC co-processing

Modeling and TEA for Pyrolysis Oil Co-Processing Scenarios



Technical Accomplishments - Context

Relationship between (1) FCC processing capacity, (2) fast pyrolysis oil biorefinery capacity, (3) % pyrolysis oil in FCC feed and (4) feedstock demand



FCC unit capacity for analysis is 50,000 Bbl / Day

2,000 DMTPD Biorefinery Feeds FCC at ~20 Wt%

400 DMTPD Biorefinery Feeds FCC at ~5Wt%

DMTPD = dry metric tons per day

Technical Accomplishments
Raw Pyrolysis Oil Production Scenarios

Assessment Parameter	Current Commercial	Mature Commercial
Geographical Region Match	Alabama, Arkansas, Louisiana, Mississippi	
Biomass Processing Capacity	400 Dry Tonnes / Day	2,000 Dry Tonnes / Day
Woody Biomass Feedstock Cost	$85 – $100 / Dry Ton	$90 – $120 / Dry Ton
Demonstrated Raw Py-Oil Yield from Biomass from NREL-TCPDU	59.1 ± 3.7 Wt% Organics 157.1 ± 9.9 Gallons / Dry Ton Pyrolysis Oil Intermediate	
MSP for Raw Bio-Oil (for FCC Co-Processing Analyses)	**$1.80 – $2.15 / Gallon ($75 – $95 / Barrel)**	**$1.10 – $1.55 / Gallon ($45 – $65 / Barrel)**

Py-oil production TEA enables co-processing breakeven analysis

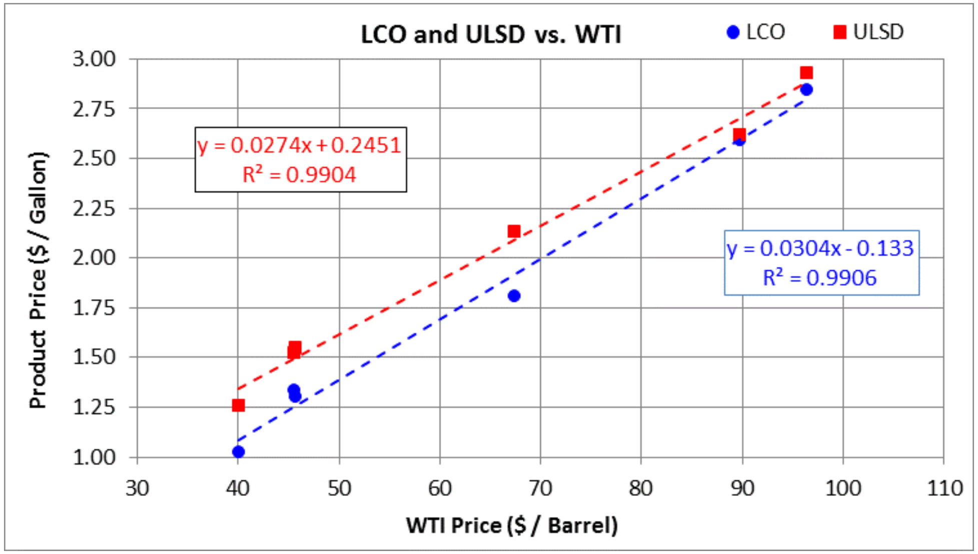
- TEA parameters are consistent with those applied for BETO-funded analysis per MYPP.
- Capital and operating costs estimated based on BETO-funded 2013 Fast Pyrolysis Design Report from Jones et al (PNNL-23053).
- Raw, stabilized pyrolysis oil with oxygen content of ~50 Wt%, specific gravity of 1.2, moisture content of 25wt%. **Consistency between Ensyn, BTG, PNNL and TCPDU yields / qualities**.

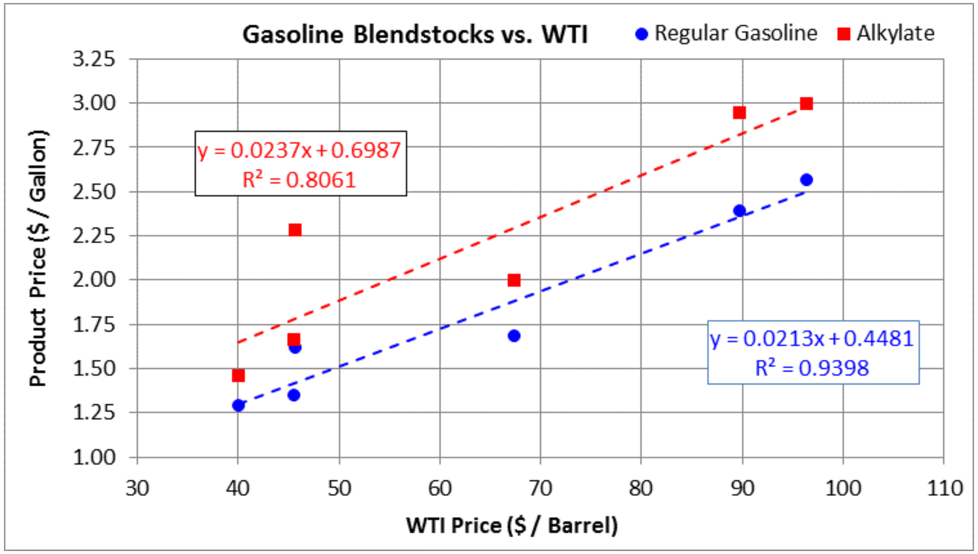
Technical Accomplishments
Petroleum Feed and Product Pricing Basis

Feed and product prices for TEA vary with crude oil price

- West Texas Intermediate (WTI) benchmark
- Feed and product prices are functions of WTI price
- Basis for values of Octane and Cetane
- Enables TEA across range of \$40 to \$100 / barrel

Source of Pricing Data: OPIS International Feedstocks Intelligence Reports (http://www.opisnet.com)

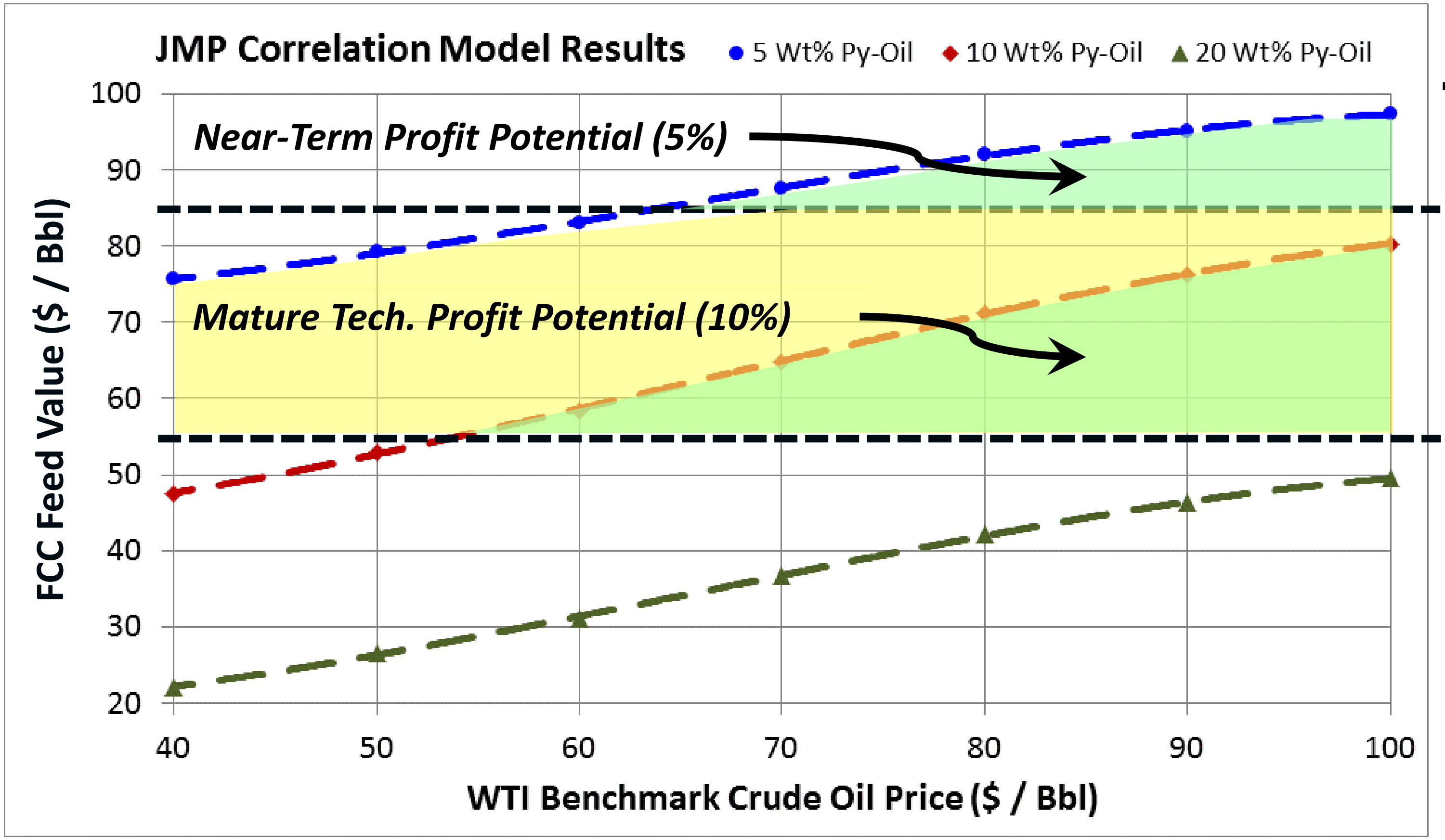




Technical Accomplishments
TEA Results: Pyrolysis Oil Breakeven Value

Breakeven Analysis

- Revenue equals cost at the "Breakeven Point"
- "Pyrolysis Oil Breakeven Value" = f (value of products)
- Profit can be realized when cost < "Breakeven Value"



Py-Oil Cost
400 Dry Tonnes / Day
$75 – $95 / Barrel
2000 Dry Tonnes / Day
$45 – $65 / Barrel

Technical Accomplishments
CRADA Experimental Data Published

Petrobras and NREL published all the data generated by the CRADA in the open literature

Fuel 188 (2017) 462-473

Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production

Andrea de Rezende Pinho [a,*], Marlon B.B. de Almeida [a], Fabio Leal Mendes [a], Luiz Carlos Casavechia [b], Michael S. Talmadge [c], Christopher M. Kinchin [c], Helena L. Chum [c]

[a] *PETROBRAS, Centro de Pesquisas e Desenvolvimento Leopoldo A. Miguez de Mello (CENPES), Ilha do Fundão, Av. Horácio Macedo, 950, Rio de Janeiro, RJ, Brazil*
[b] *PETROBRAS-SIX, Rodovia do Xisto BR 476, km 143, São Mateus do Sul, PR, Brazil*
[c] *NREL – National Renewable Energy Laboratory, 15013 Denver West Parkway Golden, CO 80401-3305, USA*

In addition, we used the early data Petrobras published with pine oil from a small demonstration facility going from 5% to 20% bio-oils

Fuel Processing Technology 131 (2015) 159-166

Co-processing raw bio-oil and gasoil in an FCC Unit

Andrea de Rezende Pinho [a,*], Marlon B.B. de Almeida [a], Fabio Leal Mendes [a], Vitor Loureiro Ximenes [a], Luiz Carlos Casavechia [b]

[a] *PETROBRAS, Centro de Pesquisas e Desenvolvimento Leopoldo A. Miguez de Mello (CENPES), Ilha do Fundão, Av. Horácio Macedo, 950, Rio de Janeiro, RJ, Brazil*
[b] *PETROBRAS-SIX, Rodovia do Xisto BR 476, km 143, São Mateus do Sul, PR, Brazil*

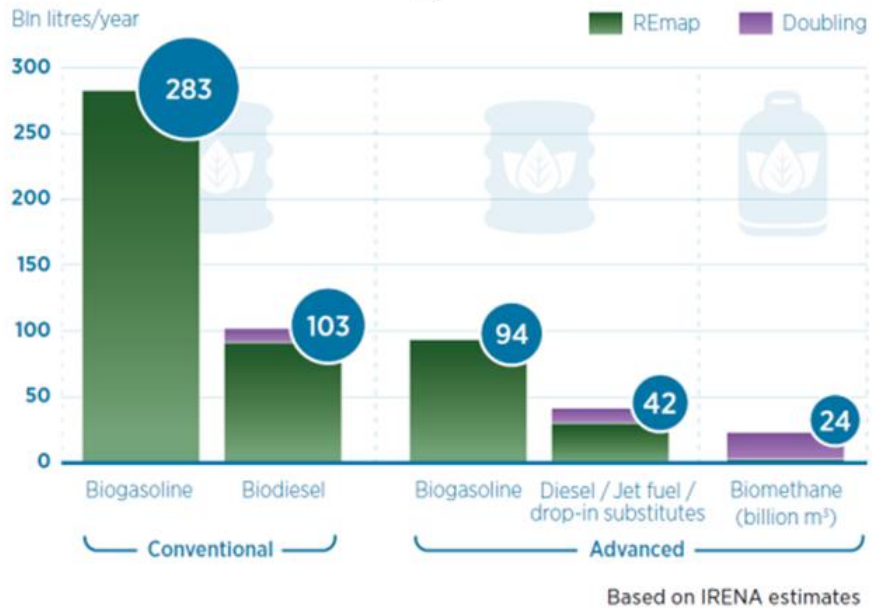
Accomplishments and On-Going Efforts

- NREL is finalizing ***techno-economic and lifecycle analyses based on yield data using CRADA results*** and previous data from Petrobras from a small scale demonstration pyrolysis oil from BTG.
- NREL and Petrobras continue to assess the ***impact of bio-oil co-processing on the bioeconomy*** (national / global)
- California Air Resources Board (CARB) is interested in co-processing. Chum and Talmadge are members of the CARB Co-processing Working Group to ***help the industry and regulators understand the impact of renewable addition***.

Relevance: Potential Impact of FCC Co-Processing

Near-term commercially viable route to biofuels in U.S. and global

IRENA Renewable Energy Roadmap 2016



U.S. Potential for ~5 Billion Gallons (GE) (20 B-Liters) biofuels per year with 10% pyrolysis oil in FCCs. Global doubles

PETROBRAS NREL

Preliminary Estimated Yearly Potential	United States	Global
FCC Processing Capacity (Bbl / Day)	6.0 Million	14.6 Million
Biofuels at 5 Wt% Pyrolysis Oil (B-GGE / Year)	1.0 – 2.8	2.4 – 6.8
Biofuels at 10 Wt% Pyrolysis Oil (B-GGE / Year)	2.0 – 4.4	4.9 – 10.7
Biofuels at 20 Wt% Pyrolysis Oil (B-GGE / Year)	5.0 – 6.3	12.1 – 15.2

Relevance: Successful Collaboration

- Established ***collaborations with credible commercial partners*** --
  - Ensyn produced 2000 gallons of raw pine pyrolysis oil (2013) for co-processing runs and Fibria delivered to Petrobras SIX
  - Bagasse (4 ton) supplied by INL from U.S. to Ensyn; Ensyn/Fibria supplied bagasse pyrolysis oils (275 gallons) to Petrobras (1/2016).
- Petrobras generated pine ***co-processing yield data at steady-state from FCC unit*** at Petrobras demonstration refinery SIX (scale of 200 kg / hr = 32 bbl / day)
  - Pyrolysis oil age from production in tests conducted: (1) **8 mo-old** and (2) **21 mo-old** – only small operational issues; test data fit previous trends.
- Petrobras SIX facility used 5 % pine bio-oil (8 mo-old) in ***uninterrupted co-processing for 70 hours*** collecting coprocessed crude
  - Subsequently distillation made 400 gallons of gasoline and 400 gallons of diesel precursors. FIBRIA shipped coprocessed fuels to the U.S. in 3/2014
- Ensyn's partners ***hydrotreated the precursors to U.S. specification gasoline and diesel*** containing biomass-derived hydrocarbons sent to Southwest Research Institute for fuel testing. Coprocessing pathway approved
  - ***Part 79 EPA diesel (2/2015) and gasoline (11/2015) and CARB both on 2/2016***

Relevance: BETO Program and Global Initiatives

- Supported BETO Strategic Mission and goal:
  - Develop and demonstrate transformative and revolutionary bioenergy technologies for a sustainable nation
  - Encourage the creation of a new domestic bioenergy and bioproducts industry
- Supported U.S. and Brazil Strategic Energy Dialogue goals in advanced biofuels and fostered industrial partnerships across these and other countries and commercialization.
  - Bilateral partnership started with the Memorandum of Understanding of 2007.

Summary

- ***Co-processing 5% py-oil is economically feasible in near-term*** and 10% is possible with progress in industry and technology
- Low cost pathway to refiners for ***increased renewable content*** in current fossil fuel production using assets and ***minimal additional capital*** (~$1 MM)
- Significant impact on TEA from lowering capital hurdle
- ***Product allocation method has major impact on TEA (and LCA)***
- U.S. / global FCC capacities enable opportunity for ***several billion gallons*** of gasoline equivalent of hydrocarbons containing biofuels
- CRADA is accelerating commercialization of this pathway.
- NREL (Chum and Talmadge) members of the CARB Coprocessing Technical Working Group helping understand the renewable addition impact
- ***CRADA provided significant input to the BETO State of Technology***.

Next Steps

- Publish TEA/LCA analyses results
- Biofuels Digest and other venues

Acknowledgements

The research reported was a result of the Memorandum of Understanding to Advance Biofuels Cooperation between the governments of Brazil and the United States started in 2007 and continued through the Strategic Energy Dialogue since 2011. The Brazilian Ministry of Mines and Energy (Dr. Ricardo Dornelles) provided significant encouragement to these activities. The U.S. Department of Energy (Rhia Davis), through the staff of the Office of Energy Efficiency and Renewable Energy International Programs (Dr. Robert Sandoli) and the Bioenergy Technologies Office (Dr. Valerie Reed and Dr. Jonathan Male), led the bilateral work and enabled and encouraged the collaboration. The Cooperative Research and Development Agreement Number 12-500, Biomass Pyrolysis to Hydrocarbons, in the Refinery Context, between Petroleo Brasileiro SA and the Alliance for Sustainable Energy, was conducted by researchers at Petrobras/CENPES/SIX and the National Renewable Energy Laboratory. We thank a very large number of involved managers and staff of these organizations for facilitating this productive bilateral collaboration. The information presented includes contributions of funding, materials for experimentation, experimental research, and model / analysis development from the following:

U.S. Department of Energy : Dr. Jonathan Male, Dr. Valerie Reed, Liz Moore, Alicia Lindauer, Rhia Davis, Dr. Robert Sandoli **Brazil Ministry of Mines:** Dr. Ricardo Dornelles **NREL:** Michael Talmadge, Yimin Zhang, Christopher Kinchin, Earl Christensen, Mary Biddy, Abhijit Dutta, Ed Wolfrum, Eric Tan, Esther Wilcox, Katherine Gaston, Josh Schaidle, Zia Abdulla, Adam Bratis, Tom Foust **Petrobras:** Marlon B.B. de Almeida, Fabio Leal Mendes, Luiz Carlos Casavechia, CENPES/PDEDS/QM group, Henrique Wilmers de Moraes, Marco Antonio Gomes Teixeira, Luiz Alexandre Sacorague, Cleber Goncalves Ferreira **Ensyn:** Robert Graham **Fibria:** Matheus Guimarães **PNNL:** Susanne Jones, Pimphan Meyer, Lesley Snowden-Swan, Asanga Padmaperuma **INL:** Damon Hartley, David Thompson, Patrick Lamers

Additional Slides

Abbreviations Used

AOP	Annual Operating Plan
ASTM	American Society for Testing and Materials
B Gal	Billion Gallons
BETO	Bioenergies Technology Office
BTG	Biomass Technology Group
C3's	Hydrocarbons with 3 carbon atoms
C4's	Hydrocarbons with 4 carbon atoms
CENPES	Petrobras Research Center
CRADA	Cooperative Research and Development Agreement
EERE	Office of Energy Efficiency and Renewable Energy
EIA	Energy Information Administration
FCC	Fluidized Catalytic Cracker
GGE	Gallons of Gasoline Equivalent
HCO	Heavy Cycle Oil
IP	Intellectual Property
IRENA	International Renewable Energy Agency
LCA	Life Cycle Analysis
LPG	Liquified Petroleum Gas
MM Gal	Million Gallons
MOU	Memorandum of Understanding
NBC	National Bioenergy Center
NREL	National Renewable Energy Laboratory

OPIS	**Oil Price Information Service**
POC	**Point of Contact**
R&D	**Research and Development**
RFO	**Renewable Fuel Oil**
RIN	**Renewable Identification Number**
SED	**Strategic Energy Dialogue**
SIX	**Superintendência da Industrialização do Xisto**
SwRI	**Southwest Research Institute**
TEA	**Techno-Economic Analysis**
VGO	**Vacuum Gas Oil**

Responses to Peer Reviewers

- Integration looks promising, but limited percentage may limit growth. Limited duration of testing and deep understanding of contaminants may prove to be a major problem.
  - The research now reported explains the ranges of bio-oil studied 5% to 20% by weight of bio-oil. The impact of 5 and 10% on FCCs is several billion gallons of gasoline equivalent. The understanding of the process improved further. It was not in the scope of this CRADA to complete the long term duration tests required that industry will pursue as it continues to develop the process. We explained better the difference in sizes between the two operations and the impact in more detail in the Fuel publication.

- This project provides very good initial information indicating that pyrolysis oils can potentially be blended with petroleum feedstocks into an FCC. This is potentially an important pathway for bio-oil utilization.
  - The innovation that Petrobras brought is the ability to introduce the bio-oil and the VGO in two different injection ports and at different temperatures. Bio-oil is injected from the cold (50C) to the entrance of the hot catalyst from the regenerator thus leading to significant cracking at a high catalyst to oil ratio. The VGO enters at the normal temperature.. It is not necessary to blend the oils with VGO. Very low capital equipment is needed to add the pyrolysis oil tank storage and the piping for the oils to enter the FCC.

- This is very important work for demonstrating the viability of adding bio-oil to an FCC unit. I assume that the unit is operated at steady state and that all material balances close tightly. Questions include: What are the oxygenates and how much is in the product? Has the project team kept weight basis constant and backed out carbon for oxygen? Results were a little confusing going from weight to volume and then on a relative basis (%). Also, double check benzene content in gasoline before and after and look at LPG; propylene in the C3 has potential chemical value. How do you rationalize the differences in results with those from W. R. Grace in the DCR?
  - Low temperature separate pyrolysis oil feeding line to FCC unit at 200 kg/h is a major difference to DCR facilities at 1/100 of the size. Coprocessing high mass balance closures were obtained with data for TEA. A modified distillation facility produced 400 gallons each of gasoline and diesel containing phenolic compounds . The CRADA provided direct oxygen measurements through neutron activation analysis of the finished fuels tested. We found 0.01 wt.% in the co-processed gasoline confirming that no oxygenates are present within this very low limit. The base diesel used by SwRI contained 1.5 vol. % of biodiesel (0.18 wt.% oxygen) , confirmed by the direct oxygen content of 0.23 wt. % oxygen in the co-processed diesel; these values agree within the errors of these two measurements. Prior to hydrotreating, there are phenolics, quantitated in the first paper. VGO alone also produces phenolics but the presence of bio-oils increases the amount.
  - Great suggestion on the propylene and butylene amounts.. We quantitate the amounts and price these streams as well.

Publications, Presentations, and Honors

- Andrea de Rezende Pinho, Marlon B.B. de Almeida, Fabio Leal Mendes, Luiz Carlos Casavechia, Michael S. Talmadge , Christopher Kinch, and Helena L. Chum, "Fast pyrolysis oil co-processing from pinewood chips with vacuum gas oil in an FCC unit for second generation fuel production," Fuel, 188 (2017) 462-473. Open access at http://dx.doi.org/10.1016/j.fuel.2016.10.032
- Andrea de Rezende Pinho, Marlon B.B. de Almeida, Fabio Leal Mendes, Victor Ximenes (2014). Production of lignocellulosic gasoline using fast pyrolysis of biomass and a conventional refining scheme. Pure and Applied Chemistry. 86: 859-865. This issue is part of a collection of invited papers based on presentations of the same topic).
- Andrea de Rezende Pinho, presenter of paper above at 2nd Brazilian Symposium on Biorefineries (II SNBr), Brasília, Brazil, 24–26 September 2013. Work conducted prior to the CRADA.
- **Michael Talmadge**, Helena Chum, Christopher Kinchin, Yimin Zhang, Mary Biddy, Andrea de Rezende Pinho, Marlon B.B. de Almeida, Fabio Leal Mendes, Luiz Carlos Casavechia, and Barry Freel. Proceedings of the 2016 Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products (forthcoming); Agenda https://www.ncsu.edu/mckimmon/cpe/opd/tcs2016/pdf/agenda.pdf
- **Michael Talmadge, Helena Chum (presenters)**, Christopher Kinchin, Yimin Zhang, Mary Biddy, Andrea de Rezende Pinho, Marlon B.B. de Almeida, Fabio Leal Mendes, Luiz Carlos Casavechia, Barry Freel, Analysis for co-processing fast pyrolysis oil with VGO in FCC units for second generation fuel production, Prepared for CARB Co-Processing Working Group, Sacramento, CA, December 13, 2016. https://www.arb.ca.gov/fuels/lcfs/lcfs_meetings/12132016nrel.pdf
- **Chum, H**. "Integrated Systems for the Bioeconomy – role of innovation." ORNL/BETO Bioenergy Study Tour in the Southeastern United States from April 10 to 14, 2016, http://web.ornl.gov/sci/ees/cbes/studytour2016/pdfPresentations/PetrobrasNRELCRADAAikenSC.pdf
- **Chum, H.L.,** June 7, 2013. Brazil-US MOU and the Petrobras-NREL CRADA Highlights, Golden, CO. Talk presented to a Brazilian government/industry delegation composed of the Senior Advisor to the CEO, Brazilian Development Bank (BNDES), International Affairs Manager of the Brazilian Agency for Industrial Development (ABDI); Heads of Innovation and New Business at BRASKEM that followed the Council of Competitiveness bilateral meeting in Washington D.C.
- Andrea de Rezende Pinho and Luiz Carlos Casavecchia, Petrobras, Supply Journal, Year 7, Number 67, pages 14-17, October 2014: Present and Future in transport fuels "Research at SIX could make viable the first route of biomass pyrolysis oils to gasoline and diesel, produced in a conventional refinery." http://asp-br.secure-one.net/v2/index.jsp?id=2225/6153/6434

Honors by the Biofuels Digest

- H. Chum "Top 100 People in the Advanced Bioeconomy" 2017
- H. Chum "Top 100 People in the Advanced Bioeconomy" 2016
- H. Chum "Top 125 People in the Advanced Bioeconomy" 2015

Press releases from Ensyn Corp.'s and partners efforts

Acknowledged contributions from the Petrobras/NREL/BETO CRADA

http://www.biofuelsdigest.com/bdigest/2015/11/25/epa-grants-ensyn-title-40-cfr-approval-for-rfgasoline/

http://www.biofuelsdigest.com/bdigest/2015/08/27/ensyn-gets-epa-approval-for-rfdiesel/

https://www3.epa.gov/otaq/fuels1/ffars/web-fuel.htm

http://biomassmagazine.com/articles/12874/ensyn-receives-key-regulatory-approvals-from-carb

https://www.arb.ca.gov/fuels/lcfs/fuelpathways/pathwaytable.htm
with four entries for two different oil transport distances;

https://www.arb.ca.gov/fuels/lcfs/2a2b/apps/ensyn-121715.pdf
Pathway Codes: RNWG001, RNWG002, RNWD028, and RNWD029

Hydrocarbon Processing: January 2017,
Commercialization of pyrolysis oil in existing refineries—Part 1
By Arbogast, S., Bellman, D., Paynter, D., Wykowski, J., AOTA Energy Consultants LLC

Uncertainty in Carbon-14 ASTM Method

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

BETA

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Tel: 305-667-5167
Fax: 305-663-0964
info@betalabservices.com

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.