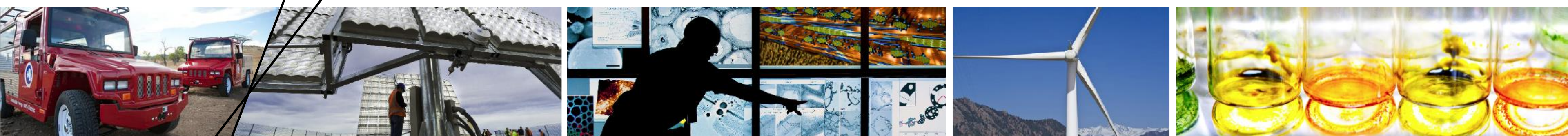
DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

2.4.2.303 Brazil Bilateral: Petrobras-NREL CRADA



March 25, 2015

BETO Area: Thermochemical Conversion
NREL AOP: Industry and Refinery Integration

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In collaboration with Barry Freel, Ensyn Corp.

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Goal Statements

Brazil Bilateral: Petrobras–NREL CRADA

- Demonstrate technical and economic feasibility of co-processing raw fast pyrolysis oil in Fluid Catalytic Cracking (FCC) operation
  - Establish collaborations with credible commercial partners
  - Produce 2000 gallons of raw pyrolysis oil for co-processing runs (2 feeds)
  - Generate co-processing yield data at steady-state from FCC unit at Petrobras demonstration refinery SIX (scale of 200 kg / hr = 32 bbl / day)
  - Perform techno-economic and sustainability analyses based on yield data
  - Assess the impact of bio-oil co-processing on bioeconomy (national / global)
  - Publish results in up to three (3) peer reviewed journal articles
- Support BETO Strategic Goals and Bioeconomy Development
  - Develop commercially viable technologies for converting biomass feedstocks into energy dense, fungible, liquid transportation fuels
  - Supports U.S. and Brazil Strategic Energy Dialogue goals in advanced biofuels and industrial partnerships across these and other countries

Quad Chart Overview

Timeline

Actual Start Date	February, 2013
End Date	September, 2015
Overall % Complete	75%
NREL % Complete	50%

Budget

	Total Costs FY10 to FY12	FY 13 Costs	FY 14 Costs to Q1 FY15	Total Planned Funding FY15-End Date
DOE Funded BETO		$41K	$58K	$265K
EERE Intl.	$37K	$71K	$56K	$250K

Project Cost Share

1. Petrobras $1,976K

2. Ensyn Corp. $100 K

4 : 1 partners : DOE funding

Barriers

Addressed:

- **Tt-S. Petroleum Refinery Integration of Bio-Oil**
- **Tt-R. Process Integration**
- **Tt-K. Product Finishing**

Other:

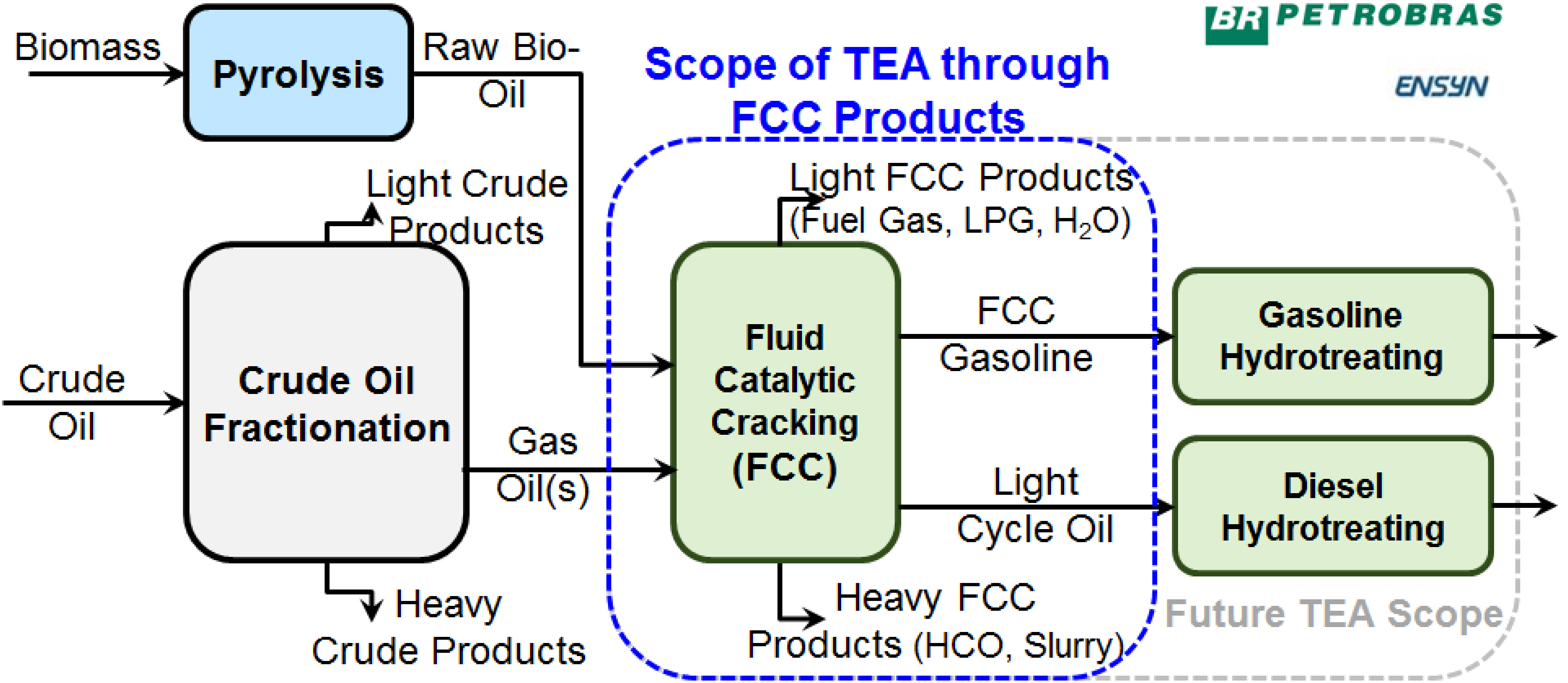
- **Commercial Suppliers of Bio-oils**
- **Direct Bio-Oil Coprocessing in FCC deemed not possible because of coke formation**

Partners

- Petrobras R&D, CENPES, Rio de Janeiro, RJ
- Petrobras SIX facility, Sao Matheus do Campo, PR, Brazil
- NREL – National Bioenergy Center, Alternative Fuels and Strategic Energy Analysis
- Ensyn Corp. and partners, principally Fibria Celulose, Brazil

Conventional Petroleum Refinery Integration of Bio-Oil Tested in Demo scale

BETO Barriers Tt-S & Tt-R



Techno-economic Analysis Basis

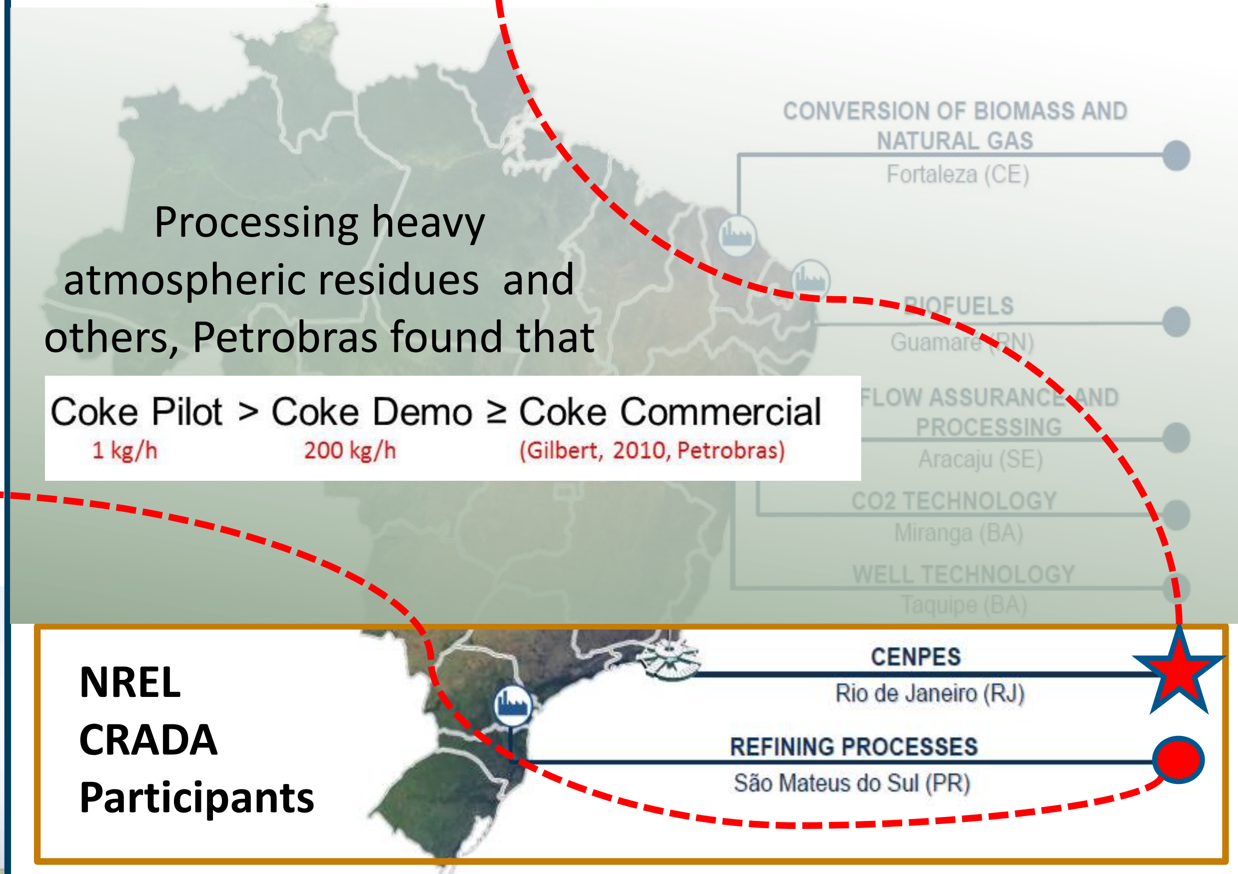
- VGO and intermediate prices from EIA Bloomberg and OPIS
- Pyrolysis oil price(s) from BETO-funded TEA
- FCC costs and savings discussed with Petrobras and Ensyn
- FCC intermediate yields from Petrobras SIX pilot plant facility

Petrobras–NREL CRADA: Petrobras Facilities

Petrobras SIX Facility
São Mateus do Sul, Parana

Infrastructure
Petrobras R&D Facilities

Petrobras Research Center
CENPES, Rio de Janeiro, Andrea Pinho



Processing heavy atmospheric residues and others, Petrobras found that

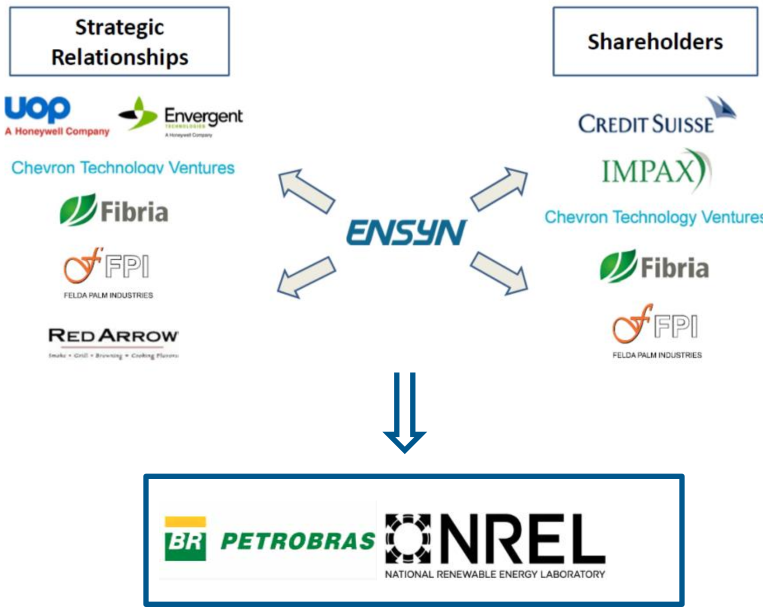
Coke Pilot (1 kg/h) > Coke Demo (200 kg/h) ≥ Coke Commercial (Gilbert, 2010, Petrobras)

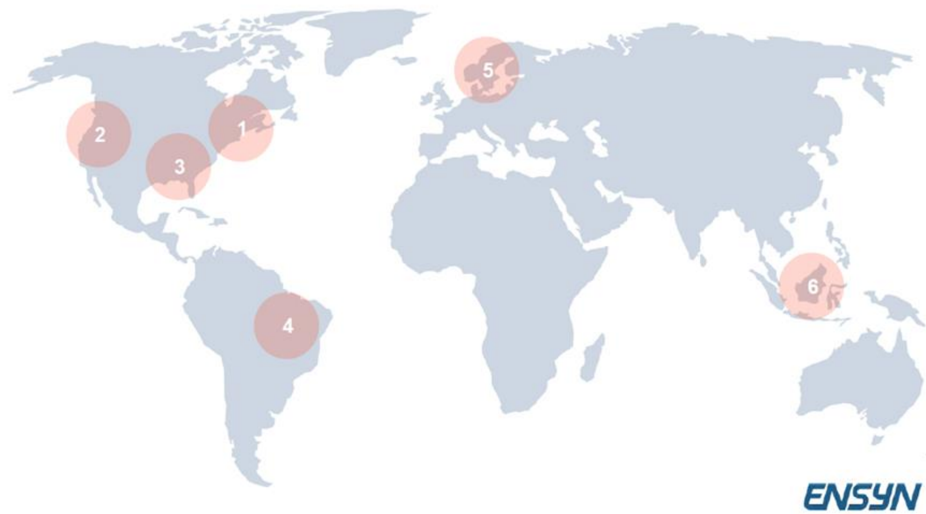
NREL CRADA Participants

PETROBRAS

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

Petrobras–NREL CRADA: 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™ plant

1 – Project Overview

Scale kg/h 200kg/h	• CENPES coprocessing run on U.S. feedstocks and analyses • SIX coprocessing runs for products, heat/mass balances
Scale 10kg/h; Analyses	• Produce oak/bagasse pyrolysis oils for CENPES coprocessing • Chemical, technical, economic, environmental analyses
U.S.-Brazil Agreements	• Strategic Energy Dialogue **2011** • MOU to Advance Cooperation on Biofuels **2007**

PETROBRAS

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Outcome: Technoeconomic and Lifecycle analyses of FCC products with/without bio-oil

Original CRADA to end in March 2015

2 – Management Approach

- 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
  - **Go/No-Go** 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
- Ensyn Corp. selected as supplier of commercial pyrolysis oil
  - NREL enabled through the CRADA & SED the Materials Transfer Agreement with ENSYN and Petrobras for bilateral shipping of samples. ENSYN Corp. partnership with Fibria, a Brazilian company, eliminated timing uncertainties
- The project coprocessed by 12/2013 enough bio-oil to produce 1000 gal of un-distilled products from coprocessed VGO and bio-oils. The milestone of 12/2013 was surpassed
  - Petrobras modifications at the SIX facility also enabled distillation of these products into gasoline and diesel coproduced samples that Fibria sent to the U.S. in 4/2014
- 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 enabled reaching the milestone of 12/2014 with the preliminary technoeconomic analysis on time

3 – Technical Accomplishments/ Progress/Results

<table>
<tr><th>Barrier</th><th>Accomplishments/Progress/Results</th></tr>
<tr><td>Commercial Supplier</td><td>Ensyn Corp./Fibria provided 6 ton pine bio-oils on 11/ 2013</td></tr>
<tr><td>Direct Bio-Oil Co-processing in FCC
not possible because of high coke formation from literature g/min to kg/h</td><td>Petrobras demonstrated in processing heavy oil residues that
Flow Rate: Coke Pilot > Coke Demo ≥ Coke Commercial
1 kg/h 200 kg/h (Gilbert, 2010, Petrobras)
The relationship holds for co-processing bio-oils at 200 kg/h:
<table>
<tr><td></td><td></td><td>Bio-oil weight %</td><td></td></tr>
<tr><td></td><td>VGO</td><td>+5%</td><td>+10%</td></tr>
<tr><td>Coke, wt. %</td><td>6.4%</td><td>6.0%</td><td>6.5%</td></tr>
</table></td></tr>
<tr><td>Tt-R. Process Integration

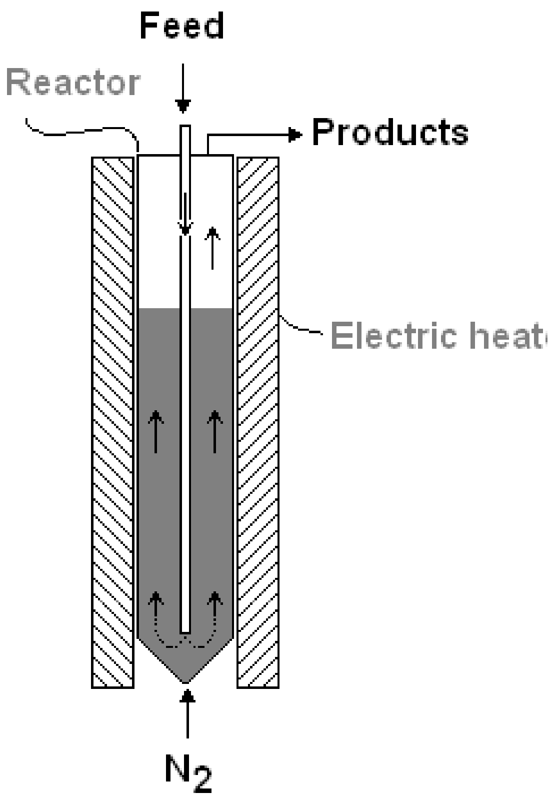
VGO=vacuum gas oil</td><td>Changes made: a separate feeding line (<80^{o}C) and bio-oil injection point in a way to cause thermal degradation so that the cracked molecules undergo further cracking in the riser without substantial coking formation on the catalysts.</td></tr>
<tr><td>Petroleum Refinery Integration of Bio-Oil</td><td>Pine pyrolysis oil coprocessing with VGO at 200 kg/hour flow rate at Petrobras reached a cumulative 400 operating hours.</td></tr>
<tr><td>Tt-K. Product Finishing (ENSYN and collaborators)</td><td>At 5 % bio-oil, uninterrupted processing for 70 hours collected crude that subsequently was distilled to 400 gallons of gasoline and 400 gallons of diesel materials. FIBRIA shipped the coprocessed oils to the U.S. in 3/2014</td></tr>
</table>

Preliminary NREL TEA:

- 5 wt.% bio-oil VGO is positive economically relative to just VGO processing
- 10 wt.% changes in product slate has slightly negative economics vs. VGO

Proof of concept

overcomes higher coke yields of g/min to kg/h work



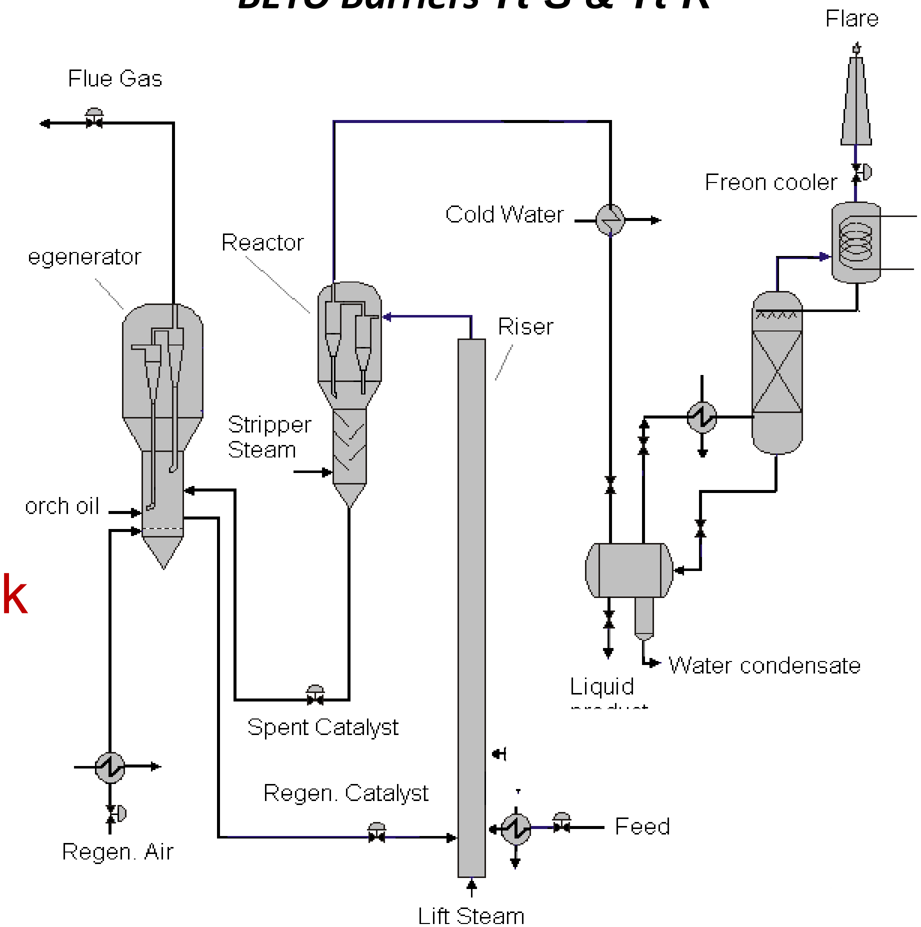
Lab (ACE unit)

- Uniformly heated at reaction temperature (510-540°C)
- Only one feed entrance

Thermal shock breaks high molecular weight compounds!

Scale matters!

BETO Barriers Tt-S & Tt-R



Pilot/Demonstration/Commercial

- Demo/Commercial: possible to have multiple feed points

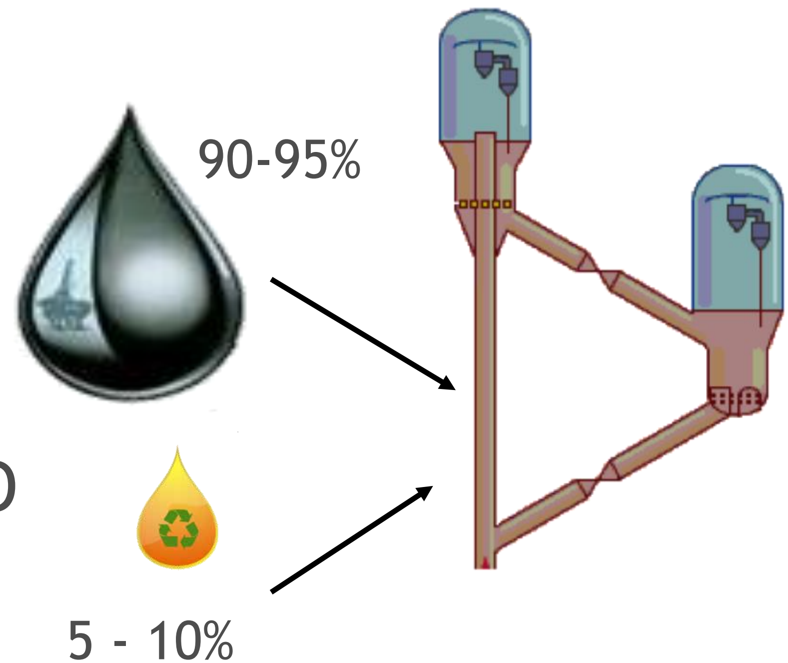
Barrier: Integration of Bio-Oil in Commercially Relevant Scale FCC

- Same type of hardware used in industrial units
  - Feed nozzles
  - Riser closed-coupled cyclone (catalyst-hydrocarbons separation device)
  - Structured packing stripper
  - Heat balanced
  - Mass flowrate: 200 kg/h
  - Riser: L=18 m, d= 2”
- Process
  - Mass balances: 96-98%
  - 3 hours-long tests
  - # tests using bio-oil: 78
  - Cumulative time w/bio-oil > 400 hours
  - Up to 20% of bio-oil

Tt-R: Process Integration

Tt-K: Product Finishing

- Ensyn/Canada bio-oil: 6 tons from pine woodchips
- Tankage and feed lines retrofitted
- 70 hours uninterrupted production w/5% bio-oil/VGO
- Products distilled into FCC gasoline and LCO in 4/2014
- Fibria shipped FCC intermediates to U.S. for hydrogenation and testing of final gasoline and diesel



Oil Stability at Petrobras
Oil Production: ~3/2013, Canada
SIX Production runs: 11-12/2013
SIX Process R&D runs: 1-4/2014
Oil viscosity increased; remaining solid sample disposed: 11/2014

Enablers of TEA: Yields/Catalyst

Weight %	100% VGO	95% VGO + 5% Bio-oil	90% VGO + 10% Bio-oil
Dry Gas	3.5	2.8	2.8
LPG (C3-C4)	13.8	13.8	12.5
Gasoline (C5-220°C)	39.9	40.6	38.8
Diesel (220-344°C)	20.3	19.6	19.2
Bottoms (+ 344°C)	16.1	14.4	14.4
Coke	6.4	6.0	6.5
CO	0.0	1.0	1.7
CO_2	0.0	0.4	0.6
Water	0.0	1.4	3.5

- Negligible catalyst deactivation caused by alkaline metals was found after 24h with 5 wt.% bio-oil.
- Longer test runs are necessary to address this issue.

Enabler of TEA: Oxygen Mass Balances

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Oxygen balance during co-processing at 540 °C

(kg of oxygen / 100 kg of feed)

	5% Bio-Oil Co-Processing		10% Bio-Oil Co-Processing	
Feedstock	2.54	100.0 %	5.07	100 %
CO	0.57	22.4 %	0.97	19.1 %
CO_2	0.29	11.4 %	0.44	8.7 %
Water	1.24	48.8 %	3.11	61.3 %
Liquid Products	0.05	2.0 %	0.05	1.0 %
Not Classified	0.39	15.4 %	0.50	9.9 %
Balance Closure	2.15	84.6 %	4.57	90.1 %

Improved oxygen mass balance closure at demo-scale

Previous work

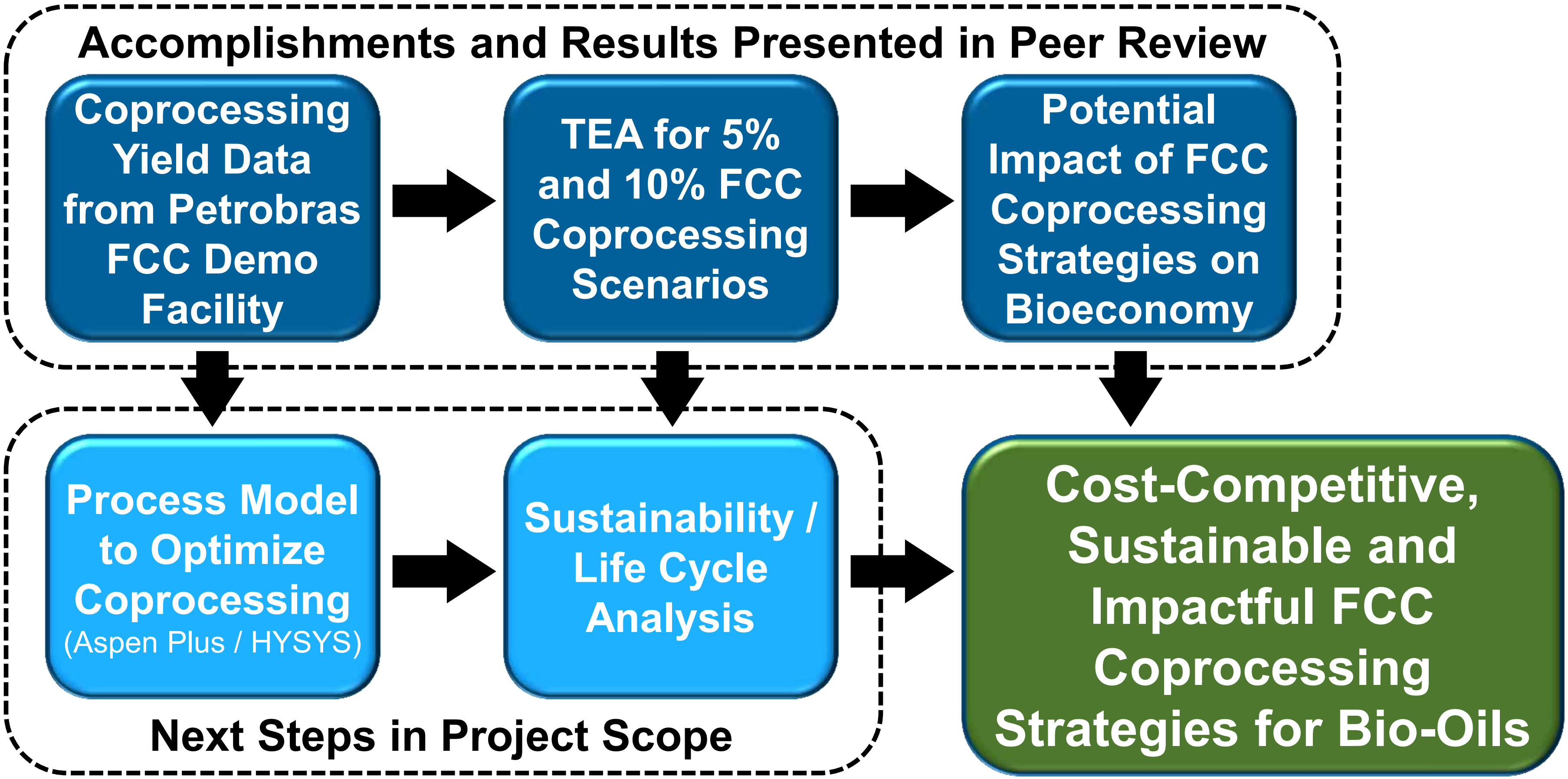
- **Petrobras / demo scale:**
  - BTG bio-oil
  - closure ~70 and 87 wt. %

  Pinho et al. 2015. Fuel Processing Technology. v. 131, p. 159-166

- **Literature / lab scale:**
  - Oxygen balance around 50 wt. %

  Fogassy et al., 2010. Applied Catalysis B: Environmental. v. 96, p. 476-485

Analysis Approach

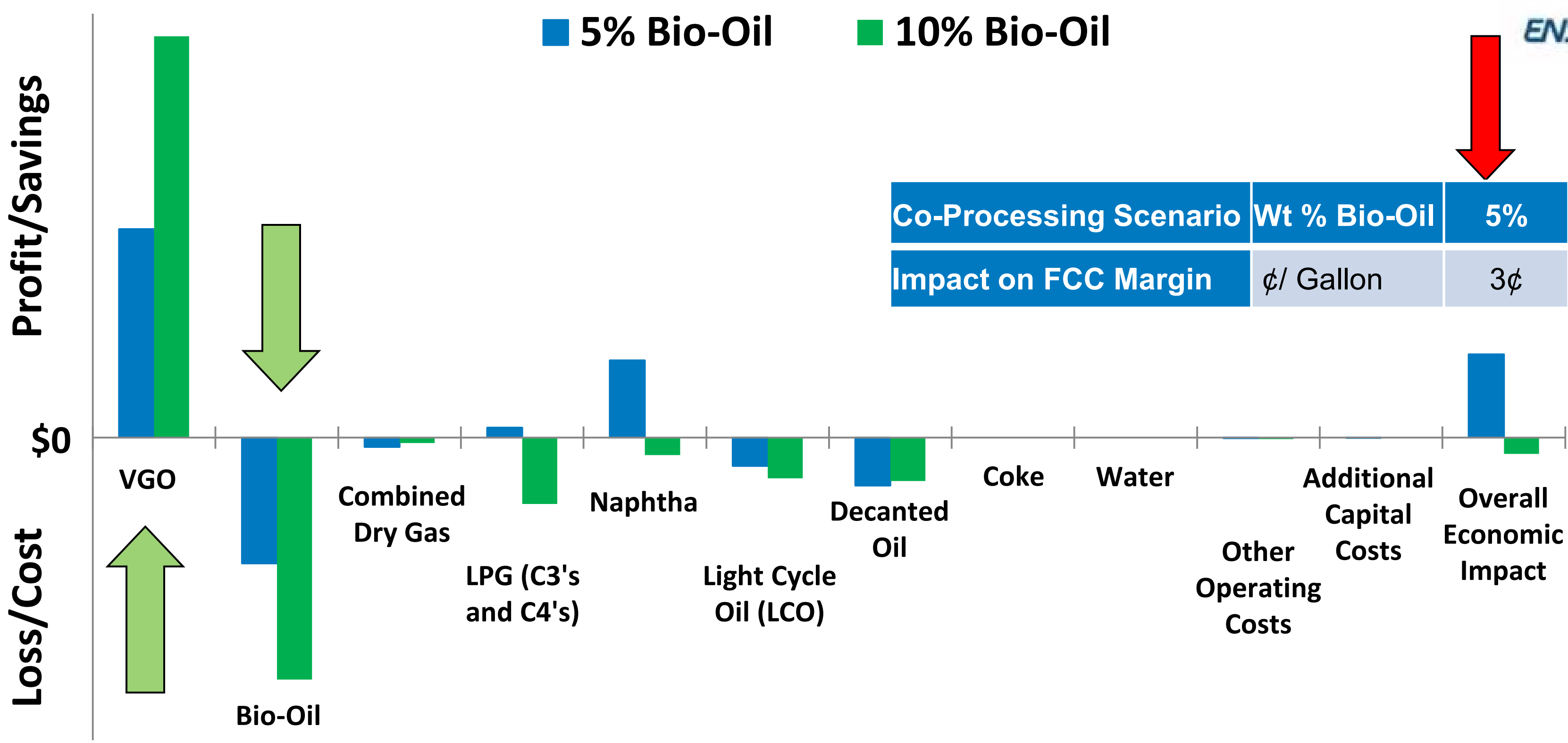


Initial **techno-economic analysis** represents feasibility study

- Provides justification for continuing project effort (Go / No-Go)
- Establishes basis for sustainability and impact analysis (Relevance)

3 – Accomplishments and Results

Relative Magnitude of Additional Costs and Profits

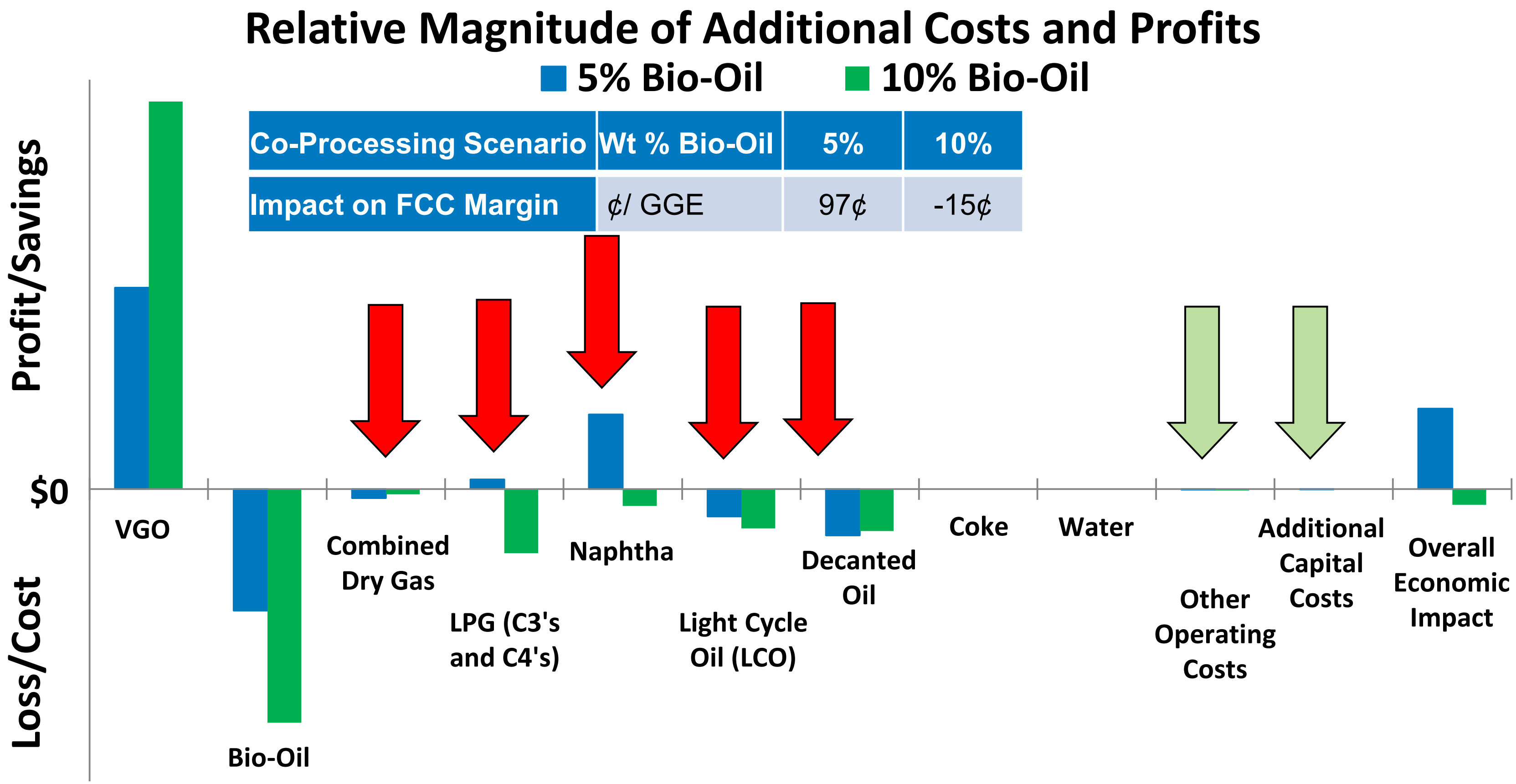


Co-Processing Scenario	Wt % Bio-Oil	5%	10%
Impact on FCC Margin	¢/ Gallon	3¢	-1¢

Overall blending has a positive impact on profits for 5% bio-oil, slightly negative for 10% Bio-oil. Process not optimized

Most significant impact on profitability is the cost of feed to the FCC Unit

3 – Accomplishments and Results



Co-Processing Scenario	Wt % Bio-Oil	5%	10%
Impact on FCC Margin	¢/ GGE	97¢	-15¢

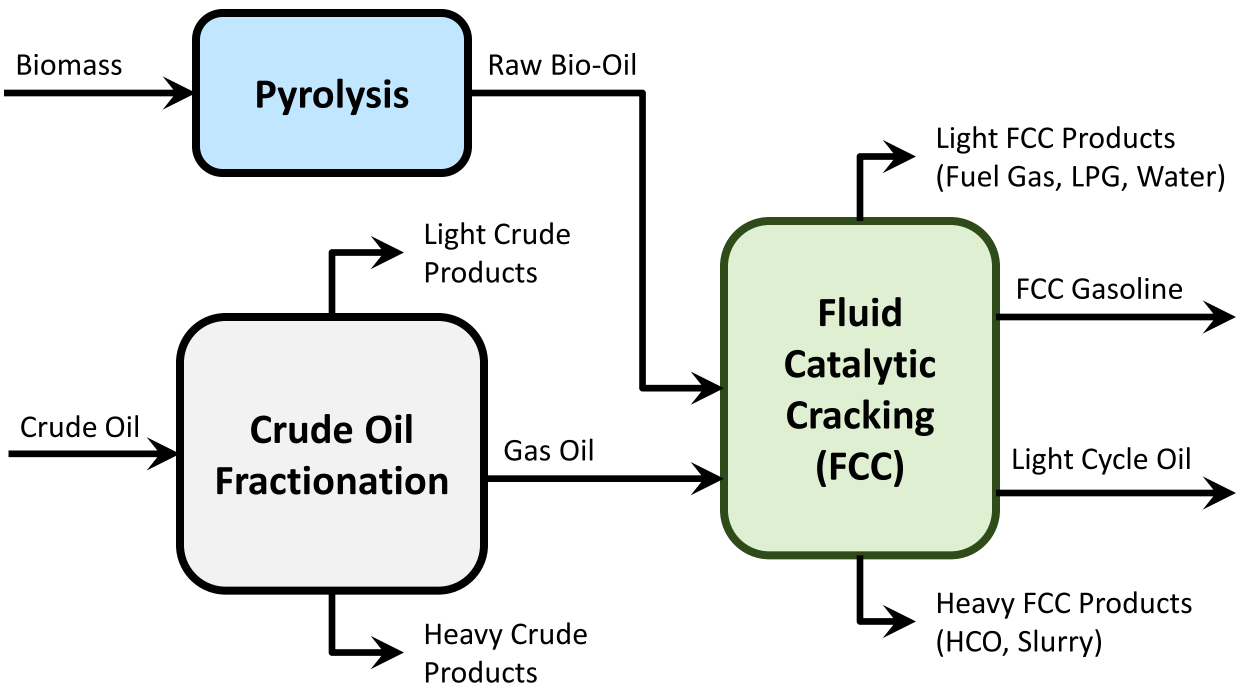
- **Value of products have less significant impact relative to feed cost, but is significant relative to the overall economic impact**
- **Additional capital and operating costs are insignificant compared to the value of VGO, bio-oil, and FCC products**

4 – Relevance

Impact of Co-Processing: 50,000 Barrel / Day FCC Unit

Bio-Oil Ratio	Feedstock	Raw Bio-Oil	Products
5 wt%	500,000 Tons / Yr	300 MM Lb / Yr	28 MM GGE / Yr
10 wt %	1,000,000 Tons / Yr	600 MM Lb / Yr	36 MM GGE / Yr

Note: 5 wt % bio-oil in FCC equates to ~3.9 vol % due to substantially higher density of bio-oil relative to VGO



Roughly same fuel energy obtained from 1,000 – 1,200 ton/day cellulosic fuel facility with minimal refinery investment

Potential Impact of FCC Co-Processing

	FCC Capacity (Barrels / Day)	**FCC Capacity** (MM Gal / Yr)	**5 wt % Bio-Oil Products** (MM Gal / Yr)	**10 wt % Bio-Oil Products** (MM Gal / Yr)
TEA Basis	50,000	770	28	36
Brazil	587,000	9,000	330	420
United States	6,000,000	92,000	3,300	4,300
World	14,600,000	224,000	8,100	10,400

	Annual Biomass demand, Million Tons	Annual Biomass–Derived Products, Billion GGE (Billion Gal EtOH Equiv.)
U.S.A.	50-70	3.3 (5.0-6.5)
World	130-170	8.1-10.4
UN SE4ALL initiative, 2030 projected*		60 (advanced) 100 (conventional)

*IRENA (2014), REmap 2030: A Renewable Energy Roadmap, Summary of Findings, June 2014.

FCC co-processing has potential to contribute significantly towards U.S. and global volumetric biofuel goals

5 – Future Work

Next Steps

- Petrobras SIX data obtained after July 2014 will be incorporated into the TEA by NREL
- Comparative LCA with and without bio-oil will be conducted
- ENSYN Corp. will prepare the bagasse pyrolysis oils from bagasse in preparation by INL
- Bagasse oils to be shipped to Petrobras for co-processing

Key Upcoming Milestones

- TEA modeling, sensitivity analysis, and initial LCA by 6/30/15
- Final CRADA report by 9/31/15

Publish Results

- Publish three (3) papers in peer reviewed literature

Project Summary

- Petrobras and NREL selected a commercial pyrolysis oil supplier
- Ensyn Corp. provided 2000 gallons of pine pyrolysis oil to Petrobras demonstration unit SIX, through its partnership with Fibria Celulose, Brazil
- By 12/2013, Petrobras SIX operated continuously its demonstration FCC unit at 200 kg/hour for 70 hours producing coprocessed VGO and bio-oil, without problems. Subsequent distillation isolated gasoline and diesel fractions.
- The SIX facility produced significant technical data of coprocessing analyzed by Petrobras CENPES and shared with NREL to generate the preliminary TEA
- Fibria shipped 400 gallons each of gasoline and diesel to the U.S. (3/2014)
- A cumulative 400 hours of operation of the SIX unit coprocessing VGO and bio-oils was completed
- Preliminary NREL TEA results:
  - 5 wt.% bio-oil VGO is positive economically relative to just VGO processing
  - 10 wt.% changes in product slate has slightly negative economics vs. VGO
  - Impact of 5% bio-oil in 50,000 bbd FCC co-processing similar to 1,000 – 1,200 ton per day cellulosic fuel facility with minimal refinery investment
  - FCC co-processing has the potential to contribute significantly towards U.S. (RFS2) and global (UN Sustainable Energy for All) volumetric biofuel goals

Thank You

Petrobras Project Collaborators and Supporters

US Department of Energy:
BETO: Steven Thomas (POC), Kevin Craig, Nichole Fitzgerald, Prasad Gupte, Liz Moore (*TC Conversion*); Zia Haq, Kristen Johnson, Alison Goss Eng, Alicia Lindauer (*Analysis & Sustainability*)
DOE EERE International: Rob Sandoli
DOE International: Rhianon Davis

U.S. Dept. of State: Dan Birns

NREL: Helena Chum (POC) *Chemical analysis*: Kim Magrini, Steve Deutch, David Templeton, S. Black; *Technoeconomic Analysis*: Mike Talmadge, Chris Kinchin, Mary Biddy; *Fuel characterization*: Earl Christensen, Bob McCormick; *Sustainability:* Helena Chum, Yimin Zhang; *Management:* Adam Bratis, Mark Davis,
Tom Foust ; C*RADA and Materials Transfer Agreements with Ensyn*: Anne Miller, Eric Payne, Rich Bolin, LaNelle Owens.

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Petrobras/CENPES:

Biomass Conversion (Process):
Andrea Pinho (POC), Marlon Almeida, Vitor Ximenes, Fabio Mendes,

CENPES Analytical: Marco Antonio Gomes, Rosana Cardoso, Roberta M. T. de Mattos, L. Alexandre Sacorague

Sustainability: Cristiano Machado Silveira

*Managemen*t: Andre Fachetti, Raul Rawet, Alipio Ferreira Pinto Jr., Oscar Chamberlain

Petrobras/SIX

Maicon Tait, Luiz Carlos Casavechia, and their Research Production Teams

ENSYN Corporation:

Bob Graham, Barry Freel, Raymond Pirraglia

FIBRIA Celulose:

Centro de Tecnologia Aracruz

Matheus Antunes Guimarães

Additional Content for Reviewers

- Key numbers used in the TEA
- Future Project Milestones
- Responses to Comments from 2013 Peer Review
- References used in the Peer Review Presentation
- Project and related partner Publications, Presentations, Commercialization, IP
- List of Acronyms and Abbreviations
- Additional Slides for Petrobras – NREL CRADA Project

Key numbers for the TEA

Price Basis for Techno-economic Analysis (TEA)

Intermediate or Product	Value	Source
Biomass	$80/dry U.S. ton	DOE-BETO funded efforts at INL
VGO	$2.38/gal	OPIS, Bloomberg
Bio-oil	$1.43/gal	DOE, discussed with Ensyn
Dry Gas	$0.26/kg	EIA, valued as NG based on heating value
LPG	$1.65/gal	OPIS
Naphtha	$2.48/gal	OPIS, Bloomberg
LCO	$2.59/gal	OPIS
Decanted Oil	$1.55/gal	Discussed with Ensyn

Future Project Milestones

Milestones

Milestone Name/Description	End Date	Type
Technoeconomic analysis (TEA) and scope of lifecycle analysis (LCA).Report will define the conditions for the lifecycle analysis to be followed and will provide more robust data than the preliminary report in FY2014.	12/31/2014	Quarterly Progress Measure (Regular) ✓
Project will report at the Peer review presentation with the Petrobras PI presenting the process information and NREL discussing some of the modeling conducted to date and status of the chemical analysis. Presentation will also outline any remaining tests and expected timeline for completion.	3/31/2015	Quarterly Progress Measure (Regular) ✓ Peer Review
Technical write-up that summarizes results of TEA estimation and outline at least 3 sensitivity analysis cases that will be considered.	6/30/2015	Quarterly Progress Measure (Regular)
A final report of the project that summarizes the following key results for at least 2 different co-processing scenario consideration: 1) Assessment of Petrobras upgraded ENSYN pyrolysis oils products and it's applicability in US operations. 2) Techno-economic analysis of the process will assess costs with sensitivities for how the modifications would need to be made to represent US conditions. 3) LCA results compared to petroleum refining without biomass pyrolysis oils. 4) Properties of the gasoline and diesel products coproduced with pine pyrolysis oils and upgraded in the U.S. 5) Comparison of the direct pyrolysis oils routes with others using hydrotreating that the BETO program modelled. 6) Areas of major uncertainties will be highlighted (e.g., long term catalyst testing in FCC units).	9/30/2015	Annual Milestone (Regular)

Responses to Comments from 2013 Review

Responses to Previous Reviewers' Comments: Applicability of the CRADA results to the U.S.

- At the 2013 peer review the project was 3 mo. old. The described work focused on the feedstocks for the small scale experimentation at Petrobras. The difficulty of exchanging samples between the U.S. and Brazil was delaying the project. As we could not complete the preparation of the bagasse pyrolysis oils, we abandoned small scale coprocessing at Petrobras for additional demonstration scale testing. The prepared oak pyrolysis became the reference for the analytical methodology.
- The SIX facility for the CRADA work at >100 kg/hour required a commercial supplier of pyrolysis oils able to supply and deliver 3-5 tonne samples to Brazil. Taking into consideration the comments from the peer reviewers, we selected a feedstock that was applicable to the U.S. and more broadly to North America, well studied in BETO projects.
- ENSYN Corp. was starting to offer a heating oil product, the renewable fuel oil (RFO™) and had a joint venture with the pulp and paper Brazilian company, Fibria. Fibria also has shipping capabilities.
- The CRADA partners selected ENSYN Corp. as the supplier and in this way, the milestone of delivering oils to Petrobras for coprocessing was met ahead of schedule in November 2013, and by the end of the year, SIX was testing and producing 5 wt% of coprocessed VGO with pine (RFO™) products for further distillation into naphtha and LCO products for hydrogenation and engine testing in the U.S.
- ENSYN Corp. will also produce 3-5 tonne samples of bagasse (from the U.S.) for coprocessing with VGO at Petrobras SIX facility, a more relevant feedstock for Brazil and all countries producing sugarcane commercially with refineries.

Responses to Comments from 2013 Review

Responses to Previous Reviewers' Comments: Availability of Results to the U.S.

- The Publications section reports the initial research results of Petrobras, prior to the CRADA, that appeared in the published peer reviewed literature in March 2014 in electronic format: Production of lignocellulosic gasoline using fast pyrolysis of biomass and a conventional refining scheme.
- Results obtained by Petrobras in Brazil with pine pyrolysis oils are being converted to a situation in the U.S. (or other parts of the world where refineries purchase petroleum and commercial intermediates). The difference in performance of the VGO and the cases of co-processing with bio-oil will be converted into a technical, economic, and lifecycle analysis and will be published.

Oil Stability Issues

- ENSYN Corp. RFO received by Petrobras in November 2013 only had to be disposed of in November 2014 for severe increase in viscosity and phase separation. Went through a very hot summer in Brazil.
- NREL's oak pyrolysis oils samples (5) prepared in 2012 by NREL (1-micron cold filtered and cold stored at NREL) were shipped by NREL to Petrobras. In transit the samples were retained in customs during the summer of 2013. NREL's oils were single phase. Analysis at NREL and Petrobras of the oils shows that the cold stored and aged samples were identical within experimental error for elemental composition. GCxGC-TOFMS identified similar compounds for the volatile part.
- ENSYN Corp. RFO had two phases and was more difficult to homogenize for chemical analyses than the oak oil.

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for Peer Review Presentation

PETROBRAS

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- **DE MIGUEL MERCADER; GROENEVELD, M.J.; KERSTEN, S.R.A.; WAY, N.W. SCHAVERTEN, C.J.; HOGENDOORN, J.A. Production of advanced bio-fuels: Co-processing of upgraded pyrolysis oil in standard refinery units. Applied Catalysis B: Environmental. v. 96, p. 57-66, 2010.**

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- de Rezende Pinho, A., B. de Almeida Marlon Brando, L. Mendes Fabio and L. Ximenes Vitor (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).
- 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.
- 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.

Petrobras Journal Publication

http://asp-br.secure-zone.net/v2/index.jsp?id=2225/6153/6434 in Portuguese, Following pages present the original Portuguese and translated vesions.

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." (translated from Portuguese).

This publication describes the efforts that SIX undertook to modify the facility to perform the CRADA work.

Commercialization

KEY BARRIER
Commercial Bio-Oil Suppliers

ENSYN

IEA Bioenergy

Task 34 - Pyrolysis

Welcome to Task 34

By Doug Elliott, Task 34 Leader

PyNe 36
January 2015
ISSN 2040-2759

http://www.pyne.co.uk/?_id=49

RFO™= Ensyn's Renewable Fuel Oil

Ensyn providing RFO heating oil to New Hampshire hospitals

Page 13

Progress at Ensyn

Page 14

Bob Graham of Ensyn in the USA reflects on the company's successes and looks to the future

"Ensyn alliances with leading industrial partners with progressive vision, and this is our plan for the future. Our current strategic relationships include those with UOP, Fibria Celulose, Chevron Technology Ventures, Petrobras/NREL and Credit Suisse. We look forward to working with these valued partners and adding others as we work to make Ensyn the world's leading producer of cellulosic liquid fuels."

Contact
Dr. Robert Graham
c/o Ensyn Technologies Inc.
2 Gurdwara Road
Ottawa, Ontario
K2E 1A2
Canada

T: +1 (613) 248 2257

ENSYN

Page 17

See also: Cellulosic game changer, Bioenergy Insight, Volume 5, Issue 6, pp58-59, December, 2014; http://www.marketexchange.com/2014_Platts/Day%202/Lee_Torrens.pdf; http://www.nararenewables.org/2014conference/wp-content/uploads/2014/05/TallmanNWBCC2014p.pdf

Figure 1: Ensyn has recently enhanced its Ontario facility, converting it to a dedicated fuel facility with a capacity of three million gallons/year.

IP: ENSYN's recent patents issued

US 20150005547A1

(19) **United States**
(12) **Patent Application Publication** (10) **Pub. No.: US 2015/0005547 A1**
Freel et al. (43) **Pub. Date: Jan. 1, 2015**

(54) **SYSTEMS AND METHODS FOR RENEWABLE FUEL**

(71) Applicant: **Ensyn Renewables, Inc.**, Wilmington, DE (US)

(72) Inventors: **Barry A. Freel**, Ottawa (CA); **Robert G. Graham**, Ottawa (CA)

(21) Appl. No.: **14/314,785**

(22) Filed: **Jun. 25, 2014**

Related U.S. Application Data

(60) Provisional application No. 61/839,832, filed on Jun. 26, 2013.

Publication Classification

(51) **Int. Cl.**
C10L 1/04 (2006.01)
(52) **U.S. Cl.**
CPC ***C10L 1/04*** (2013.01)
USPC **585/14**

(57) **ABSTRACT**

The present application generally relates to the introduction of a renewable fuel oil as a feedstock into refinery systems or field upgrading equipment. For example, the present application is directed to methods of introducing a liquid thermally produced from biomass into a petroleum conversion unit; for example, a refinery fluid catalytic cracker (FCC), a coker, a field upgrader system, a hydrocracker, and/or hydrotreating unit; for co-processing with petroleum fractions, petroleum fraction reactants, and/or petroleum fraction feedstocks and the products, e.g., fuels, and uses and value of the products resulting therefrom.

US 20150000186A1

(19) **United States**
(12) **Patent Application Publication** (10) **Pub. No.: US 2015/0000186 A1**
Freel et al. (43) **Pub. Date: Jan. 1, 2015**

(54) **GENERATING CELLULOSIC-RENEWABLE IDENTIFICATION NUMBERS IN A REFINERY**

(71) Applicant: **Ensyn Renewables, Inc.**, Wilmington, DE (US)

(72) Inventors: **Barry A. Freel**, Ottawa (CA); **Robert G. Graham**, Ottawa (CA)

(21) Appl. No.: **14/487,575**

(22) Filed: **Sep. 16, 2014**

Related U.S. Application Data

(63) Continuation of application No. 13/709,822, filed on Dec. 10, 2012.

(60) Provisional application No. 61/569,712, filed on Dec. 12, 2011, provisional application No. 61/646,152, filed on May 11, 2012, provisional application No. 61/673,683, filed on Jul. 19, 2012.

Publication Classification

(51) **Int. Cl.**
C10L 1/18 (2006.01)
(52) **U.S. Cl.**
CPC ***C10L 1/1802*** (2013.01)
USPC **44/307**

(57) **ABSTRACT**

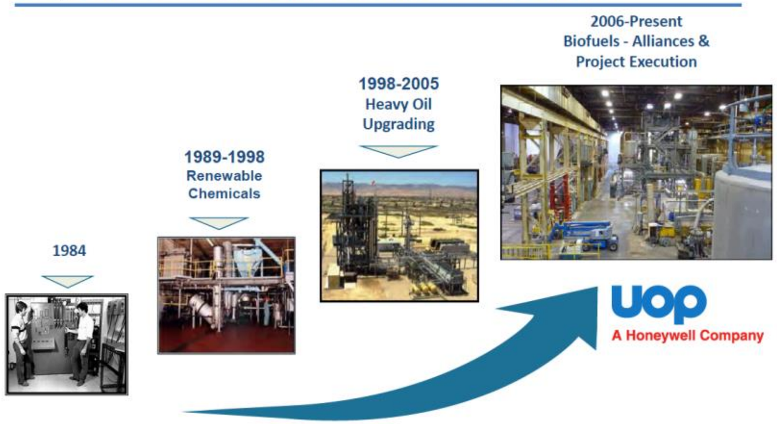
The present application generally relates to methods of generating cellulosic-renewable identification numbers by thermally processing a cellulosic biomass to form a renewable fuel oil, and then co-processing the renewable fuel oil with a petroleum fraction in a refinery to form a cellulosic-renewable identification number-compliant fuel.

http://stks.freshpatents.com/Ensyn-Renewables-Inc-nm1.php

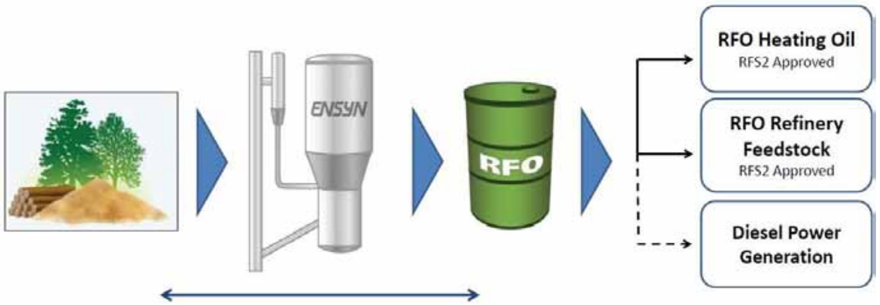
Count	Application #	Date	**Ensyn Renewables, Inc. patents** (updated weekly) - BOOKMARK this page
1	20150000186	01/01/15	Generating cellulosic-renewable identification numbers in a refinery
2	20150004062	01/01/15	Systems for fuels from biomass
3	20150004067	01/01/15	Fluidized catalytic cracking apparatus
4	20150005547	01/01/15	Systems and methods for renewable fuel
5	20150005548	01/01/15	Methods to increase gasoline yield
6	20150005549	01/01/15	Preparing a fuel from liquid biomass
7	20140363343	12/11/14	Apparatuses and methods for controlling heat for rapid thermal processing of carbonaceous material
8	20140053456	02/27/14	Systems and methods for the devolatilization of thermally produced liquids
9	20130333278	12/19/13	Low water biomass-derived pyrolysis oils and processes for producing the same
10	20130327629	12/12/13	Char-handling processes in a pyrolysis system
11	20130145683	06/13/13	Systems and methods for renewable fuel
12	20100236915	09/23/10	Mitigation of deposits and secondary reactions in thermal conversion processes
13	20130327629	12/12/13	Char-handling processes in a pyrolysis system

Commercialization

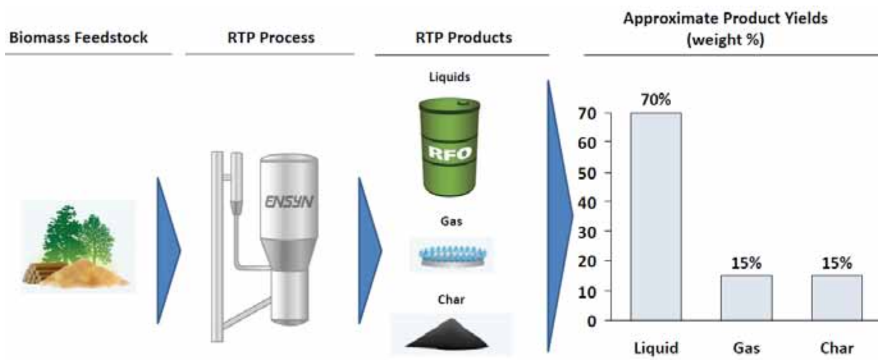
30 years of successful commercialization



CREDIT SUISSE IMPAX Chevron Fibria FPI FELDA PALM INDUSTRIES ENSYN



Modular facilities, located near the biomass feedstock, producing 5-20 million gallons year of RFO



From solid biomass to liquid fuels in less than 2 seconds

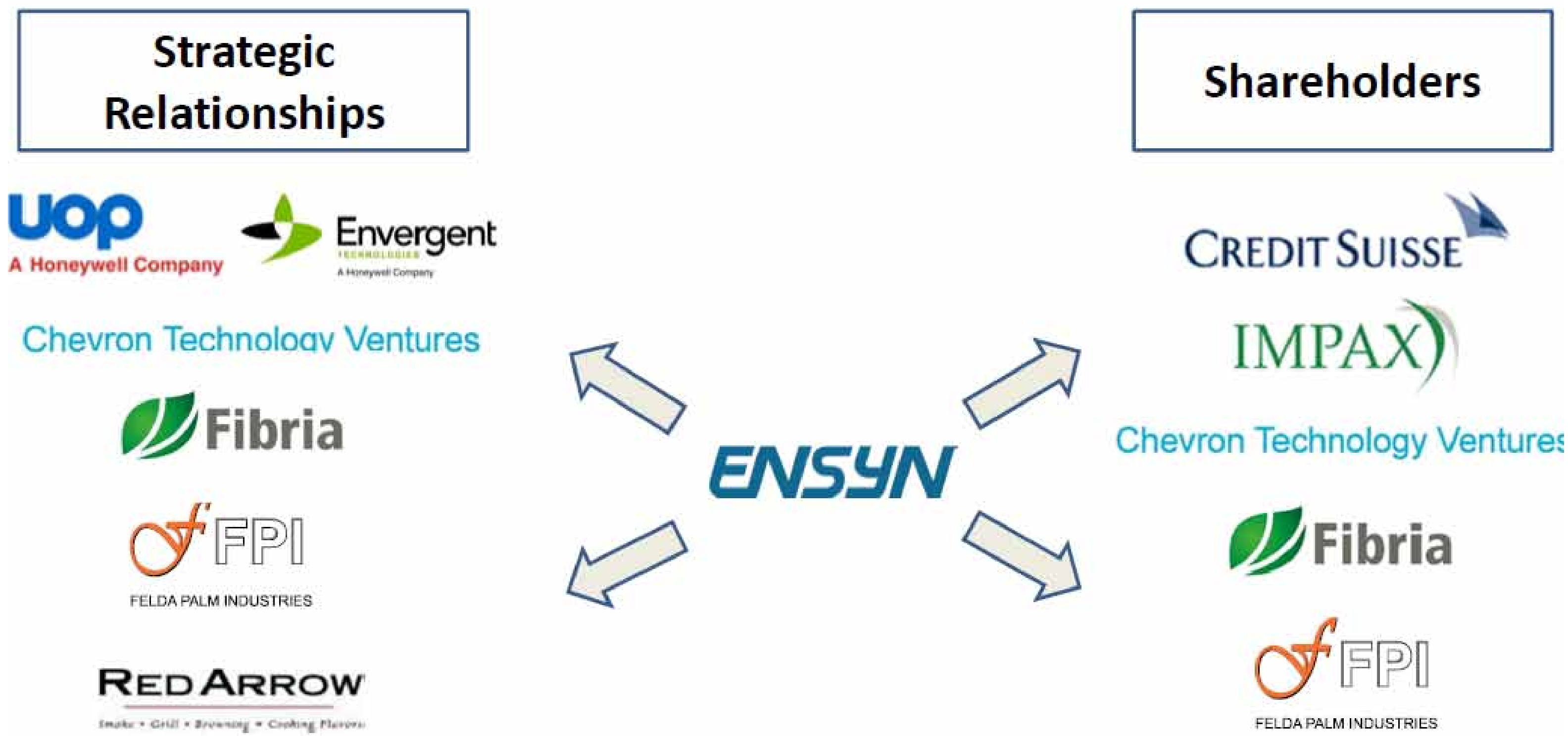
- Non-catalytic process maximizes carbon conversion from solid biomass to liquid fuels – and generates high liquid yields
- Gas and Char co-products used as source of energy to run the facility

Capacity Expansion –RTP5 & RTP 20 Facilities

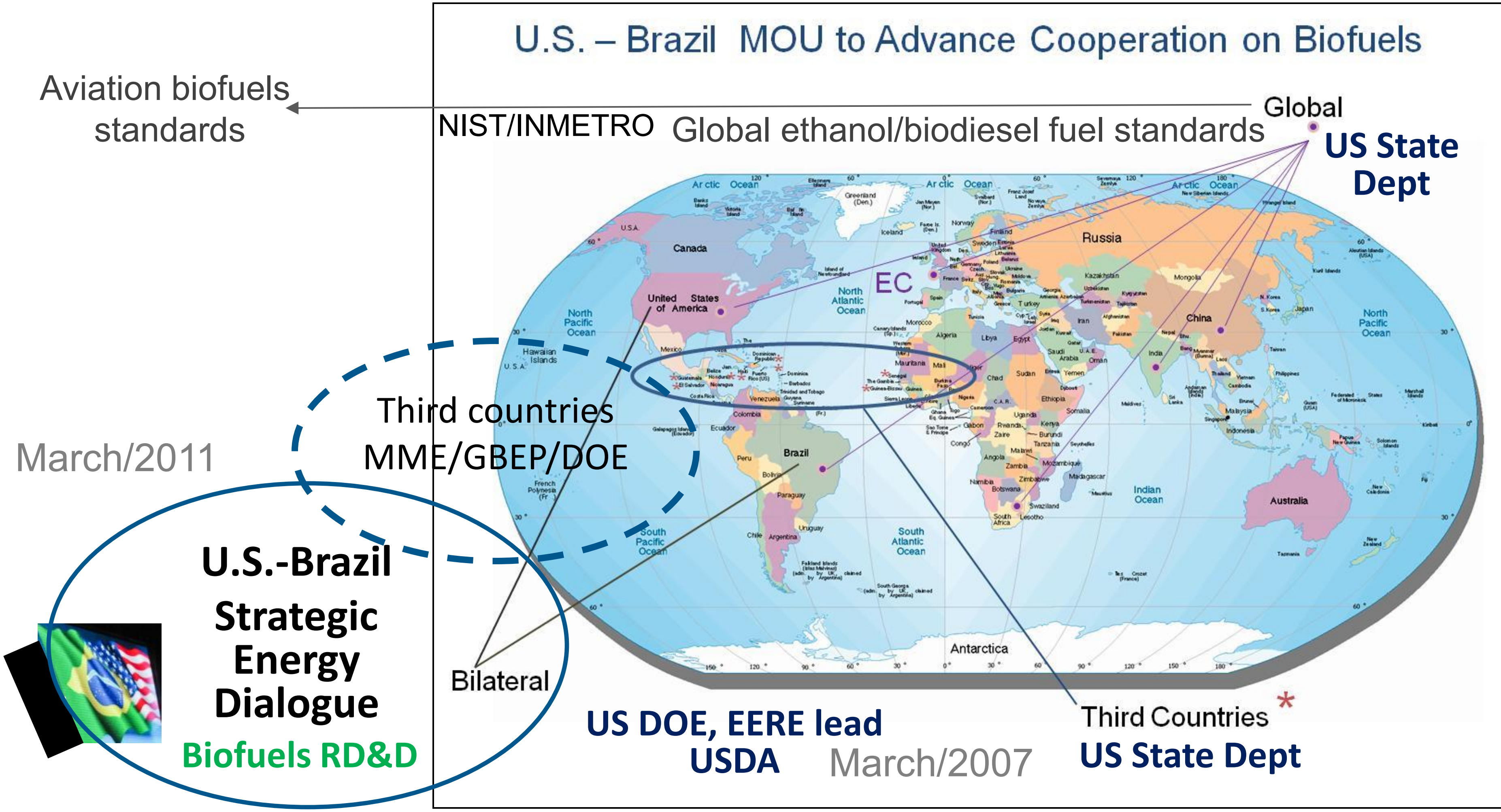
ENSYN	RTP5	RTP20
Project Cost	$25-35 million	$90-120 million
Feedstock Capacity	100 BDMT/day	400 BDMT / day
Liquid Production	~ 5 million gpy	~ 20 million gpy
Feedstock Cost	$50-100 / BDMT	$50-100 / BDMT
Production Costs	Capex: ~$5-6 /gpy Opex: ~$1.20/gallon	Capex: ~$5-6 /gpy Opex: ~$1.20/gallon

ENSYN

Petrobras/NREL CRADA provided critical large scale samples to Ensyn and partners for product quality assessment



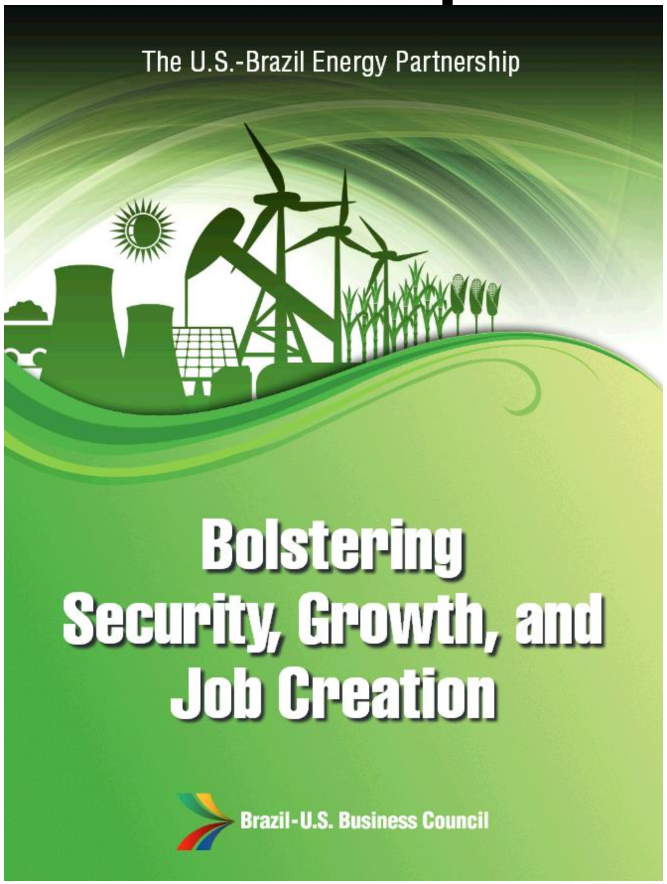
Cooperation Frameworks



Brazilian Government Ministries: Science, Technology and Innovation (MCTI); Mines and Energy (MME); Development, Industry and Foreign Trade (MDIC); Agriculture, Livestock and Supply (MAPA) -- led by the Ministry of External Relations

Strategic Energy Dialogue

Partnership Activities



http://www.brazilcouncil.org/sites/default/files/Braz

Mission

Foster understanding among the private and public sectors in Brazil and the United States to maintain and advance trade and investment between both countries through free trade, free markets, and free enterprise.

Major U.S.-Brazil Energy-Related Agreements	
1995	U.S.-Brazil Common Agenda on **Environment**
1997	Agreement for Cooperation Concerning Peaceful Uses of **Nuclear Energy**
1997	Implementing Agreement for Cooperation in the Area of **Energy Technology**
2003	MOU for the Establishment of a Mechanism for Consultations on **Energy Cooperation**
2007	MOU to Advance Cooperation on **Biofuels**
2010	MOU on Cooperation Regarding **Climate Change**
2010	U.S.-Brazil Binational Energy Working Group **Joint Action Plan**
2011	Partnership for the Development of **Aviation Biofuels**
2012	U.S.-Brazil Commercial Dialogue **Energy Work Plan**

Council Recommendations

(relevant)

- Establish a U.S.-Brazil work plan to create a global biofuels market detailing joint efforts at the bilateral, trilateral, regional, and multilateral levels, including joint action at the G-20, the United Nations Food and Agriculture Organization (FAO), and the World Trade Organization (WTO).

DOE Report: http://www.ourenergypolicy.org/wp-content/uploads/2013/07/US-Brazil-Energy-Dialogue-.pdf
US State Department summary: http://www.state.gov/r/pa/ei/bgn/35640.htm

List of Acronyms & Abbreviations (1)

ACE	Advanced Cracking Evaluation
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
EtOH	Ethanol
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

List of Acronyms & Abbreviations (cont.)

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

Additional Slides from Petrobras

1. Translation of Petrobras Journal article explaining modifications made at its SIX demonstration unit to conduct the CRADA
2. Additional detailed coprocessed fuel information from the CRADA project

Petrobras

Supply Journal

Year 7, Number 67, October 2014

(Petrobras) SIX RESEARCH co-processing pyrolysis oils from wood processing residues (bio-oil). Successful tests may enable production of gasoline and diesel from cellulosic feedstocks in a conventional refinery.

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.

VISÃO DE FUTURO

14

Fuel ecologically correct

Combustível ecologicamente correto

SIX PESQUISA PROCESSAMENTO DE BIO-ÓLEO DE SERRAGEM. SUCESSO DOS TESTES PODERÁ VIABILIZAR A PRIMEIRA ROTA DE GASOLINA E DIESEL CELULÓSICOS DO MUNDO, PRODUZIDOS EM REFINARIA CONVENCIONAL

A primeira etapa realizada na SIX foi o craqueamento do bio-óleo na Unidade de Multipropósito de FCC (U-144)

Figure Caption: The first step, bio-oil cracking, was performed at SIX FCC Multipurpose Unit (U-144)

PETROBRAS

"Com essas baterias de testes a SIX comprova que o nosso parque de pesquisa é um local adequado para fazer testes especiais que não são possíveis em outras refinarias"

Maicon Tait - engenheiro de processamento (SIX/PQ)

A Petrobras tem investido em pesquisa e desenvolvimento de combustíveis mais amigáveis ao meio ambiente. Neste sentido, a biomassa para fins energéticos possui vantagens ambientais, em virtude de seu caráter renovável e de sua contribuição para a redução dos gases de efeito estufa.

Por conta disso, processar bio-óleo produzido a partir de processo termoquímico (pirólise) da serragem de madeira para a produção de nafta e *Light Cycle Oil (LCO)*, corrente que possui a mesma faixa de destilação do diesel, tem sido um dos grandes desafios recentes das Unidades de Pesquisa e das equipes da SIX.

O bio-óleo de serragem, produzido no Canadá pela Ensyn, apresenta várias características indesejáveis, tais como teor de oxigênio e água elevados, acidez alta, alguma instabilidade química e menor poder calorífico. Sendo assim, não é possível utilizá-lo como um combustível convencional, sendo necessário convertê-lo em correntes de melhor qualidade. Uma das rotas estudadas é o craqueamento catalítico, tecnologia de amplo domínio pela Petrobras.

"Não seria possível desenvolvermos essa rota sem uma unidade de maior porte de FCC como a U-144. Outros grupos no mundo já haviam tentado processar bio-óleo em escalas menores, mas os resultados eram péssimos, justamente pelos problemas de dispersão de carga, que não podem ser resolvidos em escala de laboratório. O bio-óleo não se mistura com as correntes fósseis. Logo, em escalas pequenas, com um único dispersor, torna-se necessário utilizar um emulsificante, o que distorce os resultados e dificulta sua interpretação. A dispersão de carga torna-se muito prejudicada, pois não é possível aquecer as linhas de alimentação sem coqueá-la. Na U-144, esse problema foi resolvido pela injeção segregada das correntes fóssil e renovável em pontos de dispersão diferentes, tornando possível que a corrente fóssil seja aquecida normalmente, enquanto o bio-óleo é mantido a 40°C", explica a engenheira de processamento e consultora sênior do Cenpes/PDAB/CB Andrea de Rezende Pinho.

Dessa forma, em laboratório os rendimentos de coque são sempre muito elevados, indicando a inviabilidade do uso do bio-óleo, mesmo em proporções baixas, de 5 a 10%, em relação ao gasóleo, enquanto em escala de demonstração na SIX, o processamento de até 10% de

The thermo-chemical process (pyrolysis) Transforms the wood biomass residues Into a bio-oil.

A partir de processo termoquímico (pirólise) a serragem de madeira, é convertida para produção do bio-diesel

"With these series of tests SIX is proving that our Research Park is a suitable place to make special tests that are not possible in other refineries"
Maicon Tait - processing engineer (SIX / Pq)

Petrobras has invested in research and development of friendlier fuels on the environment. In this sense, the biomass for energy purposes has environmental advantages because of its renewable nature and its contribution to reducing greenhouse gas emissions.

As a result, processing bio-oil produced from thermochemical process (pyrolysis) of wood residues to produce naphtha and Light Cycle Oil (LCO), stream having the same diesel distillation range, has been a major recent challenges of the Research and Production teams at SIX.

The sawdust from bio-oil, produced in Canada by Ensyn Corp., has several undesirable characteristics such as high content of oxygen and water, high acidity, some chemical instability, and low heating value. Therefore, you cannot use it as a conventional transport fuel, being necessary to improve its quality. One of the routes studied is the catalytic cracking, a field of technology of great expertise at Petrobras.

"It would not be possible to develop this route without a larger FCC unit as the U-144 (see Figure). Other groups in the world had tried to process bio-oil in experiments conducted in small scale reactors, but the results were very bad with feeding problems that cannot be resolved at the laboratory scale. Bio-oil does not mix with fossil fuel processing streams. Therefore, at small scales, with a single dispersing point, it is necessary to use an emulsifier, which distorts the results and makes their interpretation difficult. The feed dispersion becomes greatly impaired as it is not possible to heat the feeding lines without coking them. In U-144, this problem was solved by injection of fossil and renewable currents in different feed nozzle axial points, making it possible to heat the fossil fuel normally, while the bio-oil is kept at 40 ° C, "explains the engineer processing and senior consultant of CENPES / PDAB / CB Andrea de Rezende Pinho.

Thus, while laboratory scale results show very high coke yields, indicating that bio-oil co-processing, even at low proportions of 5 to 10% of the heavy gas oil is inviable, demonstration scale results from the SIX U-144, processing up to 10%

PETROBRAS

Figure Caption: Processing bio-oil for the production of naphtha and Light Cycle Oil (LCO) has been one of the major challenges of the research teams of SIX.

Foto Larissa Drabeski / Acervo SIX

Processar bio-óleo para a produção de nafta e *Light Cycle Oil (LCO)* tem sido um dos grandes desafios das equipes da SIX

bio-óleo não altera significativamente o fator operacional e os rendimentos do FCC, mostrando resultados mais rentáveis e próximos à realidade comercial. Em resumo, nesse caso, a escala utilizada mostrou-se especialmente importante. Quanto maior a escala, melhores os resultados do bio--óleo, o que acabou por resgatar uma rota inicialmente descartada em nível mundial.

O processamento faz parte de um acordo de cooperação entre a Petrobras, uma companhia de petróleo americana, e o *National Renewable Energy Laboratory (NREL)*, laboratório pertencente ao Departamento de Energia americano. A hidrogenação da nafta e do LCO está sendo realizada nos EUA. Posteriormente, serão feitos testes de emissão para certificação americana como combustível de origem celulósica. O NREL irá calcular ainda a redução nas emissões de gases de efeito estufa alcançada através desta rota.

"Se formos bem-sucedidos, teremos viabilizado a primeira rota de gasolina e diesel celulósicos do mundo produzidos em uma refinaria convencional", assinala Andrea.

Craqueamento

A primeira etapa realizada na SIX foi o craqueamento do bio-óleo na Unidade de Multipropósito de FCC (U-144). Inicialmente, foram realizados diversos testes variando temperatura de reação e a percentagem de bio-óleo em relação à carga normal da unidade (gasóleo pesado). Nos testes, a corrente de bio-óleo foi injetada num determinado ponto do riser (reator) e a carga normal em outro ponto. Uma tarefa desafiadora foi o processamento de 100% do bio-óleo na U-144, em função da facilidade de polimerização, ou seja, formação de goma nos compostos presentes no bio-óleo.

"É um produto difícil de ser trabalhado porque em temperatura pouco acima de 50°C se degrada e em temperatura abaixo de 15°C não escoa, devido à alta viscosidade, mas com a ajuda de técnicos de operação, manutenção e engenharia conseguimos desenvolver um sistema que permite a injeção de bio-óleo puro no riser da U-144", esclarece o engenheiro de processamento e consultor da Gerência de Pesquisa da SIX (SIX/PQ), Luiz Carlos Casavechia.

Para o craqueamento desse produto, a U-144 passou por duas semanas de intervenções para alterar o injetor de carga, o sistema de mistura e o sistema de aquecimento, de modo que a temperatura do bio-óleo ficasse estável a 40°C e o produto escoasse adequadamente sem se degradar.

Além dos testes já descritos, foram produzidos 10 m³ de óleo oriundo do craqueamento de 5% de bio-óleo e 95% de Gás Óleo Pesado (GOP), que foram enviados à Unidade de Destilação U-2110 para obtenção de dois cortes, nafta e LCO.

bio-oil does not alter significantly the operational factor and FCC yields, showing the potential for more profitable results, near commercial reality. In summary, in this case, going to a larger scale was proved to be especially important. The higher the scale of the tests, the better the bio - oil results became, rescuing a route initially ruled out nearly worldwide.

The processing is part of a cooperation agreement between Petrobras, an American oil company, and the National Renewable Energy Laboratory (NREL), a laboratory of the US Department of Energy. Hydrogenation of naphtha and LCO is being conducted in the USA. Subsequently, emission tests will be made for American certification as cellulosic fuel source. NREL will also evaluate the reduction in greenhouse gases achieved by this route.

"If we succeed, we will have made possible the first route of cellulosic gasoline and diesel produced in the world in a conventional refinery," says Andrea.

Cracking

The first step conducted at SIX FCC Multipurpose Unit (U-144) was the cracking. Initially, several tests were conducted by varying the reaction temperature and the proportion of bio-oil and the normal FCC feedstock (heavy gas oil, VGO). In these tests, the bio-oil stream was injected at a point of the riser (reactor) and the fossil feed at another point. A challenging task was processing 100% bio-oil in the U-144, which easily polymerizes upon heating, leading to gums.

"It is a difficult product to be worked because at temperatures slightly above 50 ° C it degrades and at temperatures below 15 ° C does not flow because of the high viscosity of the oil. In two weeks, the SIX teams of technical operations, maintenance and engineering developed a system which allowed the injection of pure bio-oil in the U-144 riser", explains the processing engineer and consultant to the SIX Research Department(SIX / PQ), Luiz Carlos Casavechia.

To feed bio-oil at a stable temperature of 40 ° C into U-144 reactor, the feed nozzles, the mixing and heating feed systems were altered so that the bio-oil flowed properly without degradation.

In addition to the tests described above, **10 m³** of oil coming from cracking 5 wt % bio-oil and 95 wt % VGO were produced and sent to distillation unit U-2110 to obtain two cuts, naphtha and LCO.

PETROBRAS

"O processamento faz parte de um acordo de cooperação entre a Petrobras, uma companhia de petróleo americana, e o National Renewable Energy Laboratory"

Separação

Na Unidade de Destilação Atmosférica (U-2110), o produto passou pela etapa de separação, na qual foram feitos três cortes com faixas de temperatura distintas, produzindo 1.600 litros de nafta e de LCO, que serão enviados aos EUA, além do óleo decantado, que é o resíduo do processo.

Para realizar os testes nesta unidade, também foram necessárias modificações substituindo o refervedor existente por uma bomba e um forno. No total, foram dois meses de modificações na unidade para 15 dias de operação.

Os produtos foram enviados para os Estados Unidos, onde foram realizadas algumas análises das propriedades do diesel produzido e concluiu-se que ele estaria apto a ser hidrogenado. O diesel hidrogenado será enviado ao *Southwest Research Institute (SWRI)*, onde serão feitos os testes em motor. A certificação da gasolina seguirá os mesmos procedimentos. "Com essas baterias de testes a SIX comprova que o nosso parque de pesquisa é um local adequado para fazer testes especiais que não são possíveis em outras refinarias", destaca o engenheiro de processamento Maicon Tait (SIX/PQ).

Nesse processo, a dedicação da equipe da operação da Pesquisa foi fundamental. As equipes responsáveis pelo projeto receberam ainda apoio do Laboratório (SIX/PQ), Manutenção Industrial (SIX/MI) e Inspeção de Equipamentos (SIX/IE).

Na Unidade de Destilação Atmosférica (U-2110), o produto passou pela etapa de separação

Foto: Acervo SIX

"The processing is part of a cooperative agreement between Petrobras, an American oil company, and the National Renewable Energy Laboratory"

Separation

In the Atmospheric Distillation Unit (U-2110), the product was fractionated into three cuts with three different temperature ranges to produce 1600 liters of naphtha and of LCO, to be sent to the USA, in addition to the decanted oil, which is the residue of the process.

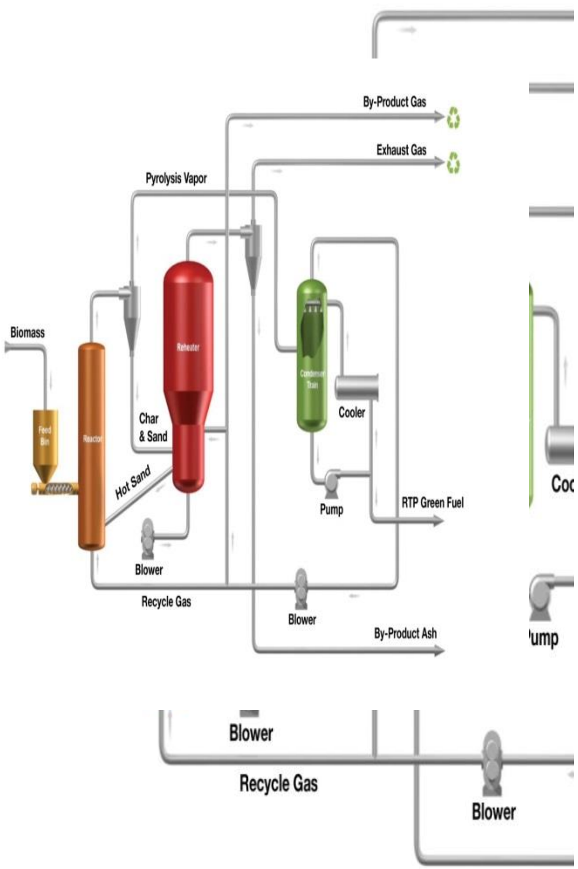
To perform the tests in this unit, modifications were also necessary such as replacing the existing pump with a reboiler and an oven. A total of two months of modifications to the unit were necessary to conduct 15 full days of operation.

The products were sent to the United States, where the LCO produced was tested and found suitable to hydrogenation as diesel blendstock. The hydrogenated diesel will be sent to the Southwest Research Institute (SWRI), to obtain U.S. motor diesel fuel properties according to ASTM specifications for meeting regulatory requirements. Naphtha hydrogenation tests are also being conducted. "With these batteries of tests SIX proves that our research park is a suitable place to do special tests that are not possible in other refineries, "said the processing engineer Maicon Tait (SIX / PQ).

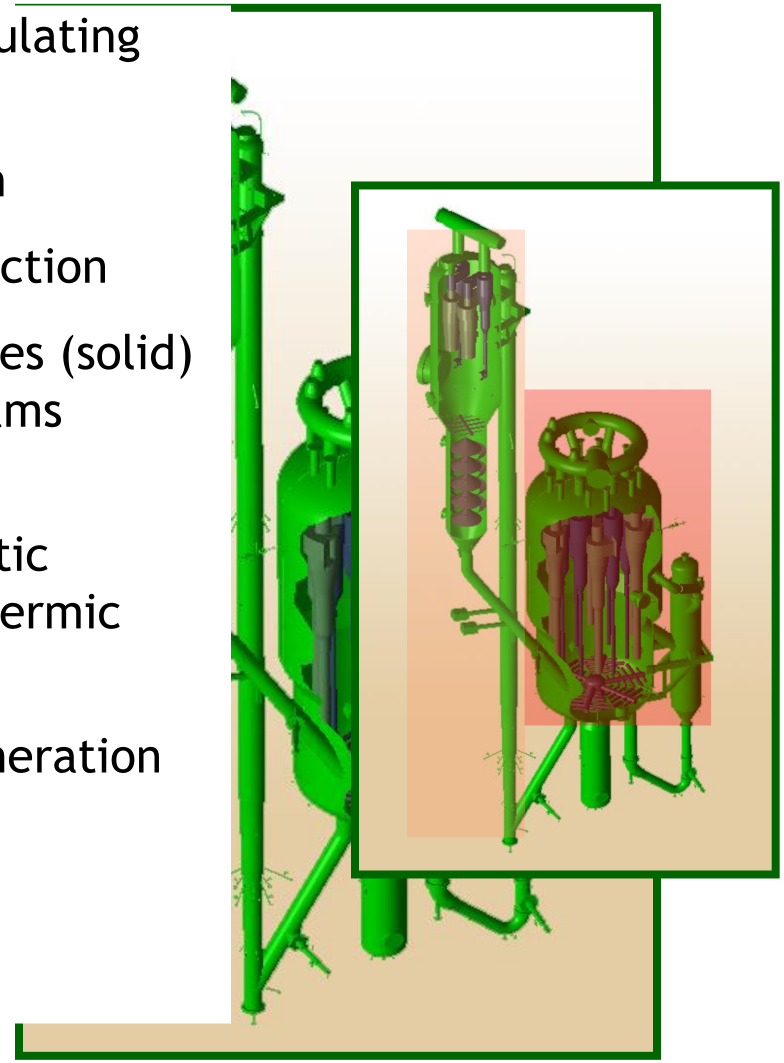
In this process, the dedication of the Research Unit and of the Operation teams was essential. The teams responsible for the project also received support from the Laboratory (SIX / PQ), Industrial Maintenance (SIX / MI) and Equipment Inspection (SIX / IE).

Figure Caption: Na Unidade de Destilação Atmosférica (U-2110), o produto passou pela etapa de separação

Biomass Pyrolysis v. FCC



- Interconnected circulating fluidized beds
  - Cracking section
  - Regeneration section
- Lignocellulosic wastes (solid) v. Heavy fossil streams (liquid)
- Pyrolysis and catalytic cracking are endothermic reactions
- Exothermic at regeneration side
- Sand v. Catalyst
- Heat recovery



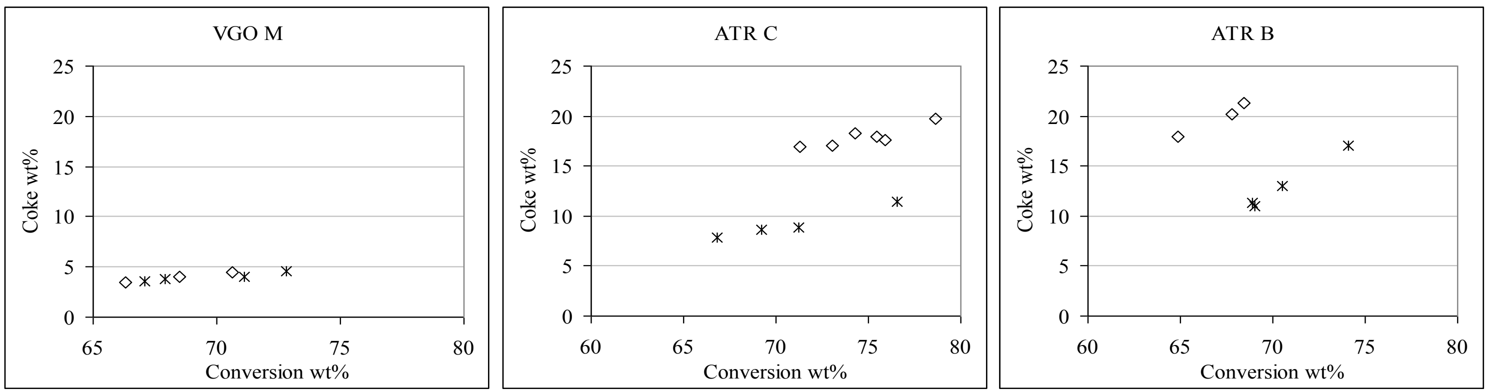
Biomass Pyrolysis Schematic Drawing
Source: Ensyn

FCC Unit PAC[RC] Petrobras Design
Source: Petrobras

Proof-of-concept

Lab scale overestimates coke yields w/ heavy feeds

- Literature states that is NOT feasible to process raw bio-oil in the FCC due to the increase in coke and hydrotreating is necessary to improve the processing characteristics of bio-oil
- Petrobras experience show that lab scale units reproduces FCC yields with light feeds, but does NOT reproduce yields with heavy feeds (for instance, atmospheric residues) *



Coke versus conversion plot for VGO M and ATRs C and B. Caption: (◊) ACE and (*) Pilot.

Coke Lab >> Coke Pilot > Coke Demo ≥ Coke Commercial

g/min 1 kg/h 200 kg/h

- Does bio-oil behave as atmospheric residue in the FCC?

* Gilbert (Petrobras), 2010

Gasoline and Diesel Quality

Before hydrogenation

	Method	Value
Density (g/cm^3, 20 °C)	ASTM D4052	0.7755
Carbon (C), %wt.	ASTM D5291	85.60
Hydrogen (H), %wt.	ASTM D5291	12.68
Sulfur, mg/kg	ASTM D5453	936
Nitrogen, mg/kg	ASTM D5453	166
RVP, kPa		48.1
Water, mg/kg	ASTM D6304	120
Phenols, wppm	UOP 262-59	4636
Tiophenols, wppm	UOP 262-59	96
Simulated Distillation, °C IBP	ASTM D2887	-20.6
5%		39.4
10%		61.2
30%		100.1
50%		134.2
70%		161.2
90%		194.9
95%		202.5
Final Boiling Point		220.7

	Method	Value
Density (g/cm^3, 20 °C)	ASTM D4052	0.9125
Carbon (C), wt. %	ASTM D5291	87.00
Hydrogen (H), wt. %	ASTM D5291	10.79
Sulfur, wt. %	ASTM D5453	0.56
Nitrogen, wt. %	ASTM D5453	0.10
RVP, kPa		14.0
Water, mg/kg	ASTM D6304	256
Phenols, wppm	UOP 262-59	5397
Tiophenols, wppm	UOP 262-59	616
Simulated Distillation, °C	ASTM D2887	
Initial Boiling Point		34.9
5%		144.4
10%		202.2
30%		234.7
50%		255.3
70%		275.8
90%		299.8
95%		310.1
Final Boiling Point		343.7