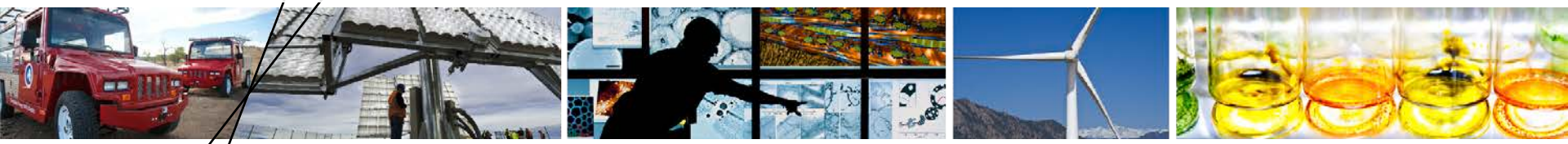
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

DOE Bioenergy Technologies Office (BETO)
Southeast United States Bioenergy Study Tour
Integrated Systems for the Bioeconomy



April 13, 2016

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Savannah River Site, Aiken, South Carolina

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

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Innovation

- Innovation is the improvement of a product or process (often in combination) which creates meaningful social/economic impact.

  "The successful translation of new ideas into tangible societal impact." — USC Stevens Institute for Innovation

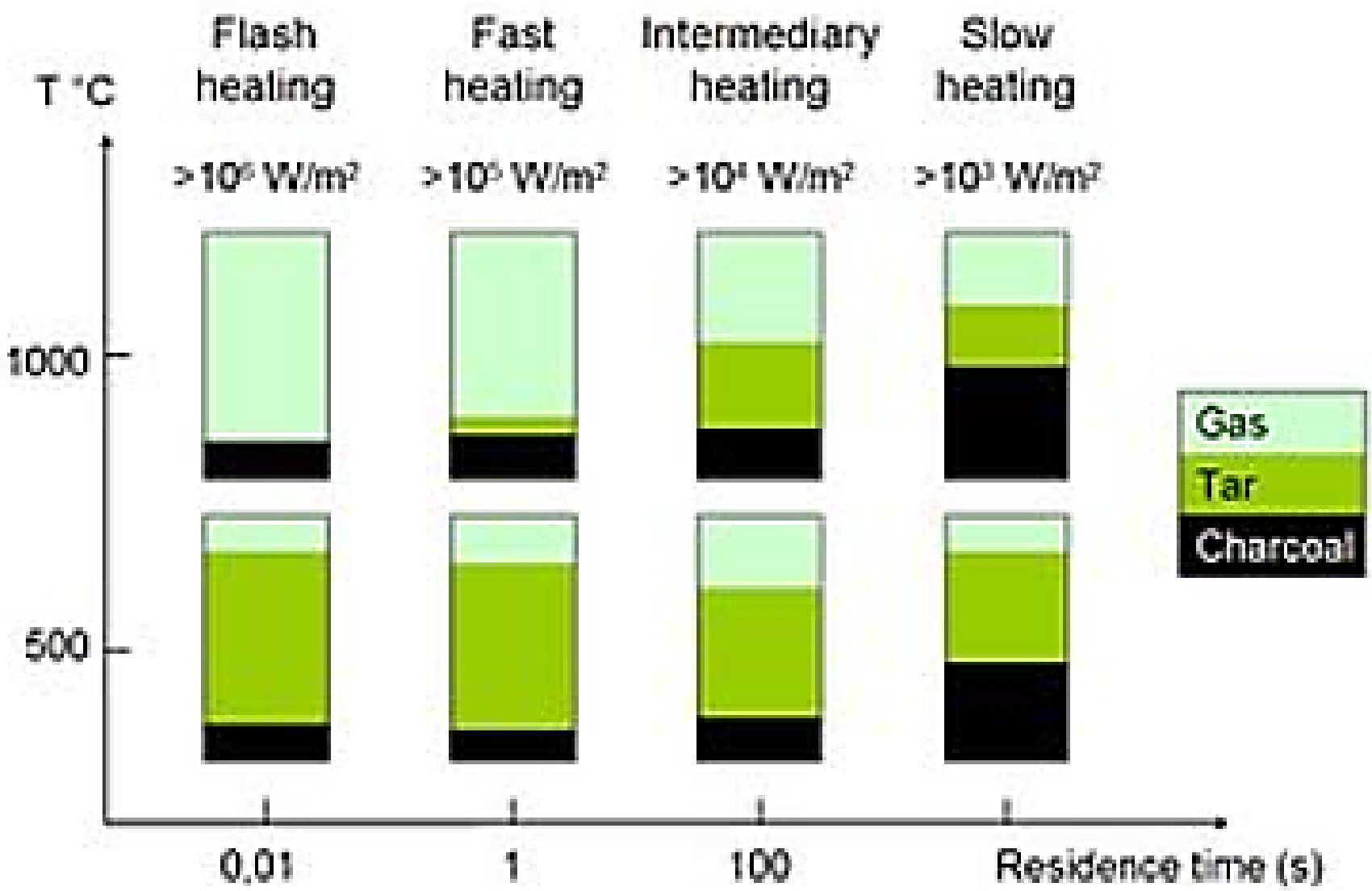
- Innovation often involves:
  - Significant advances along an entire value chain.
  - Market demand and public acceptance.
  - Correct timing – confluence of historical factors/trends.
  - Cross-cutting, interdisciplinary inputs. **including sustainability**
  - Longer term and significant impacts on economics and culture

T2Market linking innovations

Multiple inventions along value chains from many companies and skills from interdisciplinary researchers, national and international partnerships

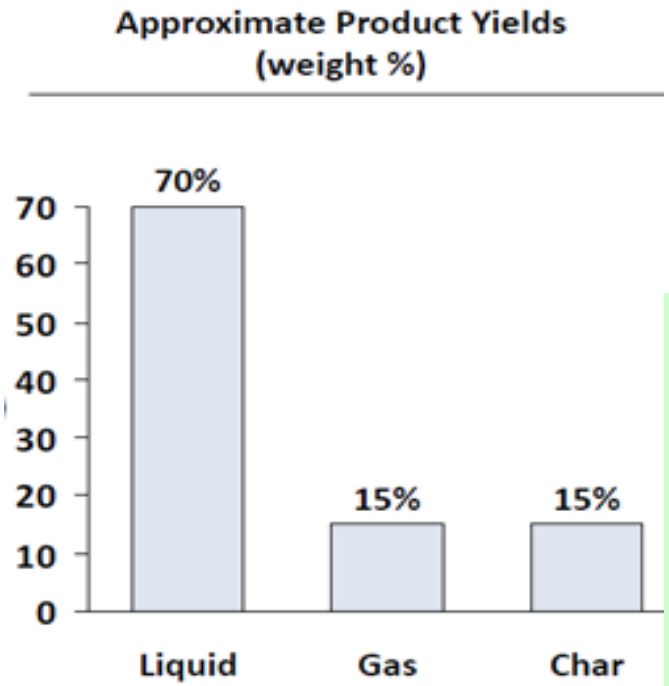
Base slide http://web.ornl.gov/sci/ees/cbes/forums/ORNL%20Presentation_Male_Final%20short.pdf; yellow boxes added

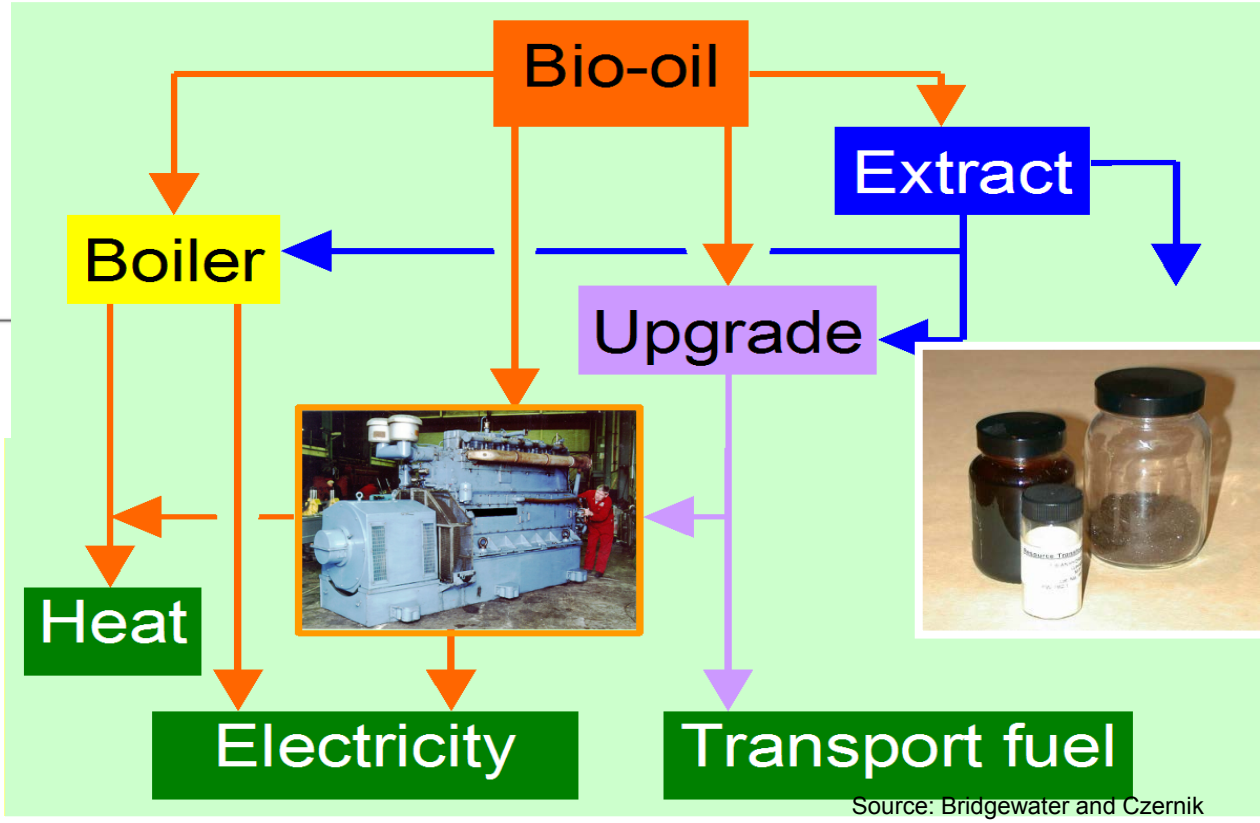
'Fast Pyrolysis Bio-oil' FPBO have many applications



http://www.eubia.org/index.php/about-biomass/pyrolysis-and-gasification/pyrolysis

'Fast Pyrolysis Bio-oil' FPBO have many applications





Source: Bridgewater and Czernik

Examples of Plants

Host Organization	Country	Technology	Feeding Capacity BDMT/day	Application	Status
Ensyn/Fibria	Brazil	Circulating Fluidized Bed	400	Fuel	Design Phase
Fortum	Finland	Fluid Bed	240	Electricity, steam and fuel oil for heating or power (1)	Operational 2013
BTG BioLiquids/ EMPYRO	Netherlands	Fluid Bed	120	Electricity, steam and fuel oil	Operational 2015
Ensyn/Ensyn Renfrew	Canada	Circulating Fluidized Bed	60-100	Heating Oil Substitution (2)	Operational 2007
Red Arrow/Ensyn	USA	Circulating Fluidized Bed	30; 35; 45	Chemicals/Fuels for power	Operational 1993; 1995; 2001
Red Arrow/Ensyn	USA	Circulating Fluidized Bed	1; 2	Chemicals	Operational 1995; 2003
Valmet	Finland	Fluid Bed	7	Fuel	Operational
Fraunhoffer UMISCHT	Germany	Ablative	2.5	Fuels, Chemicals	Commissioning

BDMT = Bone dry metric tonne

(1) Internal market (2013), exports to E.On in 2015 for peak load and reserve (http://www.fortum.com/en/mediaroom/pages/fortums-first-export-batch-of-finnish-bio-oil-to-e.on-in-sweden.aspx)
(2) In use at (1) Memorial Hospital in North Conway, New Hampshire (300,000 gallons/yr since 8/2014 (80% GHG reduction projected); (2) Valley Regional Hospital in Claremont, New Hampshire (200,000 oil/yr since 2015); (3) Youngstown Thermal, Ohio, tested successfully now up to 2.5 million gallons/year see http://www.ensyn.com/media/press-release/ and http://www.pyne.co.uk/ Newsletter July 2015

Significant Advances Along the Value Chains

uop A Honeywell Company | Envergent | NABC National Advanced Biofuels Consortium | ALBEMARLE | RTI INTERNATIONAL | NREL NATIONAL RENEWABLE ENERGY LABORATORY | Pacific Northwest NATIONAL LABORATORY | PALL Pall Corporation | TESORO | bp | IOWA STATE UNIVERSITY

Transport Fuel Upgrade

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Bioenergy Technologies Office

Pacific Northwest NATIONAL LABORATORY | GRACE Enriching Lives, Everywhere.™

PNNL and W. R. Grace will co-manage this project
Project Co-directors: John Holladay & Manoj Koranne
Principal Investigators: Ken Bryden & Alan Zacher

- Pyrolysis oil stabilization (PNNL)
- DCR piloting (Grace)
- Analysis, integration (PNNL/Grace)
- Marketing/Commercialization (Grace)

TESORO

Refinery Lead: Rick Weyen
- Integration
- RINS

VTT | Aston University Engineering & Applied Science

Pyrolysis — Yrjö Solantausta
Stabilization – Tony Bridgwater

Los Alamos NATIONAL LABORATORY EST. 1943

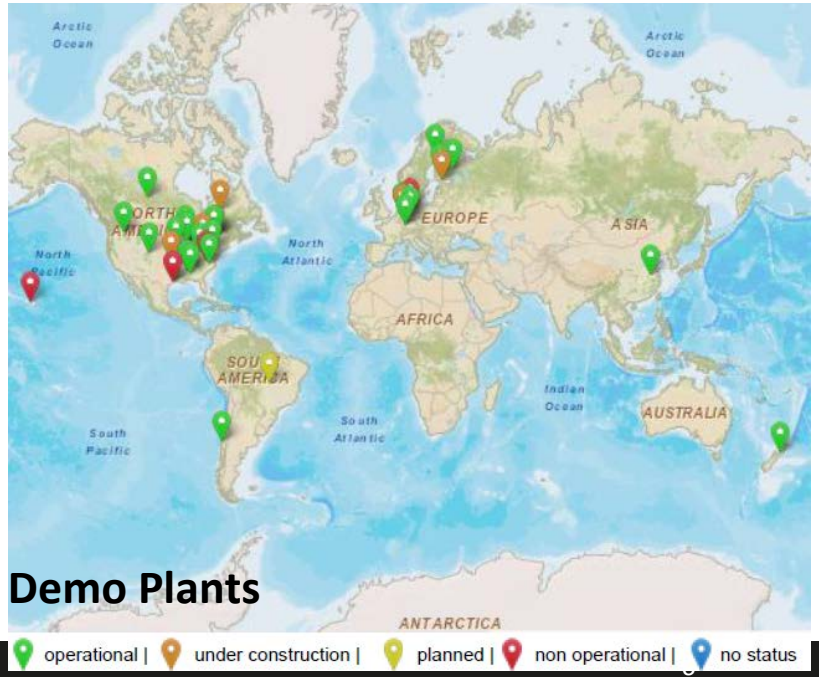
Biogenic Carbon Analyticals: Claudia Mora

OAK RIDGE National Laboratory

Materials– Jim Keiser

Some countries active in pyrolysis technologies RD&D from IEA Task 34 and member countries

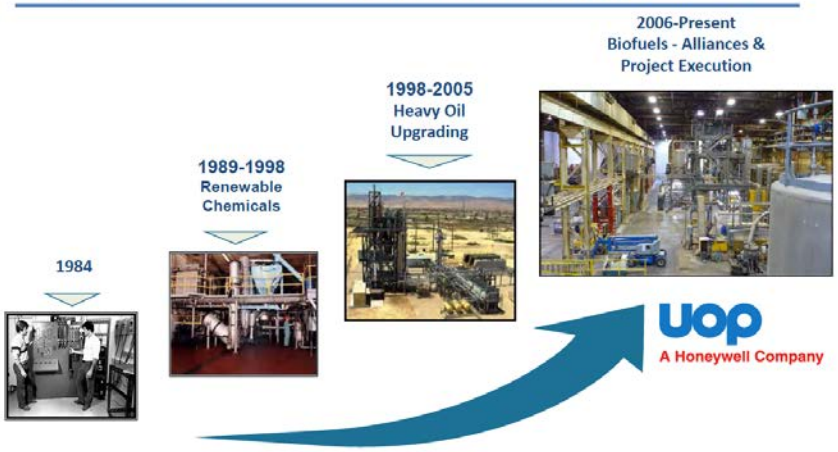
http://www.pyne.co.uk/

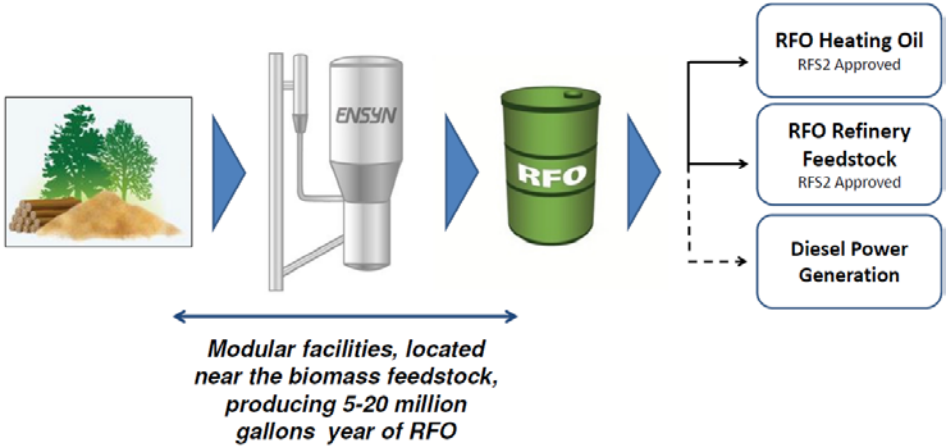


Demo Plants

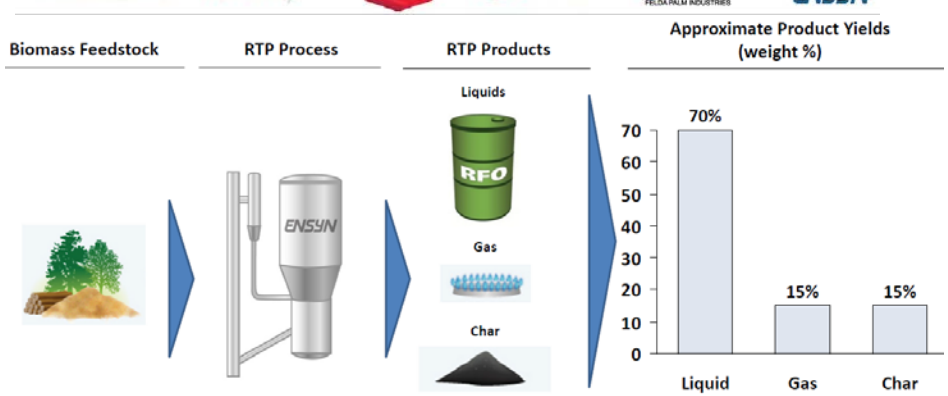
Commercialization

30 years of successful commercialization





CREDIT SUISSE IMPAX Chevron Fibria FPI ENSYN



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

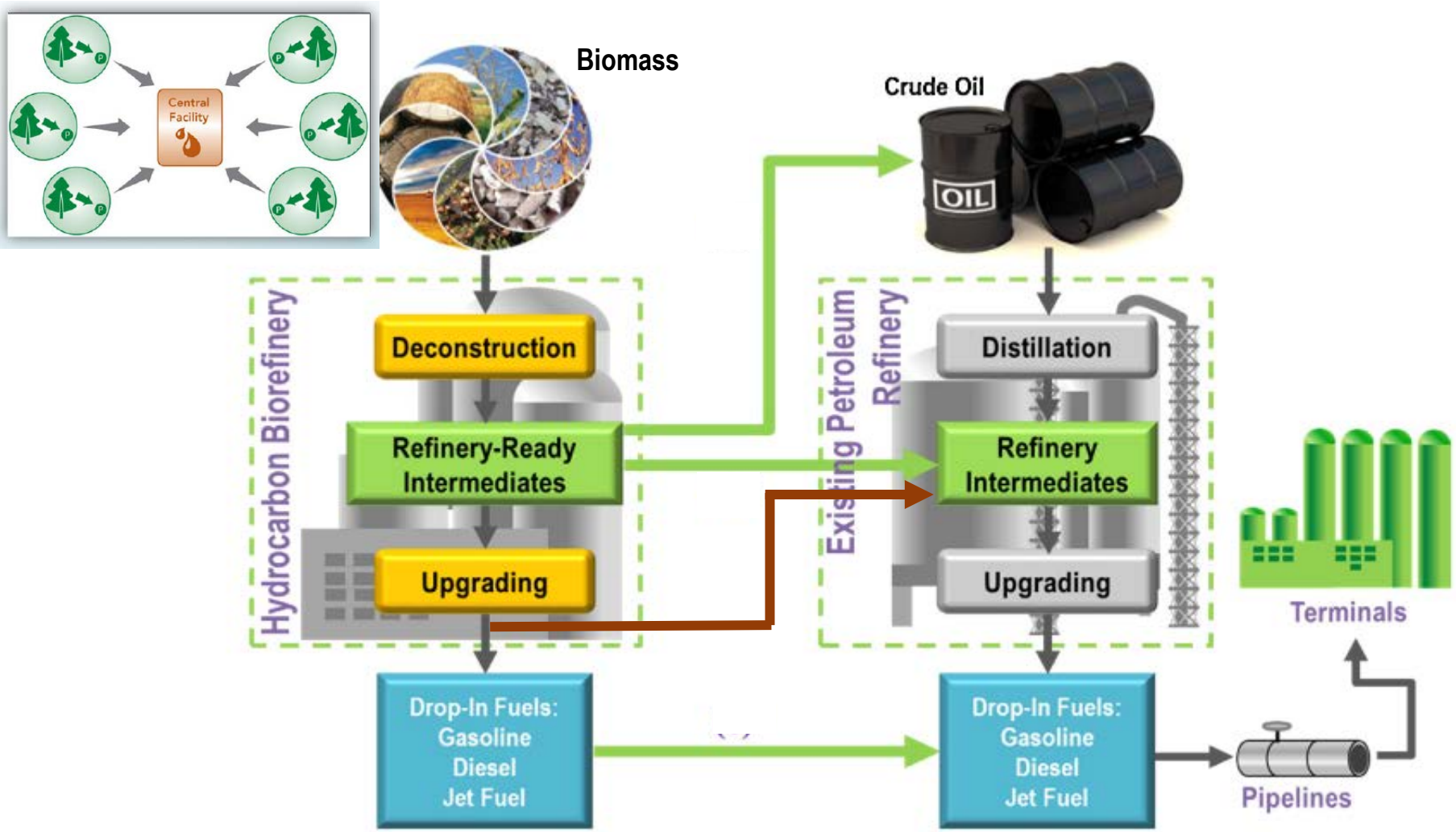
Capacity Expansion –RTP5 & RTP 20 Facilities

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

http://energy.gov/sites/prod/files/2015/07/f24/graham_bioenergy_2015.pdf

Biomass Refining with Petroleum Refining

Integrating Systems to Use Existing Infrastructure



Ye et al. Biomass-to-bioenergy and biofuel supply chain optimization: Overview, key issues and challenges, Computers and Chemical Engineering 66 (2014) 36–56 https://isen.northwestern.edu/doc/pdf/news/scholarlypapers/Booster_YouF_CompChemEng_8aug2014.pdf

Petrobras–NREL CRADA - Example

CRADA Partner and POC: Andrea Pinho, CENPES

CRADA Partner and POC: Helena Chum, NREL

Collaborator/pyrolysis oil supplier: Barry Freel, Ensyn

Goal: Demonstrate technical and economic feasibility of co-processing raw fast pyrolysis oil in Fluid Catalytic Cracking (FCC) operation.

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

CRADA=Cooperative Research and Development Agreement

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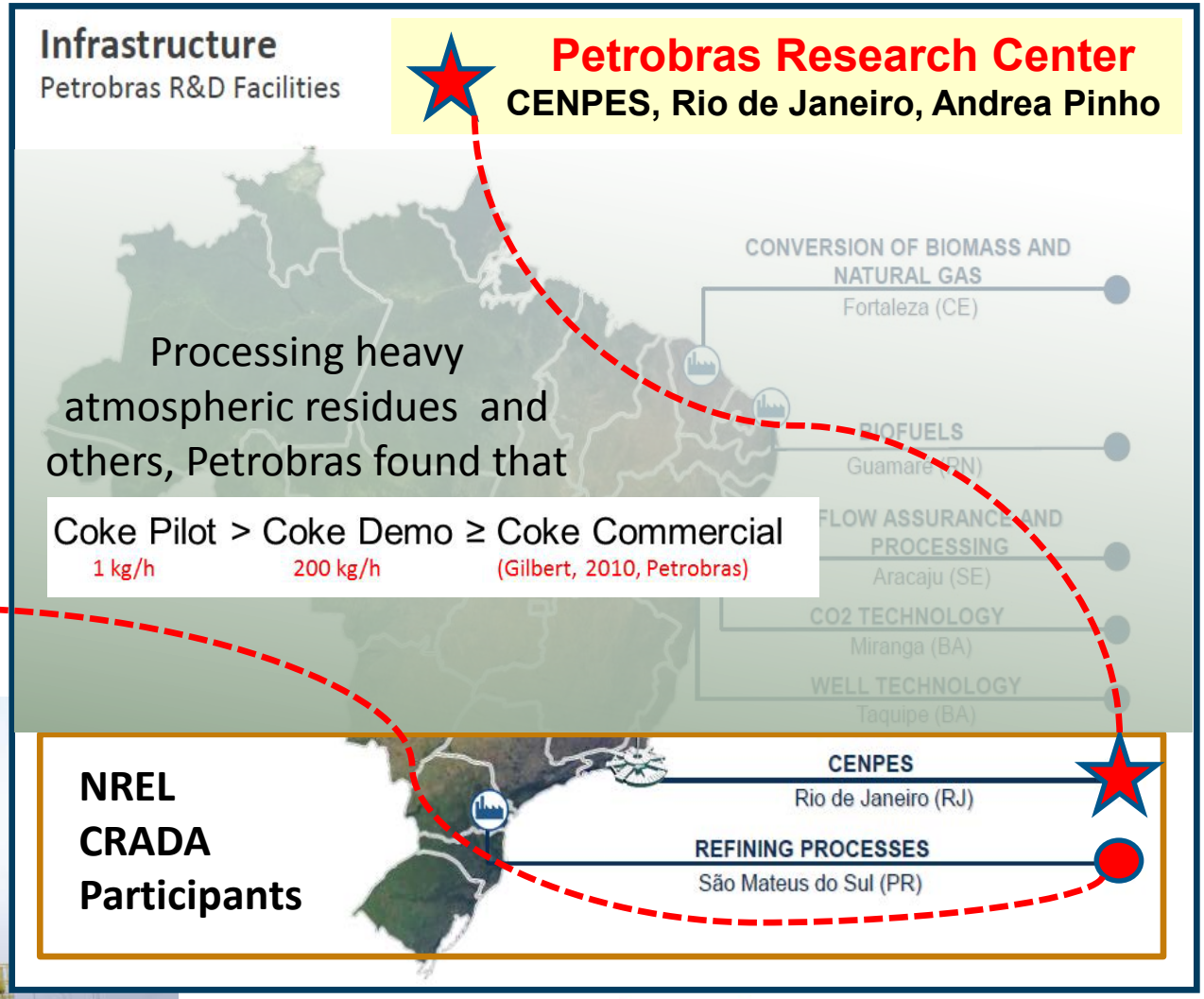
Petrobras–NREL CRADA: Petrobras Facilities

Petrobras SIX Facility
São Mateus do Sul, Parana



Processing heavy atmospheric residues and others, Petrobras found that

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

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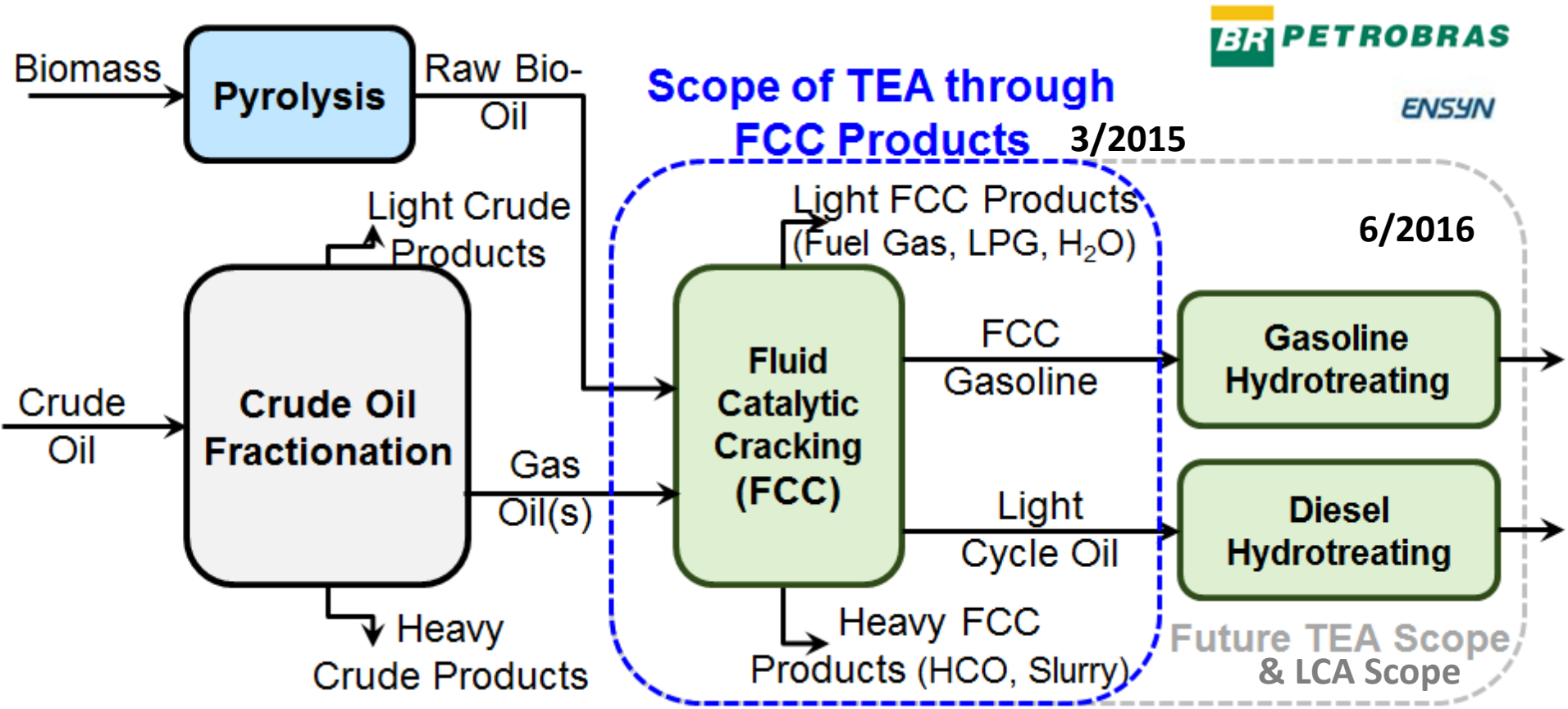
Petrobras, Supply Journal, Year 7, Number 67, 14-17, October 2014
http://asp-br.secure-zone.net/v2/index.jsp?id=2225/6153/6434

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



Techno-economic Analysis Basis

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

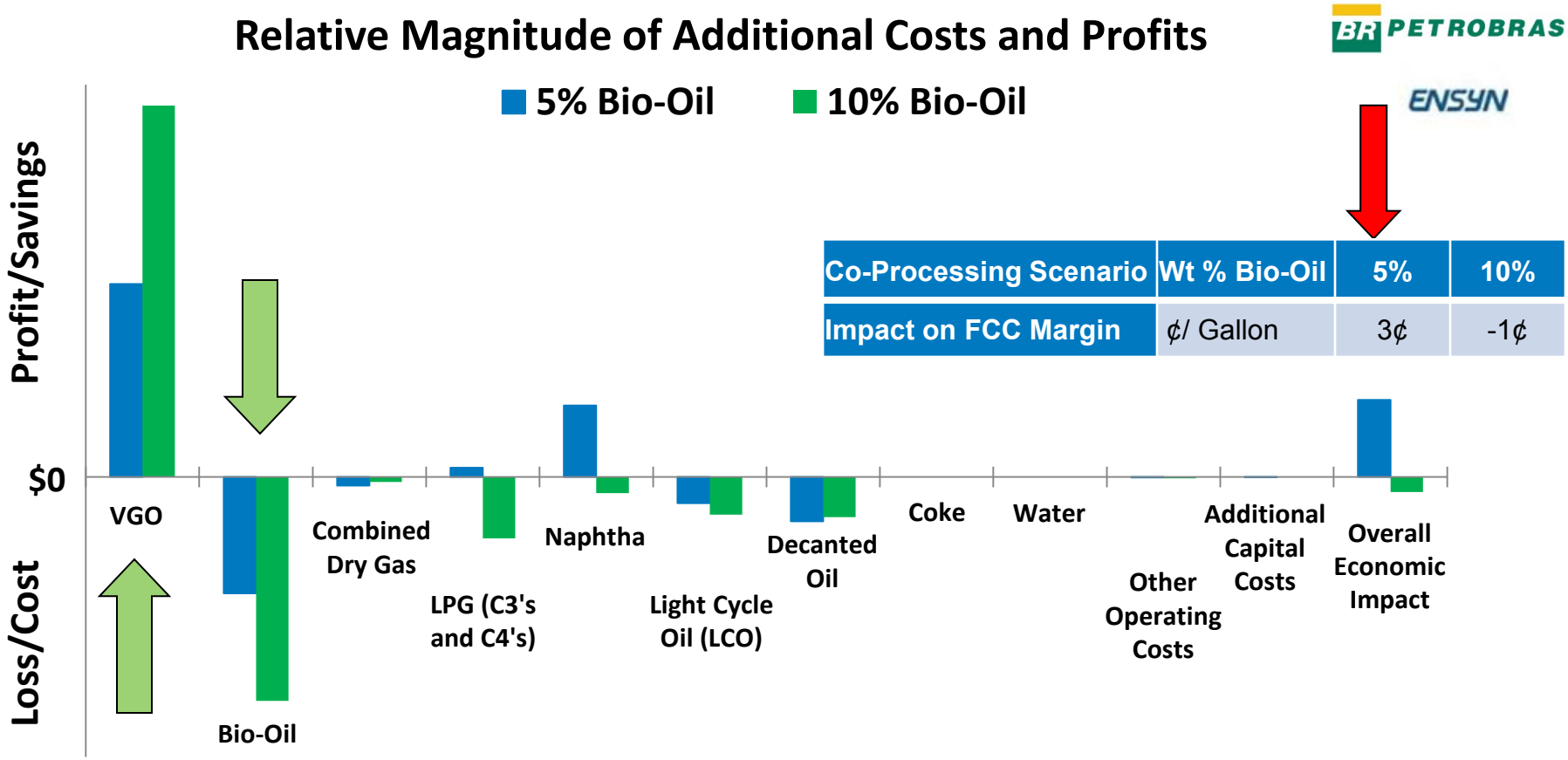
2015 DOE BETO Project Peer Review meeting http://www.energy.gov/sites/prod/files/2015/04/f21/thermochemical_conversion_chum_242303.pd

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.

Technoeconomic Results



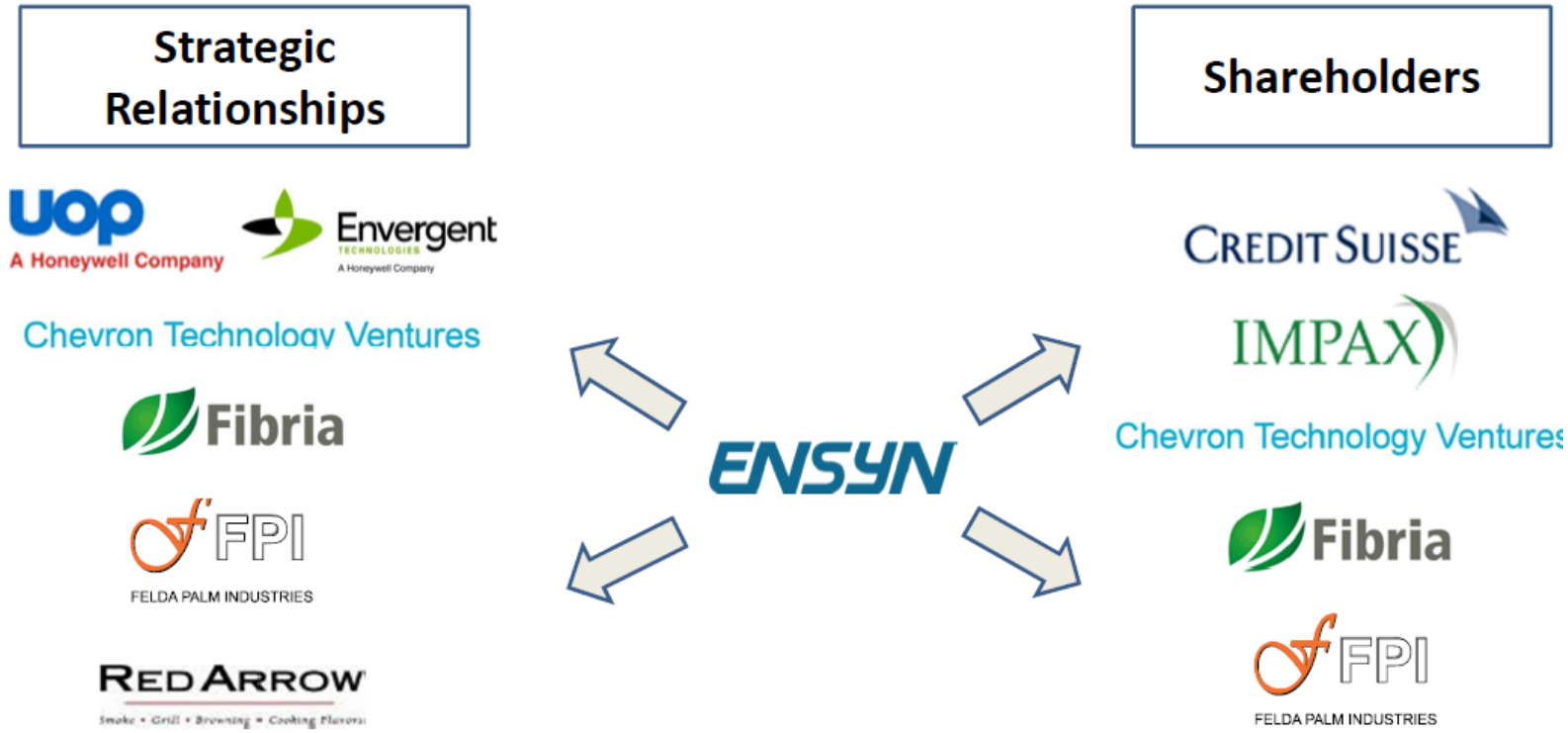
Co-Processing Scenario	Wt % Bio-Oil	5%	10%
Impact on FCC Margin	¢/ Gallon	3¢	-1¢

Overall coprocessing 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

2015 DOE BETO Project Peer Review meeting
http://www.energy.gov/sites/prod/files/2015/04/f21/thermochemical_conversion_chum_242303.pdf

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



2015 DOE BETO Project Peer Review meeting http://www.energy.gov/sites/prod/files/2015/04/f21/thermochemical_conversion_chum_242303.pd

Accelerating commercialization - US

- **Petrobras produced for the CRADA by operating 70 hours of continuous feeding at a rate of 200 kg/h rate bio-oils 5% (mass) and of vacuum gas oil (95%) a significant amount of raw gasoline and diesel precursors. The fraction was distilled into boiling points fractions of naphtha and light cycle oil containing pyrolysis oils. 400 gallons of each fraction.**
- **The precursors were shipped to the US by ENSYN's partner's to a refiner partner for hydrotreating to U.S. specification fuels.**
- **Hydrotreated fuels containing pyrolysis oils were sent to Southwest Research Institute, a certified facility, which found them to pass EPA regulations (Clean Air Act Part 79) thus permitting these renewable fuels to enter commerce in the United States.**
  - http://www.ensyn.com/2015/08/26/ensyn-receives-key-regulatory-approval-for-its-renewable-diesel/
  - http://www.ensyn.com/wp-content/uploads/2015/11/Part-79-Gasoline-Press-Release-as-Issued-rev.pdf
- **USDA Loan Guarantee awarded (conditional) to retrofit a particle board manufacturing facility in Dooly County, Georgia to produce 20 million gallons of renewable fuel from waste wood annually**
  - http://www.ensyn.com/wp-content/uploads/2015/12/USDA-9003-Loan-Guarantee-Release-as-Issued-12.10.2015-with-USDA-link.pdf

http://forestnet.com/LSJissues/2015_Feb/Renewable%20fuel%20oil%20that%20can%20help%20fuel%20a%20sawmill%E2%80%99s%20bottom%20line.pdf

http://www.ascension-publishing.com/ABLC-2014/Doherty-Ensyn.pdf

U.S. Refineries

Figure 2.2. Map of U.S. Refineries in 2011 EIA Database based on Categories Reflecting Biofuel Processing Potential

Good Match with Southeast US

http://www.pnl.gov/main/publications/external/technical_reports/PNNL-22432.pdf

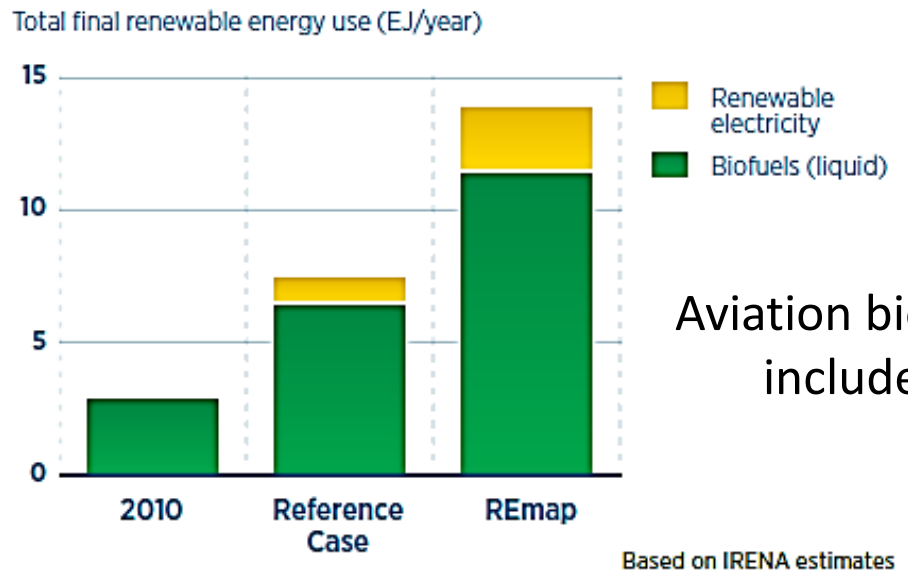
Summary

- 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 and LCA:
  - 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
  - **The renewable portion of the fuels provides very significant reductions of GHG emissions compared to the petroleum fuels, ranging from 80% - 86%, depending on the transportation mode used to ship bio-oil to a petroleum refinery.**

2030 Global Goals

- **UN Sustainable Energy for ALL goals Double share of renewable energy, double efficiency improvement rate, and give universal access to modern energy by 2030**
- **How? IRENA Renewable Energy Map 2030 2016 edition of the roadmap:**

Liquid biofuels account for 85% of the renewable energy use in transport, which represents a fourfold increase in their use by 2030 from 2014.



Aviation biofuels included

Integrated Systems for the Bioeconomy

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, E. Berger
DOE International: Rhianon Davis

U.S. Dept. of State: Dan Birns

NREL: Helena Chum (POC) Engineering: Rich Bain, Calvin Feik; *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.

Brazilian Ministry of Mines and Energy:
Ricardo Dornelles

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:

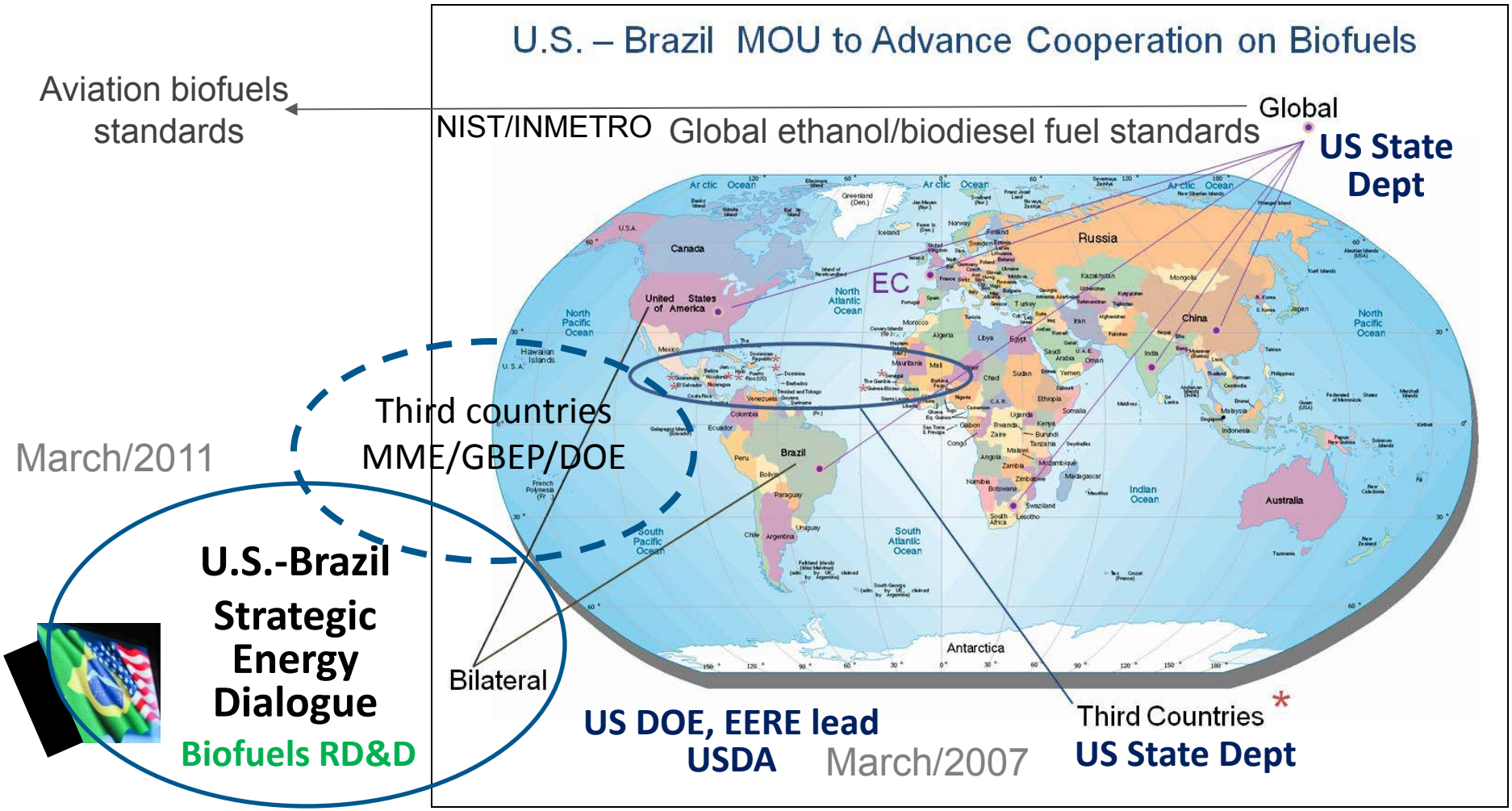
Bob Graham, Barry Freel, Raymond Pirraglia

FIBRIA Celulose:

Centro de Tecnologia Aracruz

Matheus Antunes Guimarães

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

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

2015 DOE BETO Project Peer Review meeting http://www.energy.gov/sites/prod/files/2015/04/f21/thermochemical_conversion_chum_242303.pd

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"Brazil Bilateral: Petrobras-NREL CRADA" Presented at the 2015 DOE BETO Project Peer Review meeting, Arlington, VA, on March 25, 2015, http://www.energy.gov/sites/prod/files/2015/04/f21/thermochemical_conversion_chum_242303.pdf

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- **PINHO, A.R.; ALMEIDA, M.B.B.; MENDES, F.L.; XIMENES, V.L. Production of lignocellulosic gasoline using fast pyrolysis of biomass and a conventional refining scheme. Pure and Applied Chemistry. v. 86, n. 5, p. 859-865, 2014.**
- **PINHO, A.R.; ALMEIDA, M.B.B.; MENDES, F.L.; XIMENES, V.L. Co-processing raw bio-oil and gasoil in an FCC unit. Fuel Processing Technology. v. 131, p. 159-166, 2015.**
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- **FOGASSY, G.; THEGARID, N.; TOUSSAINT, G.; VAN VEEN, A.C.; SCHUURMAN, Y.; MIRODATOS, C. Biomass derived feedstock co-processing with vacuum gas oil for second-generation fuel production in FCC units. Applied Catalysis B: Environmental. v. 96, p. 476-485, 2010.**
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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.**

Publications and Presentations

- 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.

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

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List of Acronyms & Abbreviations (cont.)

OPIS	Oil Price Information Service
PAC	Petrobras Advanced Converter
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 (Shale oil)
SwRI	Southwest Research Institute
TC	Thermochemical
TEA	Techno-Economic Analysis
VGO	Vacuum Gas Oil

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