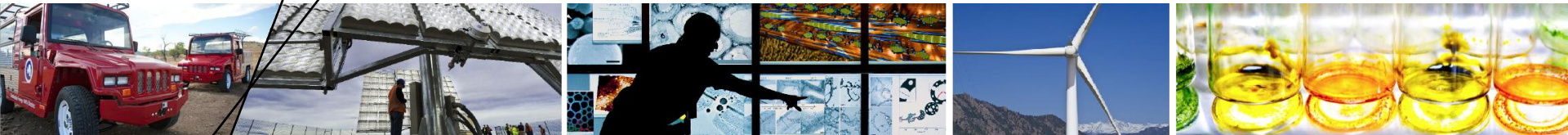


## Biomass Pyrolysis to Hydrocarbon Fuels in the Petroleum Refining Context



Brazil Bilateral: Petrobras – NREL RD&D CRADA  
WBS: 6.5.1.1

May 21, 2013

Bio-Oil Technology Area Review

Helena L. Chum  
National Renewable Energy Laboratory

Andrea Pinho, Petrobras/CENPES



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

# Context: The 2011 U.S.-Brazil Strategic Energy Dialogue (SED)

## Biofuels Area

- Incorporated Memorandum of Understanding to Advance Biofuels Collaboration (2007):
  - Promote Energy Security
  - Reduce GHG Emissions
  - Expand Economic Development
- Implemented in the two countries (Bilateral R&D led by EERE), expanded deployment in appropriate countries, and joint work with other countries to make biofuels global commodities



# Joint R&D Areas Defined – EERE led

Brazilian Delegation at NREL  
September 12, 2007

Reciprocal Visits to Define Areas



Participants reached a better understanding of each country's capabilities and limitations in the production of biofuels

## Sharing Best Practices

1. Biomass chemical characterization  
NREL

2. Techno-economic analysis (TEA) models/NREL; Lifecycle (LCA) methodology GREET/ANL

3. Biofuels Sustainability  
ORNL/ANL/NREL



Dedini



CTBE



Usina da Pedra

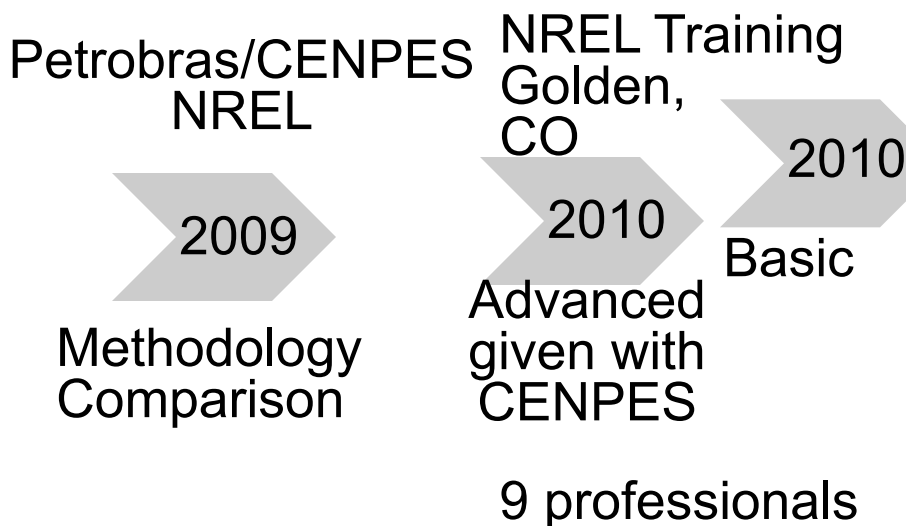
U.S. Delegation (DOE, USDA) in Brazil, May 30-June 6, 2008

# Context: 2008 MOU Petrobras-NREL

## Part 1 – Biochem: Biomass Compositional Analysis Methodology



### Brazilian Biomass Characterization Network



CTC large bagasse sample

2011

NREL prepared bagasse common sample



2012

NREL PI in Brazil

CENPES  
CTBE  
CTC

Joint Data Analysis

EMBRAPA  
INT  
IPEN  
IQ/UNESP  
IQSC/USP  
EEL/USP  
INMETRO

2013

Joint Peer Reviewed Paper in Review

Analytical Round Robin #1



# Goals

## Brazil Bilateral: Petrobras – NREL RD&D CRADA

- Facilitate technical, economic and sustainability assessment of traditional fast pyrolysis, followed by upgrading to gasoline, diesel, fuel oils, LPG, or alternatively, syngas in the refinery
  - Leverage expertise in the US and Brazil (heavy crude processing)
  - Address technical barriers
- Supports BETO's Bio-Oil Pathway R&D
  - Fast Pyrolysis Technology
  - Bio-Oil Characterization, Stabilization, and Upgrading
- Supports BETO's Strategic Goal
  - Develop commercially viable technologies for converting biomass feedstocks into energy dense, fungible, liquid transportation fuels


*Collaboration highlighted as an accomplishment  
at SED meeting, 3/19/13, Brazil  
by U.S. and Brazil Energy Deputy Secretaries*

# Project Quad Chart Overview

## Timeline

- Joint RD&D start date: 2/2013  
CRADA Finalized: 12/2012
- Project end date: 2/2015
- Percent complete: **10% NREL subject of peer review**

## Budget

- Total project funding:  
\$ 500K DOE  
**\$1,976K**  **PETROBRAS**  
**CRADA cost share**
- FY11 (EERE Intl.) \$250K
- FY12: \$0K
- FY13(BETO): \$50K
- FY14,15 (BETO): \$200K

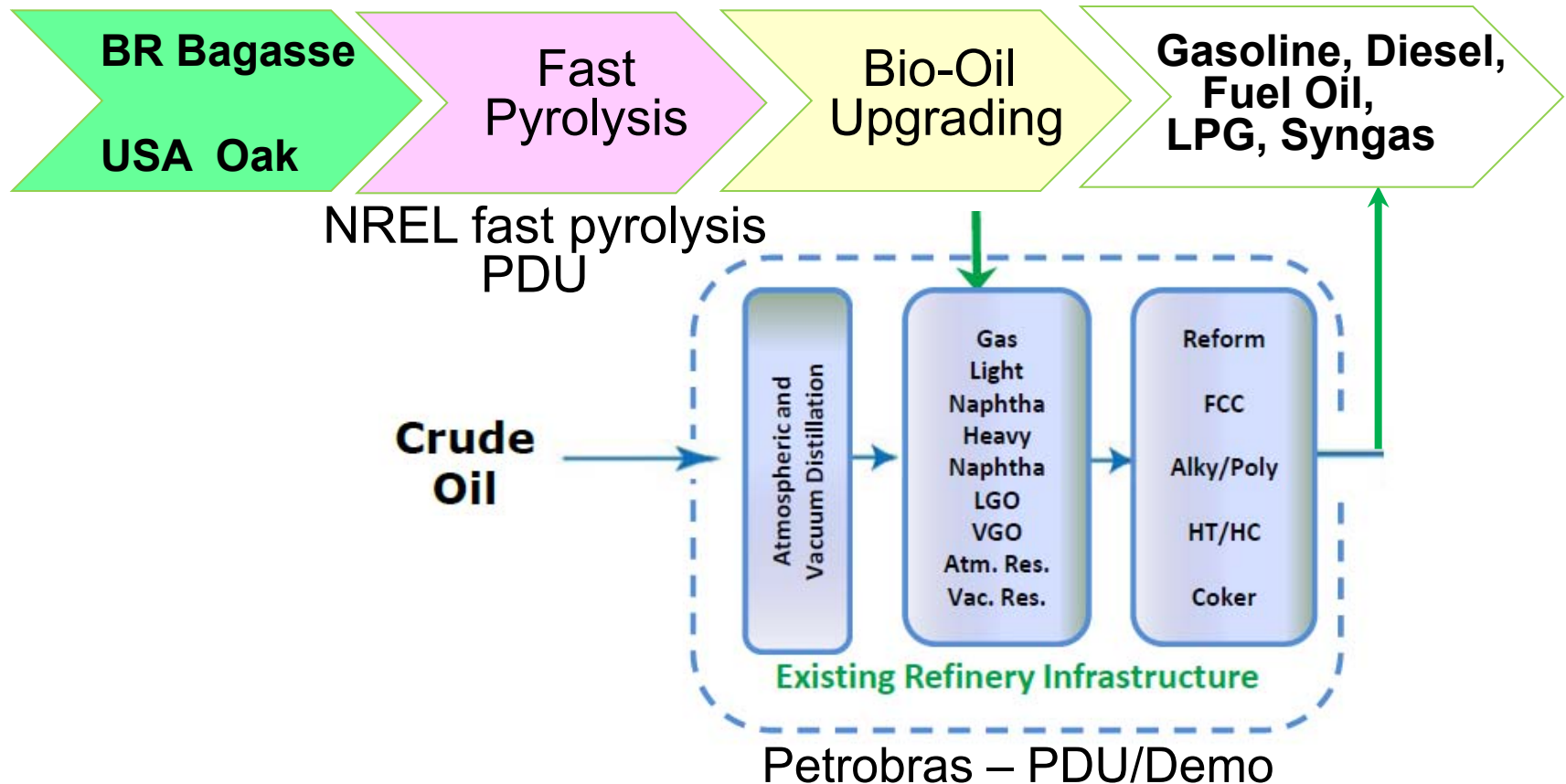
## Barriers

- Tt-E: Pyrolysis of Biomass and Bio-Oil Stabilization
- St-C: Sustainability Data

## Partners and Roles

- NREL: Bio-oil production; upgrading small scale
- Petrobras: Bio-oil upgrading
- Petrobras and NREL: joint characterization of bio-oils and upgraded products
- NREL and Petrobras: TEA/LCA
- External analytical, Beta Analytic Inc., FL, US, etc.

# Project Overview



- Joint characterization of pyrolysis oils and upgraded products
- Validation of some analytical methodology
- NREL and Petrobras collaboration on TEA/LCA from bagasse & oak 7

# 1 - Approach

*Barriers: Oil quality for upgrading & characterization; renewable C yield; costs & LCA*

Petrobras: 1000 kg bagasse pellets packaged BR

Ship to USA

BR Bagasse  
USA Oak

Fast Pyrolysis

Bio-Oil Upgrading

Gasoline, Diesel, Fuel Oil  
LPG, Syngas

USA: kg Oak pellets  
NREL fast pyrolysis PDU 20 kg/h continuous

Ship oak & bagasse oils to Brazil  
10/2013

Petrobras PDU & DEMO tests continuous

Petrobras/NREL characterization: **feedstock**, oils, upgraded products

USA Analytical Samples BR


**Outcome:** Preliminary Estimated Production Cost and LCA data by 2/2015

## Management Approaches

- Monthly phone calls setting data and materials exchanges necessary to coordinate the efforts of the two teams
  - Monthly telephone conference, emails, highlight reporting, monthly/quarterly reporting
- Milestones established in the project management plan



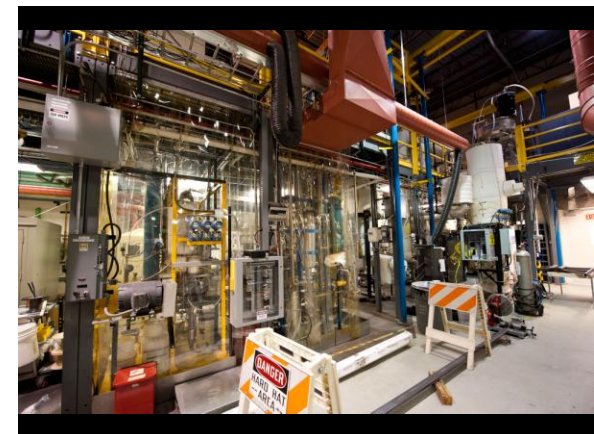
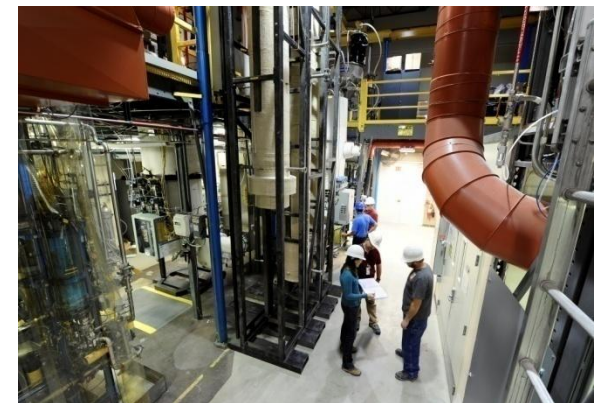
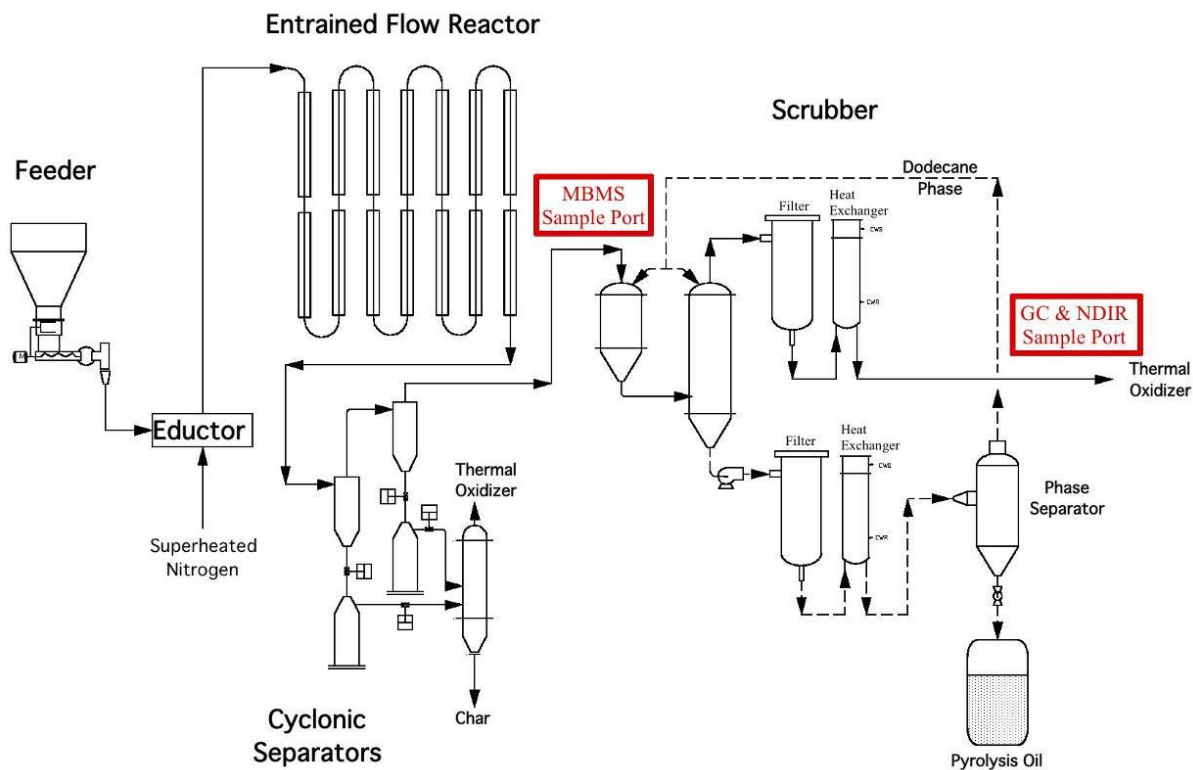
## 2 - Technical Accomplishments/ Progress/Results

Task	Description and Timing	Status
<b>Phase 1 – Bio-oil Production</b> White American Oak Brazilian Bagasse	FY12 completed Anticipated completion 10/2013*	 Not Started
<b>Phase 2-1: Co-processing of Bio-oil in Refinery Operations</b>	Oils arrive 11-12/2013 BR One year duration	Not Started
Phase 2-2: Syngas from Bio-oil	Oils arrive 11-12/2013 One year duration	Not Started
<b>Phase 2-3: Bio-oil and Upgraded Products Characterized</b>	Small samples U.S. oak and pyrolysis oils sent to Petrobras 4/2013; continued sample exchange to 10/2014	Underway
<b>Phase 2-4: TEA, LCA, Sustainability Analysis</b>	8/2014-2/2015	Not Started

\*pending shipping and customs clearing times

# 2 - Technical Accomplishments/ Progress/Results (cont'd)

## Bio-Oil Production Pilot Plant



# 2 - Technical Accomplishments/ Progress/Results (cont'd)

## Task 1: Bio-oil Production from American White Oak (KY)

Total Feed Amount Processed, kg; N <sub>2</sub> :Oak=2:1	Feed Rate, kg/h	Temp, °C	Mass Yield (wt%)			Material Balance %
			Oil	Char	Gas	
622	10	500	51.8	11.9	36.7	101.7

### Bio-Oil - Ultimate Analysis, wt% as received

Moisture	Ash	C	H	N	S	O by difference
24.6	0.06	42.8	4.65	0.01	0.02	27.9

Molar Composition:  $\text{CH}_{1.3}\text{O}_{0.5}$

TAN Number, mg KOH/g: **68±1.5** [Range: 66-70 in 5 drums]

### Metals in Bio-oil, mg/kg

Ti	Fe	Ca	Mg	Na	K	P
5.9	26	316	40	839	111	<10

### Char Ultimate Analysis, wt% as received

C	H	N	S	Cl	Ash	M
82.6	2.73	0.29	0.02	0.01	4.38	0.0

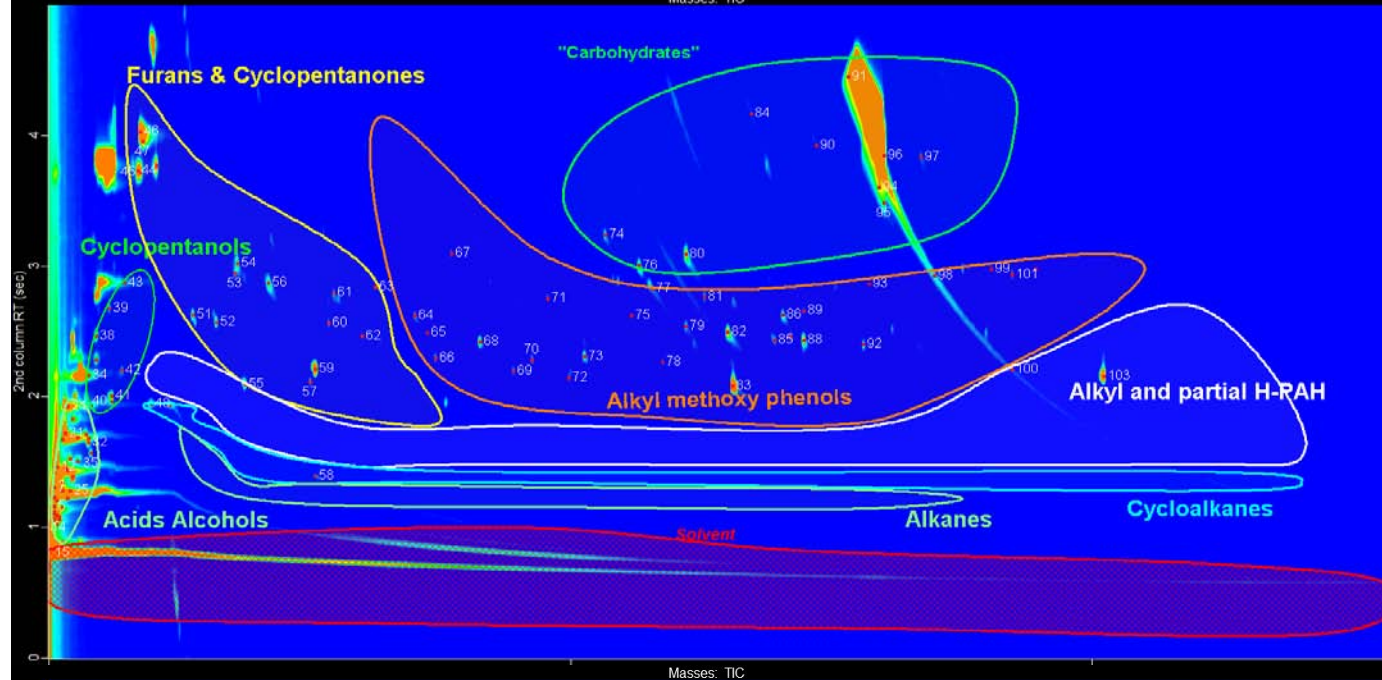
### Gas Composition, mole%, N free

H <sub>2</sub>	CO	CO <sub>2</sub>	C <sub>2</sub> -C <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>8</sub> (all)	H <sub>2</sub> O
0.3	37.1	19.2	2.2	1.0	0.9	0.7	28.5

## Other Analyses

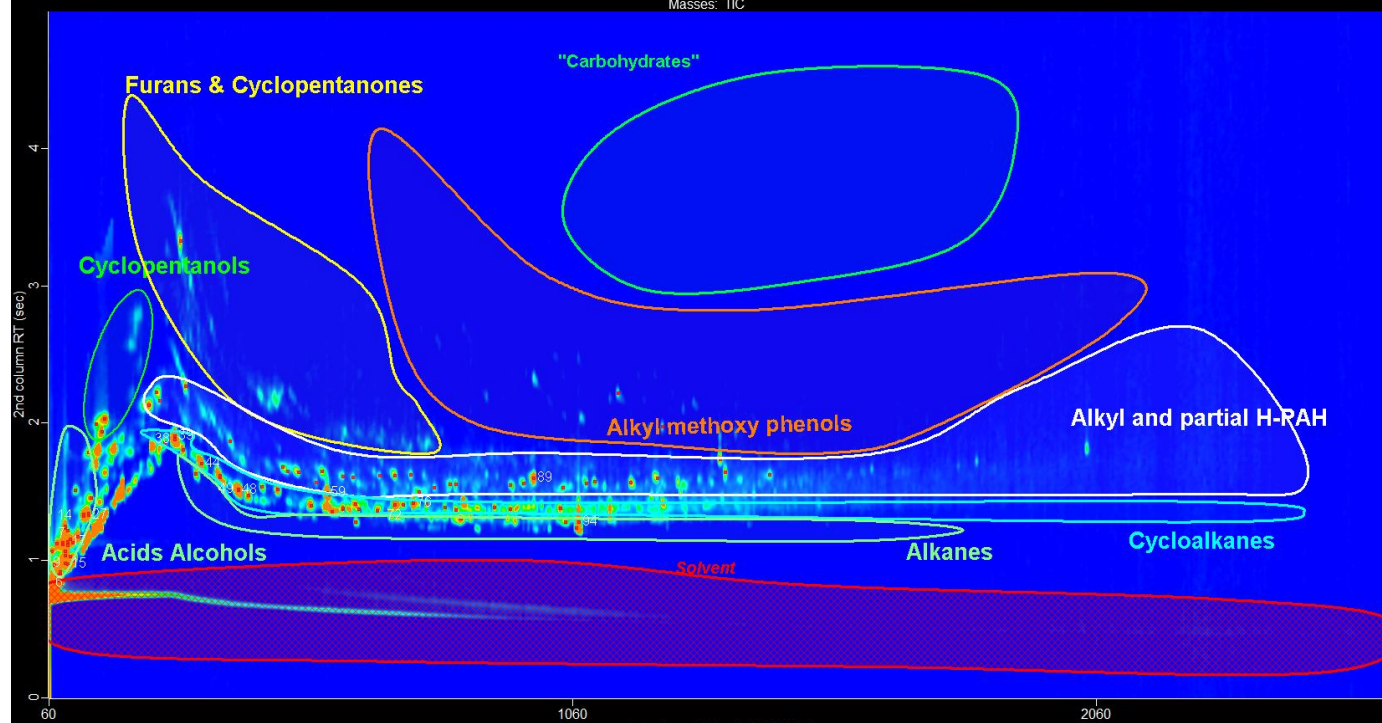
# Example GCxGC- TOFMS

Oak Pyrolysis  
Oil (500°C)



Hydrotreated

Distillate from early  
reaction product  
5%Pt on Char,  
280°C, 166 Bar



# 3 - Relevance

- Project supports the assessment of an alternative route (proprietary) that can contribute towards BETO's MYPP goal:
  - *By 2017, achieve a conversion cost of \$1.83 per gallon of total blendstock (\$1.73 /GGE, \$2011) via a bio-oil pathway.*
  - Also towards understanding technical performance cost and sustainability drivers
- Towards the Bioenergy Industry:
  - Contribute to the expansion of the biomass pyrolysis industry producing oils that can be upgraded in refineries by providing alternative processing



# 4 - Critical Success Factors

## Generic

- Technical: Achieving bio-oil technical specification in metals, acidity, viscosity, etc. as required for upgrading
- Market: Bio-oil that can be processed in a conventional refinery with reasonable cost
- Business: Technology that is technically and financially superior to other biomass conversion process

## Specific











- Demonstrate viability of technical approaches
- Demonstrate product compatibility with infrastructure
- Successful project could positively impact commercial viability of biomass pyrolysis intermediates in the context of petroleum refineries

# 5. Future Work

- NREL prepares bagasse pyrolysis oils– anticipated 10/31; pending arrival of bagasse pellets from Brazil – Milestone and deliverable
- Petrobras and NREL exchange samples, analytical methodology, and results to improve techniques. Analytical methodology report prepared 2013
- Petrobras co-processes bagasse and oak (reference) oils in pilot and demo scales during calendar year 2014
- Petrobras and NREL address syngas production with catalysts from both organizations
- Analyses of results in preparation for the TEA/LCA/ Sustainability analysis – US conditions (NREL); Brazilian conditions (Petrobras)
- Major timing uncertainty is the shipping of large and small samples both ways.
- Management: Monthly calls, emails and technical meetings as necessary.

# Petrobras – NREL RD&D CRADA

## WBS: 6.5.1.1

	2013				2014				2015	
	2/1	4/1	7/1	10/1	1/1	4/1	7/1	10/1	1/1	3/1
<b>Phase 1 Bio-Oil Production</b>										
Oak Oil Production	Complete									
Bagasse Pellet Shipment										
Bagasse Oil Production										
Bio-Oil Shipment										
<b>Phase 2</b>										
Phase 2-1 Coprocessing in Refinery Operations - Petrobras										
Phase 2-2 Syngas from Bio-oil-both organizations										
Phase 2-3 Bio-oils & Upgraded Products Characterization-both										
Phase 2-4 TEA,LCA, Sustainability Analysis - joint										
<b>Reporting</b>										
2013 Annual Report										
2014 Annual Report										
Final Report										

# Summary

- The bilateral RD&D activities leverage technical expertise and capabilities in two organizations and have significant cost share.
- Work is relevant to bio-oil pathways BETO's MYPP is assessing and will provide alternate (proprietary) assessment of developing hydrocarbon fuels from pyrolysis oils. Success will contribute to the expansion of the biomass pyrolysis industry providing feedstocks for co-processing in petroleum refineries.
- Joint RD&D started 2/2013. In FY 12 NREL pyrolyzed 600 kg White American Oak to generate bio-oils for comparative assessment at bench and demo scale at Petrobras. In 2013 NREL will pyrolyze 1000 kg bagasse and ship both oils to Petrobras for co-processing studies in a refinery context.
- Project is part of the Strategic Energy Dialogue between the governments of the U.S.A. and Brazil. The strategy is to increase the Western Hemisphere energy security, generate economic development in both countries, while providing environmental benefits. Sustainability analysis will be conducted.

# Abbreviations

## BRAZIL - Analytical Round Robin (2011-2013)

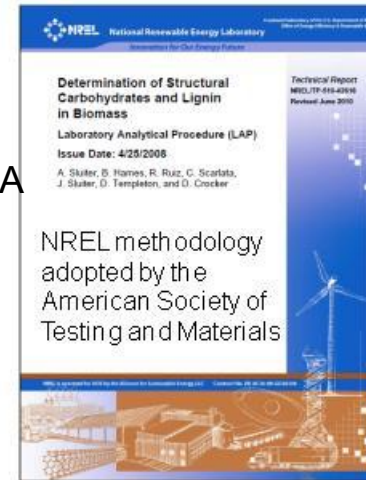
1. CENPES: R&D Center of Petrobras, Rio de Janeiro (RJ)
2. CTBE: Brazilian Bioethanol Science and Technology Lab. , Campinas/ Ministry of Science, Technology and Innovation (MCTI)
3. CTC: Sugarcane Technology Center, Piracicaba (private sector)
4. EMBRAPA AGROENERGIA: Brazilian Company on Agronomy Research, Brasilia/MAPA
5. INT: National Institute of Technology (MCTI), RJ
6. IPEN: Institute of Nuclear and Energy Research, São Paulo
7. IQ/UNESP: Chemistry Inst., State University of São Paulo, Araraquara
8. EEL/USP: Engineering School, Lorena, University of São Paulo (USP)
9. IQSC/USP: Chemistry Inst., São Carlos, USP
10. INMETRO = National Institute of Metrology, Quality, and Technology, RJ/Ministry of Development, Industry and Foreign Trade

## USA – Training, Homogeneous Bagasse Sample Preparation & Round Robin Analysis Audit and Joint Paper Preparation

- NREL: National Bioenergy Center (NBC), Biomass Analysis

• Advanced training on 9/20-24/2010 for 5 expert professionals for CTBE, CTC, INMETRO; Demo comparative analytical results by CENPES and NREL and of the need for methodology standardization and reference samples

Regular course on 9/27–10/1 for EMBRAPA, IPEN, UNESP, INT



<http://ts.nist.gov/measurement-services/referencematerials/index.cfm>



# Thank You!

## Acknowledgements

### Collaborators and Supporters:

**DOE BETO:** Paul Grabowski (POC), Melissa Klembara, Liz Moore [BETO], Alison Goss Eng

**DOE EERE International:** Dan Birns (POC), Rob Sandoli

**Brazilian Ministry of Mines and Energy:** Ricardo Dornelles

**NREL:** Rich Bain, Kim Magrini, Calvin Feik, Steve Deutch, David Templeton, Michele Myers, Stuart Black;

**NREL CRADA:** Anne Miller, Eric Payne, Rich Bolin;

Management: Adam Bratis, Mark Davis, Dale Gardner, Tom Foust

**Petrobras/CENPES/ Biomass Conversion:** Marco Antonio Gomes, Marlon Almeida, Vitor Ximenes, Fabio Mendes, Paulo Cesar Barbosa

**Petrobras/CENPES:** Andre Fachetti, Marcos Assayad



# Additional Slides

# U.S.-Brazil Strategic Energy Dialogue

Summary of the meeting between the Deputy Secretary of Energy of the United States of America, Daniel Poneman and the Deputy Minister of Mines and Energy of the Federative Republic of Brazil, Márcio Pereira Zimmermann

On the Strategic Energy Dialogue

March 19, 2013

"Through the Strategic Energy Dialogue, we are working to deliver concrete results that will help grow our economies through sustainable energy development and enhance our energy security," said U.S. Deputy Secretary of Energy Daniel Poneman. "With a strong, cooperative relationship between both our governments and the private sector, we are already advancing our shared energy goals in areas ranging from biofuels, renewables, and energy efficiency to sustainable oil and gas development and the safe operation of nuclear power generation."

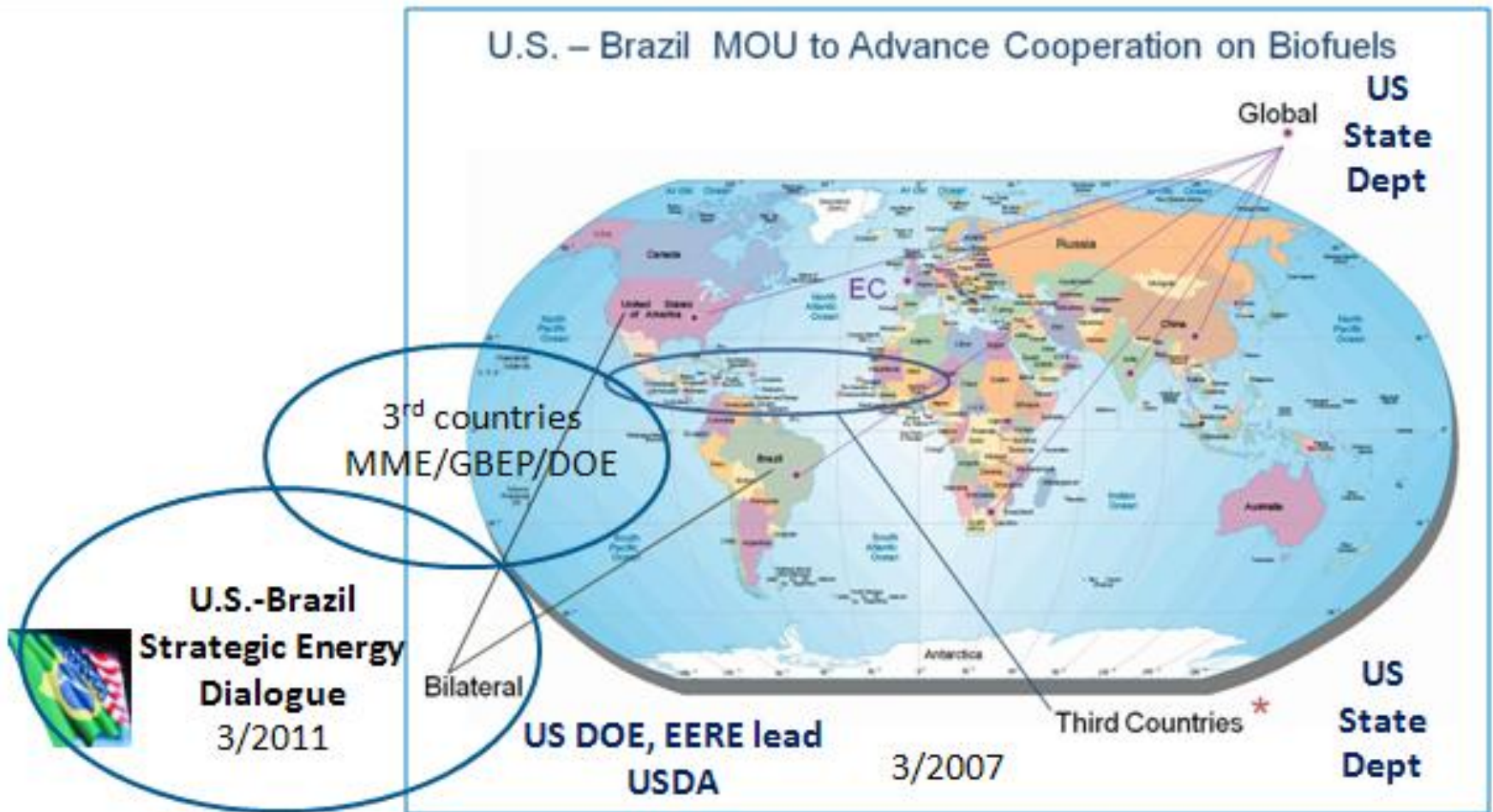
Both Parties recognized the advances achieved by this bilateral cooperation and are pleased to agree on the next steps of each of the following areas:

## I. Biofuels

The cooperation between the two countries has advanced significantly, particularly with regard to the objectives of the biofuels sustainability analysis work, conversion R&D, and the Memorandum of Understanding, which includes cooperation in third party countries and aviation biofuels. Highlights include the signing of an agreement between Petrobras/CENPES and NREL - DOE to develop technology for producing advanced biofuels and evaluating emissions, conducted jointly by NREL, UNICAMP, CTBE and CTC.

<http://energy.gov/articles/us-energy-deputy-secretary-poneman-brazil-s-deputy-minister-mines-and-energy-zimmermann>

# Cooperation Frameworks



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

# Responses to Previous Reviewers' Comments

- New Project



# Publications and Presentations

- New Project