

DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

Fractionation and Catalytic Upgrading of Bio-Oil FY13 DE-FOA-000 CHASE

March 2015

Technology Area Review

PI: Daniel E. Resasco – co-PI: Steven P. Crossley

University of Oklahoma

Goal Statement

- Current technologies:
 - low C-retention in fuel range
 - high H consumption.
- Experimental results allow
 - life-cycle analysis (LCA) and
 - techno-economic analysis (TEA)back fed to the experimentalists to refine selection of catalyst and process operations
- ultimate objective is
 - maximizing C efficiency at minimum H utilization.
- This project:
 - effective fractionation, combined with
 - catalytic upgrading for
 - C-C bond formation
 - Hydrodeoxygenationin liquid and vapor phases

Quad Chart Overview

Timeline

- October, 2013
- October, 2016
- 50 % Complete

Partners

- OU 50 %
- INL 25 %
- U. Wisconsin 12.5 %
- U. Pittsburgh 12.5 %

Barriers

Tt-F. Deconstruction of Biomass to Form Bio-Oil Intermediates

Tt-I. Catalytic Upgrading of Gaseous Intermediates to Fuels and Chemicals

Tt-J. Catalytic Upgrading of Bio-Oil Intermediates to Fuels and Chemicals

Tt-O. Separations Efficiency

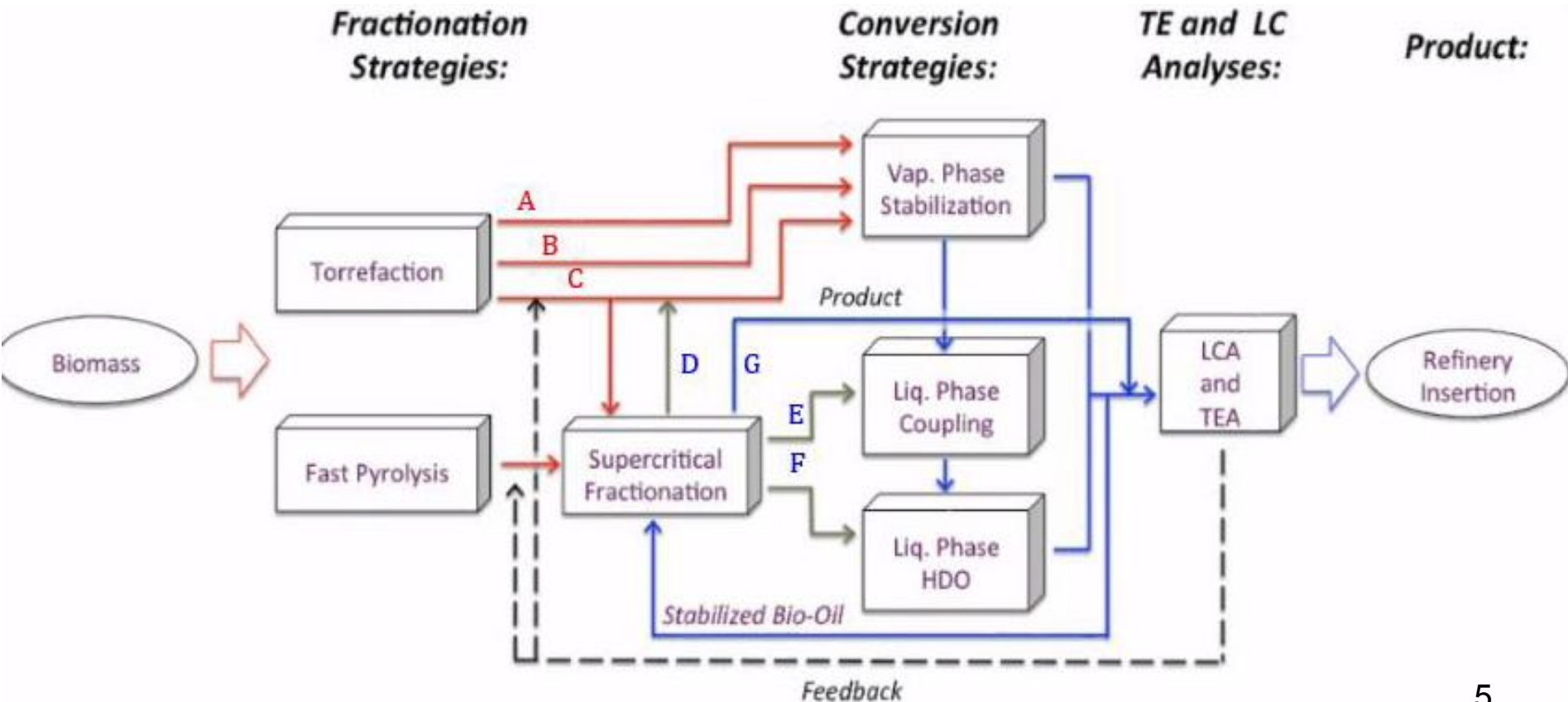
Tt-S. Petroleum Refinery Integration of Bio-Oil Intermediates

Budget

	Total Costs FY 10 –FY 12	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15- Project End Date)
DOE Funded	N/A	N/A	329,973	1,563,936
Project Cost Share (Comp.)*	N/A	N/A	155,420	562,089

1 - Project Overview

Interconnections of knowledge and samples among the various groups of the team



2 – Approach (Technical)

- **Thermal fractionation:**
 - moderate temperatures and times → deconstruction of most reactive parts → mostly small oxygenates
 - Higher temperatures and faster heating rates → mostly phenolic compounds
- **Catalytic upgrading:** Specific catalyst formulations maximize C retention in liquid phase and minimize catalyst deactivation
- **Separation:** Refining of the different fractions by supercritical extraction and selective adsorption further divides the primary fractions in purer streams
- **LCA and TEA:** Analysis LCA and TEA helps continuous improvement and feedback
- **Potential challenges** are the severely deactivating conditions imposed by the compounds involved in the streams towards the catalysts as well as the complex mixtures that make fractionation complicated.

2 – Approach (Management)

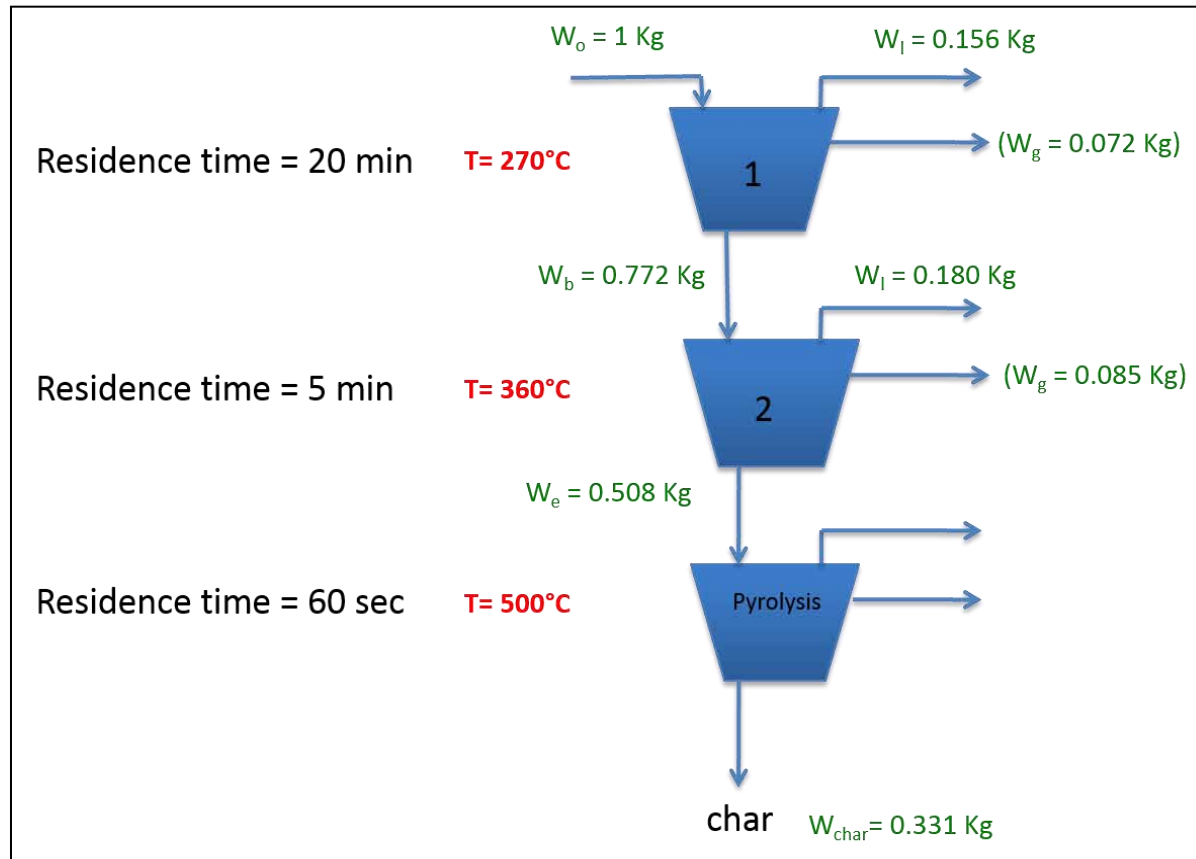
- The outcome of this project will be a series of possible process strategies to produce stabilized liquid projects that could be inserted in a conventional oil refinery.
- The most important challenge is related to process economics
- The current goal is to find thermal fractionation processes, catalysts and catalytic reactors, as well as separation processes that minimize the cost and environmental impacts, maximizing the liquid yield
- The senior personnel of the different parts of the project are responsible of planning, organizing, controlling resources, and procedures to accomplish the established goal

3 – Technical Accomplishments

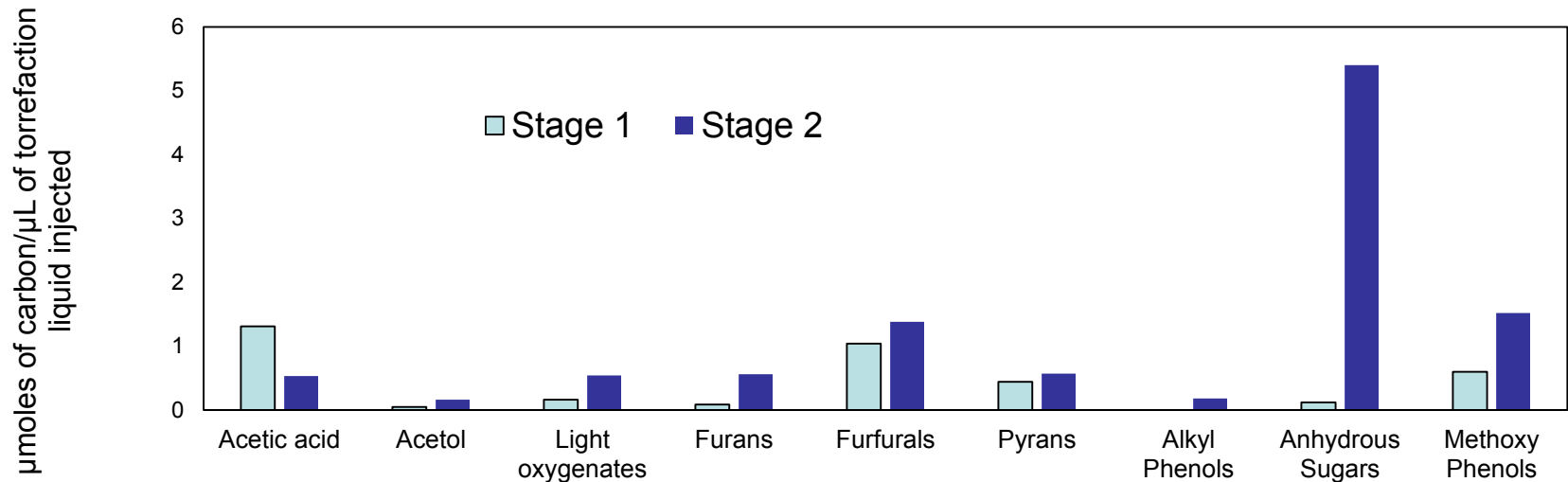
Objective A. Thermal Fractionation

Done in multi-stages, with residual solid from each stage becoming the feed of next stage. In the last one, the solid is fast pyrolyzed. The current multi-stage system contains two torrefaction stages carried out at 270° C (20 min) and 360° C (5 min) and the final pyrolysis stage at 500° C (1 min)

Mass balance measured in each of the stages



Comparison of stage 1 & stage 2 liquid compositions



Objective B. Supercritical fluid extraction of thermal fractions.

This milestone intends to examine different critical fluids for extraction of torrefaction bio-oils. The fluids examined so far included carbon dioxide (CO_2), propane (C_3H_8), dimethylether (DME), and tetrahydrofuran (THF). From these experiments the more significant results indicate that two ethers (DME and THF) were not effective as extraction solvents since they formed 1 phase with the bio-oils. Propane did form 2 phases, but had low extraction efficiencies. With the current result it can be partially concluded that CO_2 appears to be the most promising critical fluid for extraction.

Objective C. Design of novel catalysts . Synthesis and characterization of different material with catalytic properties allow us to understand the relationship between synthesis and properties of catalytic materials. This section is dedicated towards the synthesis, and characterization of different materials with potentially good catalytic performance.

C. 1 Metal catalysts

No	Catalysts	Preparation method
1	1 wt % Pt/SiO ₂ (15 g)	IWI
2	0.1,1 wt % Ru/SiO ₂ (15 g)	IWI/Reduction
3	5,10 wt % Ru/SiO ₂ (15 g)	IWI/Reduction
4	1 wt % Pd-Fe/SiO ₂ (20 g)	IWI
5	2 wt % Pd-Fe/SiO ₂ (20 g)	IWI

C.2 Oxide catalysts

Catalyst	BET Surface area (m ² /g)
TiO ₂ P25	60
TiO ₂ Anatase	165
Ce _{0.5} Zr _{0.5} O ₂	137
SiO ₂	145
Al ₂ O ₃	122

C. 3 Zeolite catalysts

Material	Volume (cm ³ /g)			Area (m ² /g)	
	Micropore	Total Pore	Mesopore	Ext Surface	Micropore
Parent Zeolite	0.186	0.222	0.035	19.5	355
Mesoporous zeolite	0.165	0.305	0.14	51.63	314.9
Mesoporous zeolite acid washed	0.189	0.357	0.168	61	361

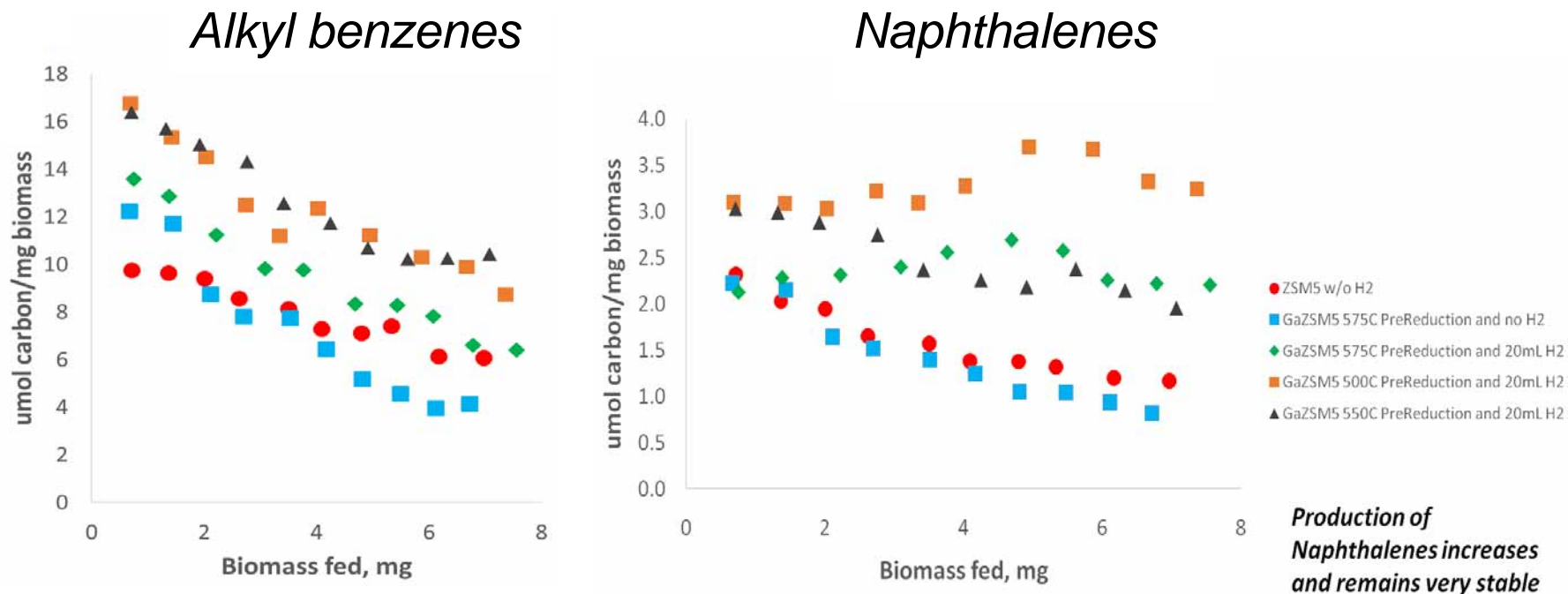
Objective D. Chemical reactions involved in the catalytic upgrading of thermally fractionated bio-oils

- Aldol Condensation
- Furfural oxidation
- Ketonization of carboxylic acids
- Piancatelli rearrangement / aldol condensation
- Acylation of phenolics
- Alkylation of phenolics
- Hydroxyalkylation of phenolics
- Hydrodeoxygenation
- Diels Alder cycloaddition

Objective D. Catalytic upgrading

D. 1 Vapor phase upgrading over Ga-ZSM5.

Incorporation of Ga causes a significant increase in production of deoxygenated alkylaromatics when the upgrade is conducted under H₂



Alkyl benzenes yield as a function of biomass feed over GaZSM5 with different pretreatment conditions

Naphthalenes yield as a function of biomass feed over GaZSM5 with different pretreatment conditions

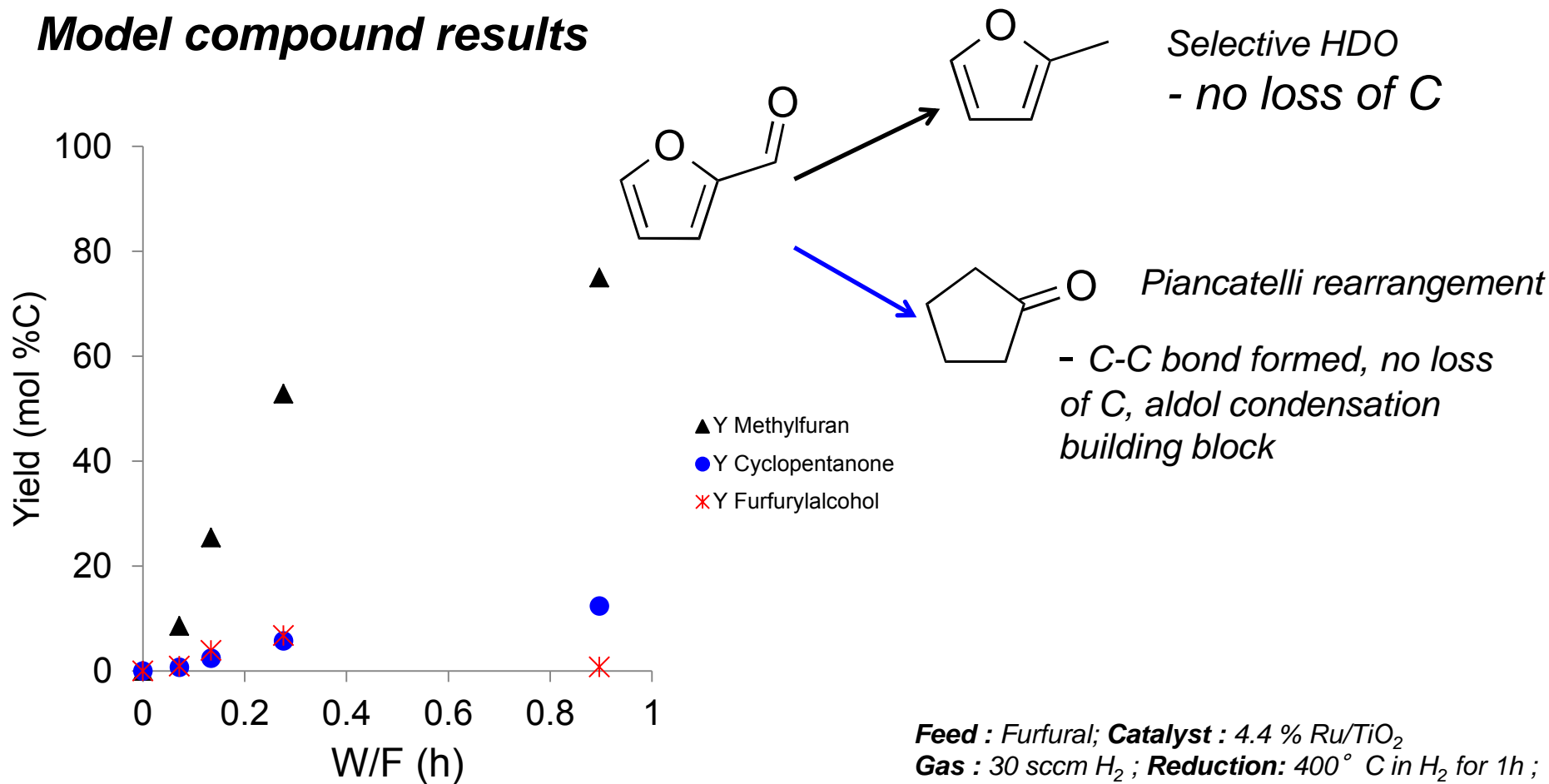
Evaluate both activity and catalyst lifetimes with real feeds for input to LCA and TEA models

Objective D. Catalytic upgrading

D. 1 Vapor phase upgrading of fraction A on Ru/TiO₂

Ru/TiO₂ catalysts show great promise with model compounds

Model compound results



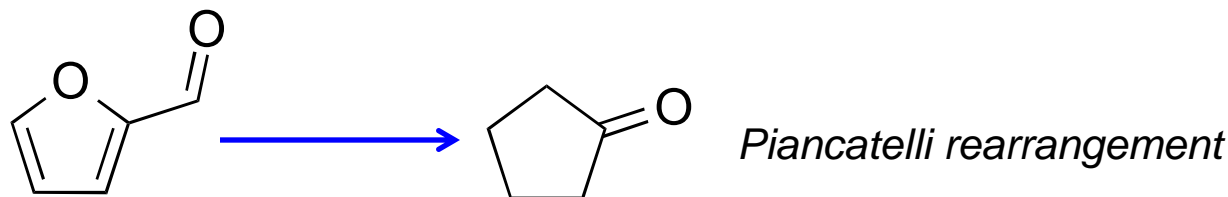
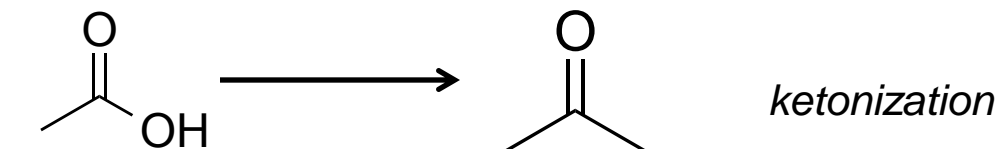
Feed : Furfural; **Catalyst :** 4.4 % Ru/TiO₂
Gas : 30 sccm H₂ ; **Reduction:** 400° C in H₂ for 1h ;
Reaction T = 400° C; **P=** 1atm;
TOS = 30 mins

Objective D. Catalytic upgrading

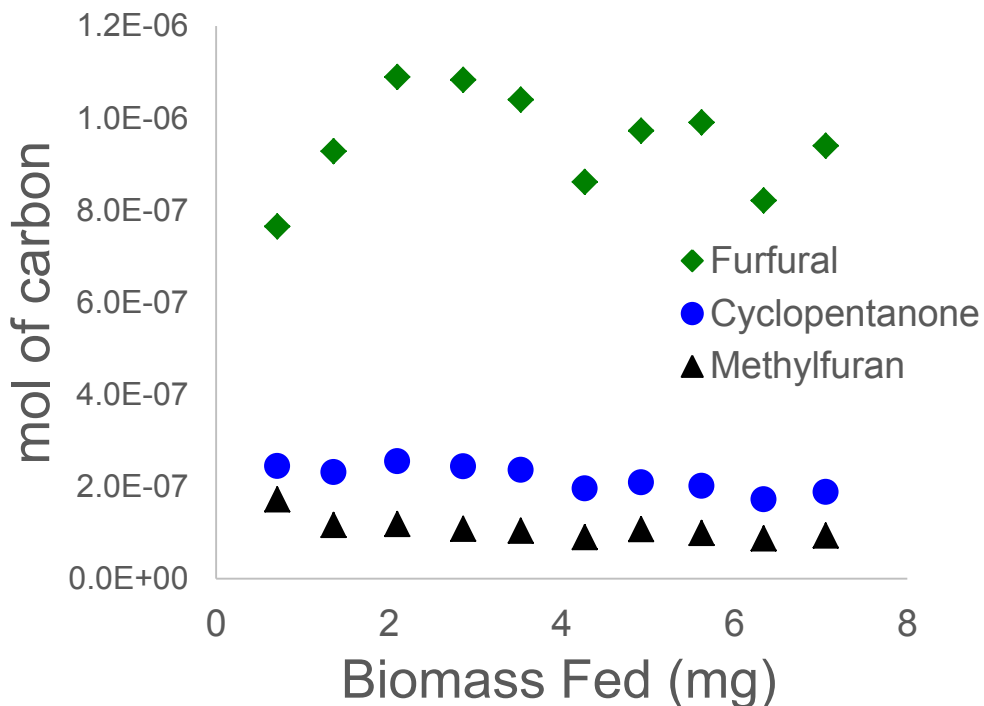
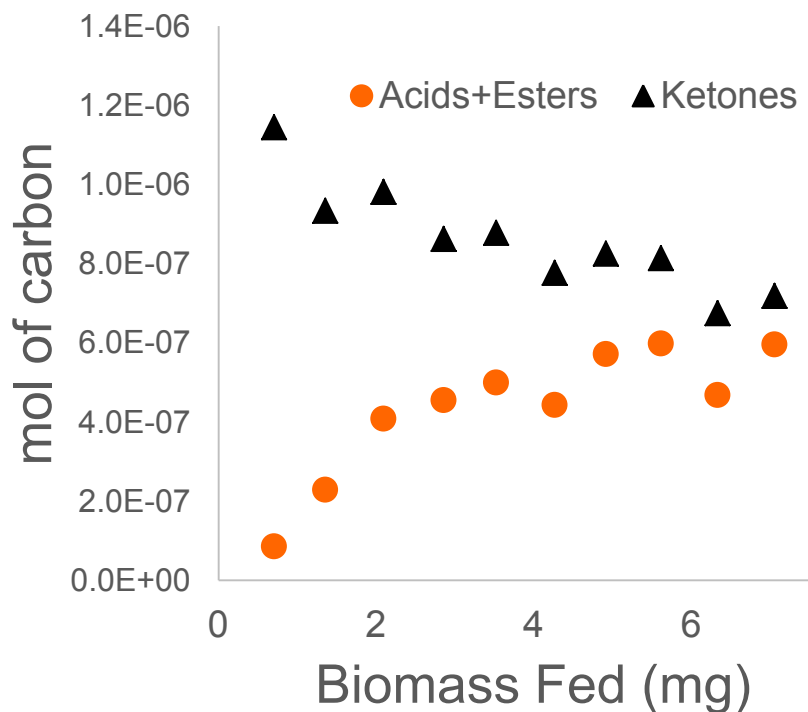
D. 1 Vapor phase upgrading of fraction A on Ru/TiO₂

Ru/TiO₂ catalysts demonstrate even more promise with real torrefaction vapors

Torrefaction vapors

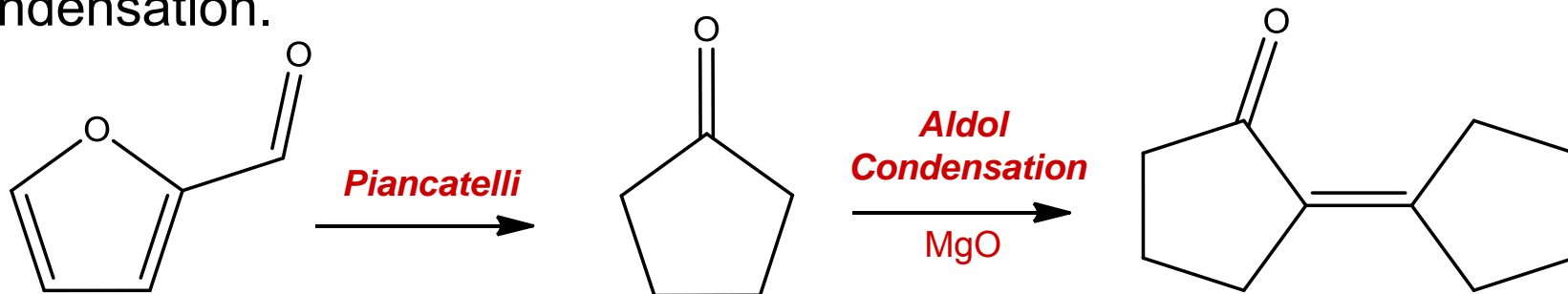


Excellent selectivity to ketone building blocks with real feed



Objective D. Catalytic upgrading

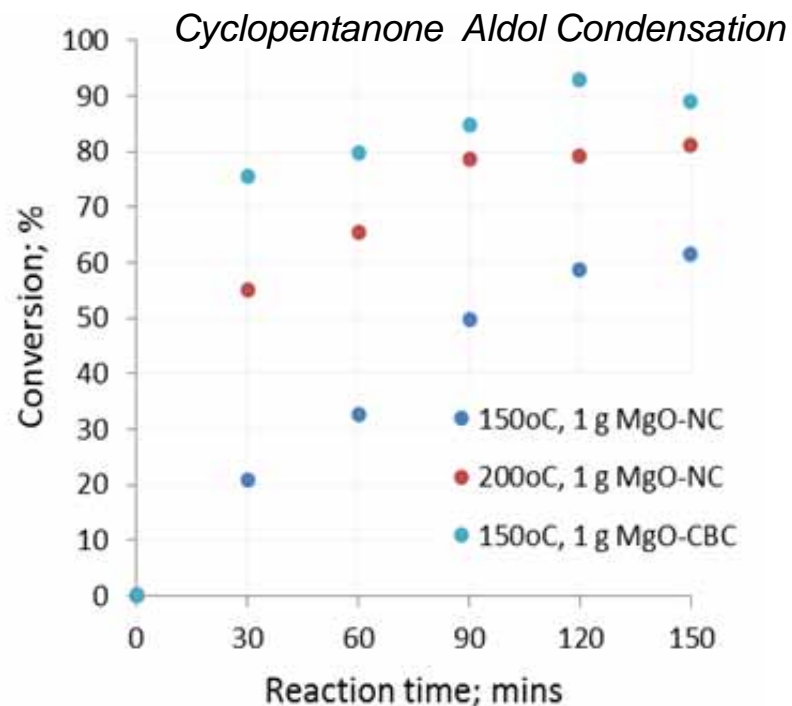
D. 2 Liquid phase upgrading of furanics (derived from fraction B)
furfural Piancatelli rearrangement followed by cyclopentanone aldol condensation.



Furfural hydrogenation Piancatelli rearrangement

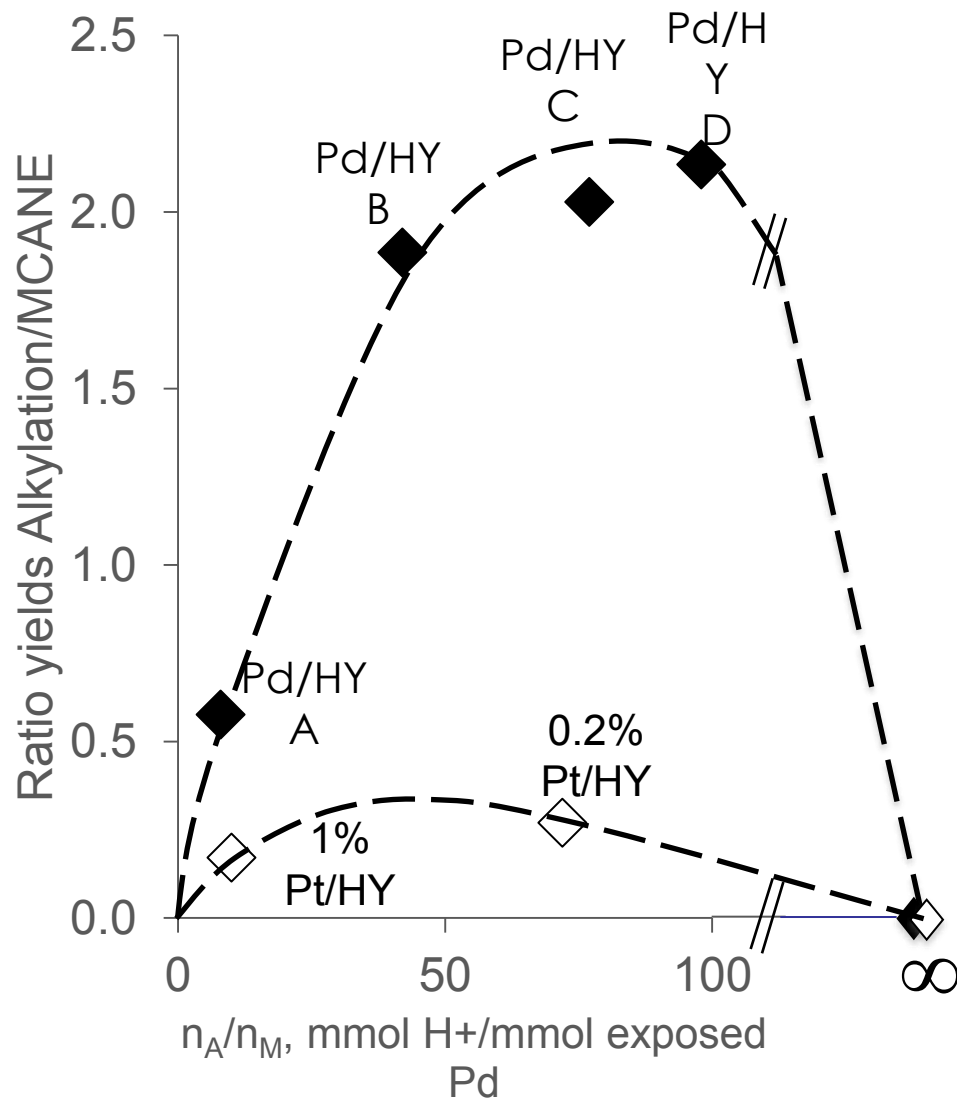
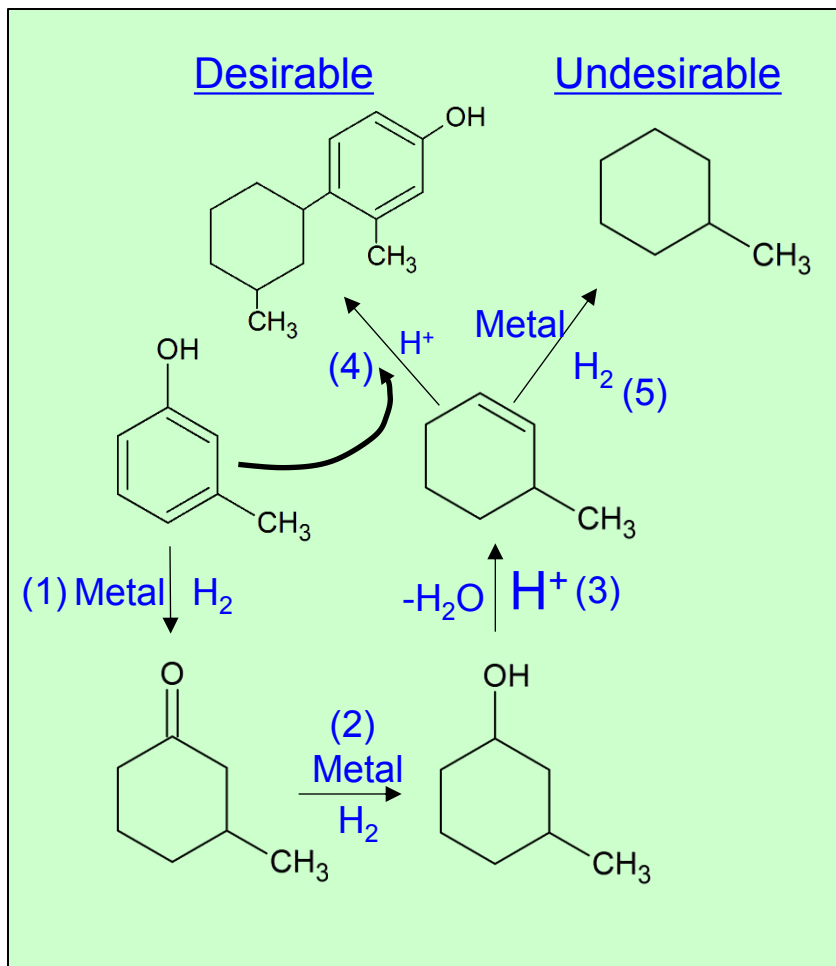
Pressure (psia)	Conversion	Cyclopentanone Selectivity
200	49%	<u>95%</u>
300	79%	<u>93%</u>
600	93%	<u>88%</u>

***Catalyst:** 2%Pd-Fe/SiO₂ (1:1) - **Solvent:** Water
***Temp:** 150°C, **time:** 6h, **Pressure:** 200-600 psia



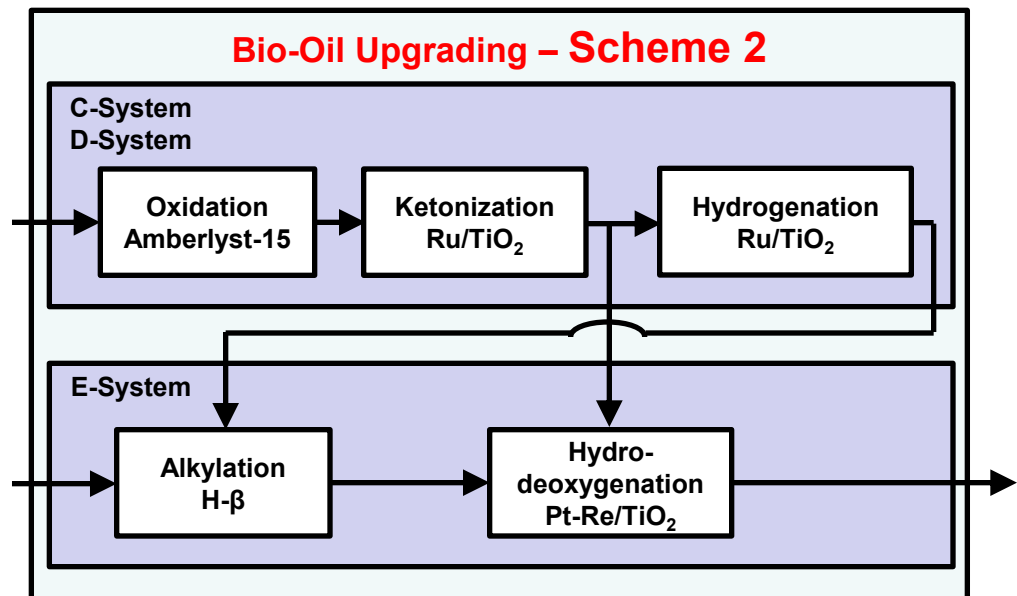
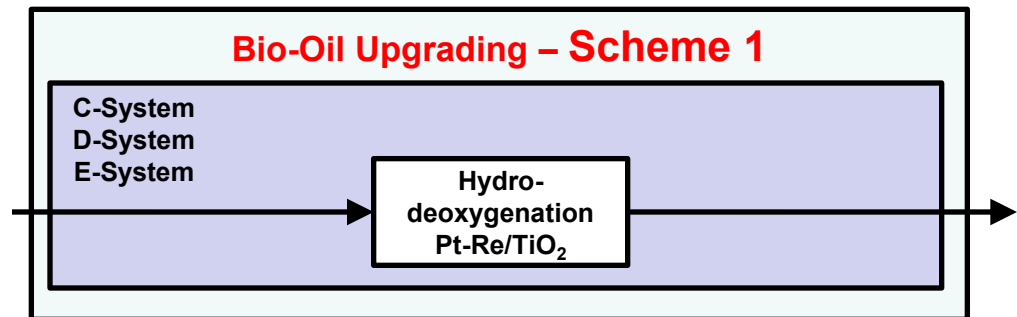
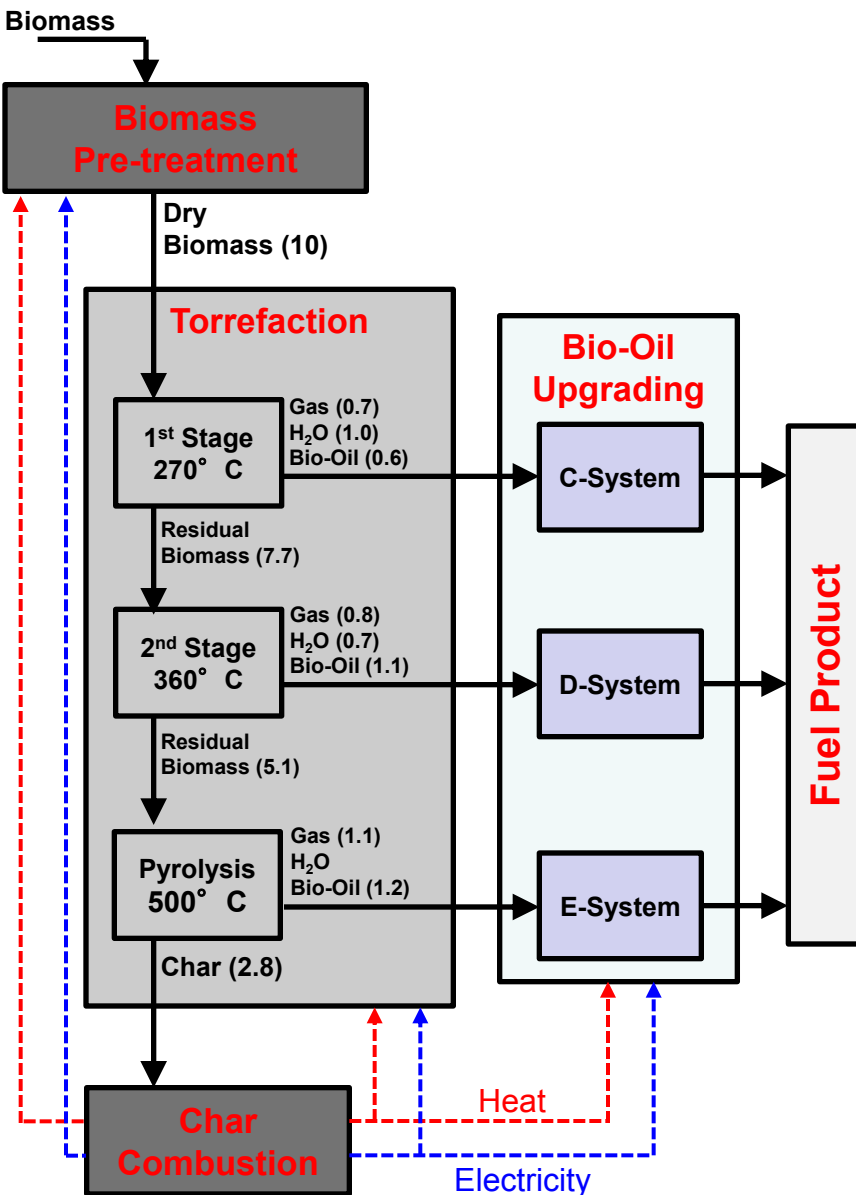
Objective D. Catalytic upgrading

D. 3 Alkylation and HDO of fraction C (phenolics)



Objective E. TEA

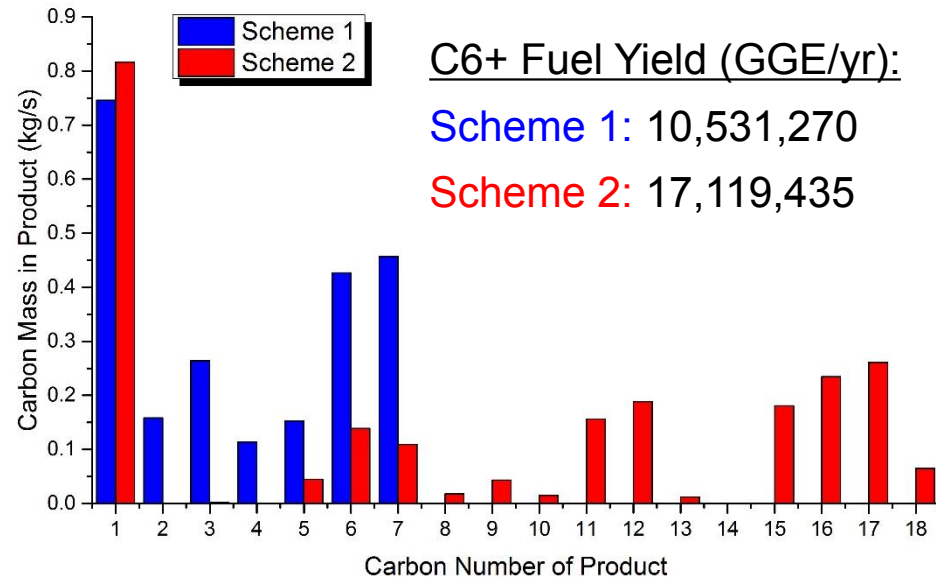
Techno-economical analysis of the current technology



Objective E. TEA

Techno-economical analysis of the current technology

- Higher upgrading complexity shifts product distribution to higher hydrocarbons
- From discounted cash flow analysis of a simplified process, we calculate minimum selling price of bio-fuel:



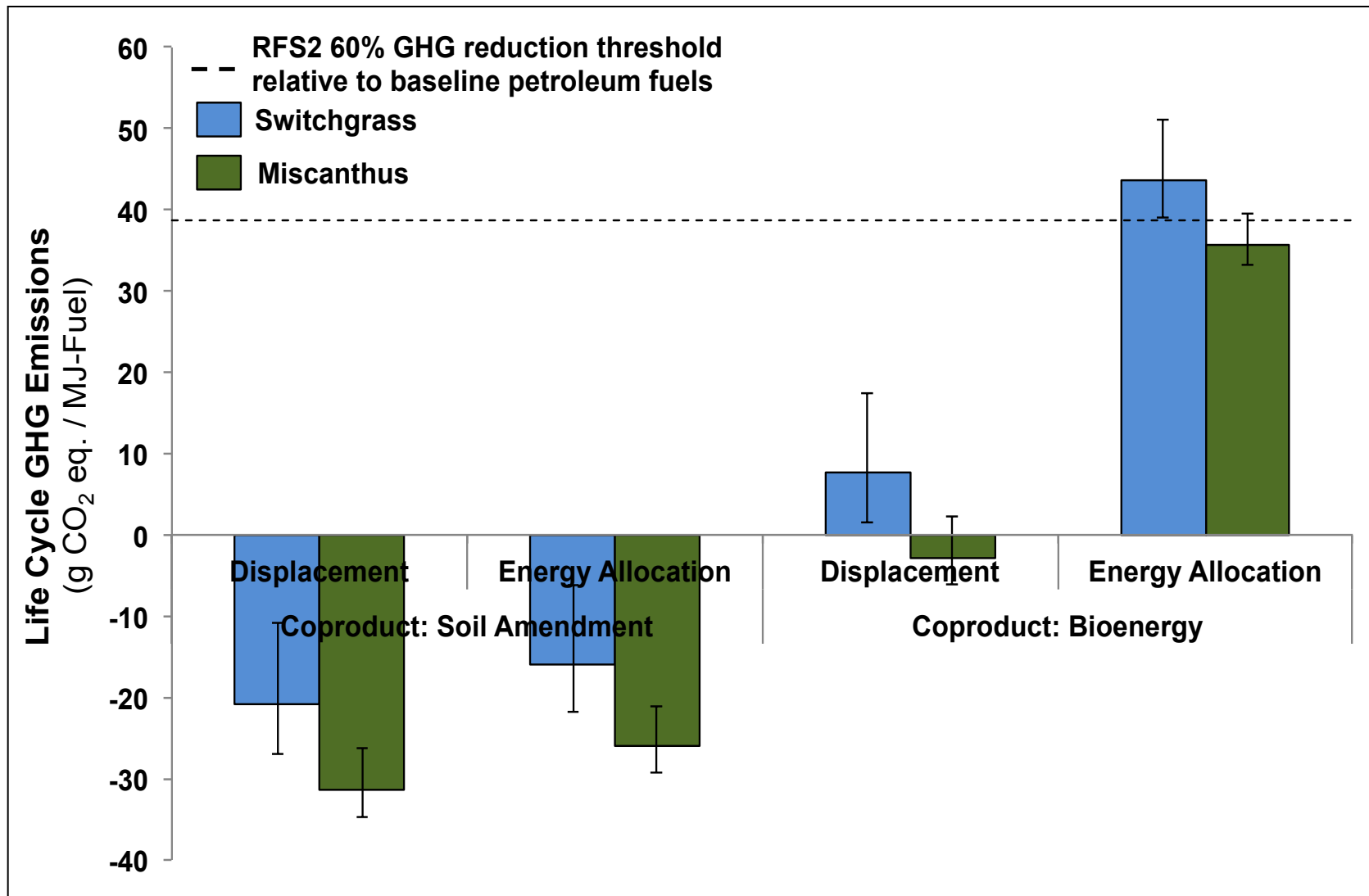
Scheme 1: 6.14 USD/GGE

Scheme 2: 5.24 USD/GGE

	Cost (Cents/GGE)	
	Scheme 1	Scheme 2
Fixed Costs	87	104
Electricity	16	8
Raw Materials		
Biomass	248	153
H ₂	97	42
H ₂ O ₂	--	30
Waste Treatment	31	14
Catalyst	8	5
Catalyst Regeneration	11	6
Total	498	362

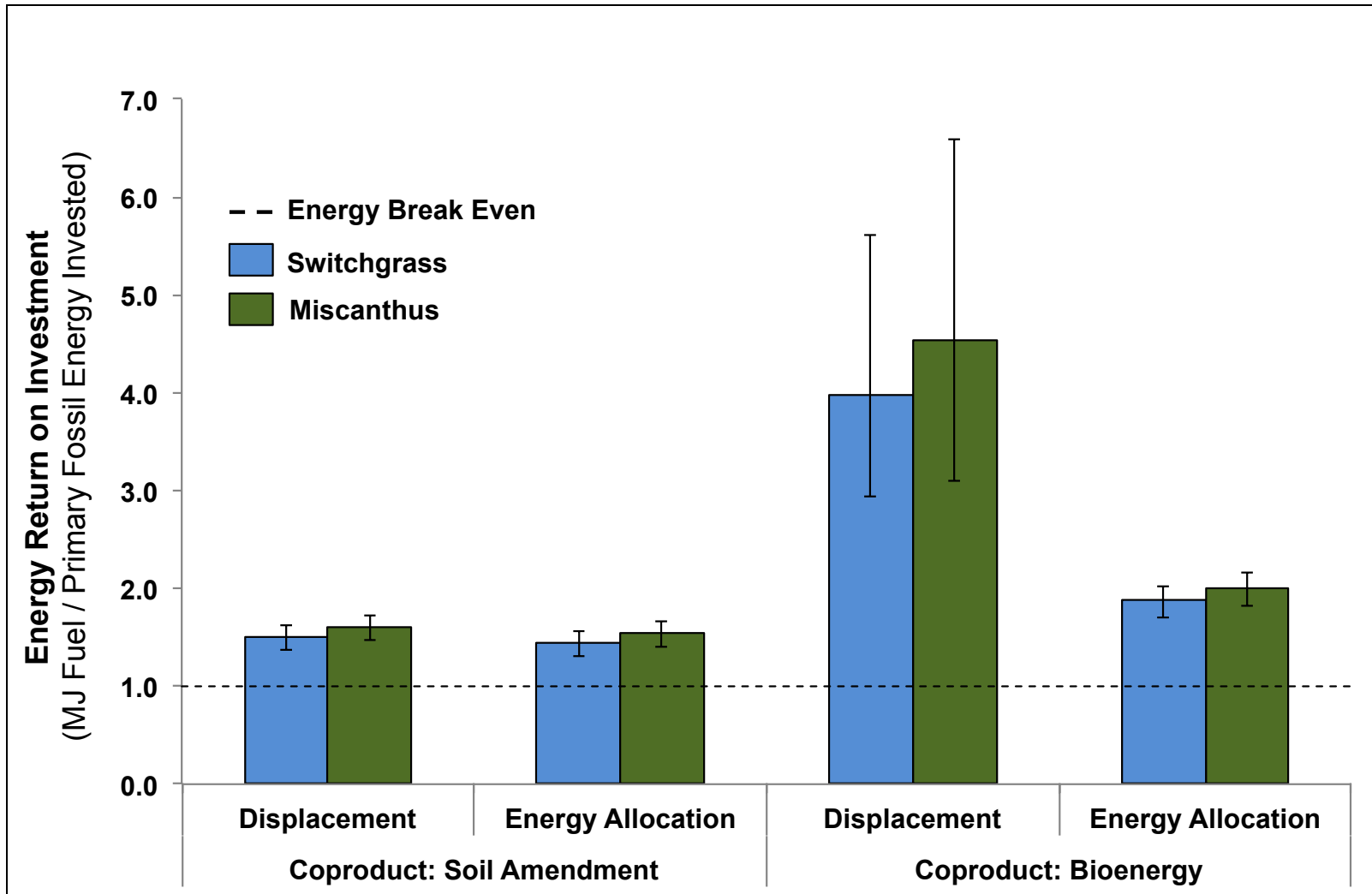
Objective F. LCA

H₂ consumption CO₂ reduction greenhouse gases reduction



Objective F. LCA

Energy Return on Investment



4 – Relevance

Tt-F. Deconstruction of Biomass to Form Bio-Oil Intermediates

Three stages are used: two Torrefaction and one Fast Pyrolysis stage to divide families of compound to be upgraded with more specialized and targeted chemistries to improve overall fuel yields.

Tt-J. Catalytic Upgrading of Bio-Oil Intermediates to Fuels and Chemicals

Demonstrated conversion of bio oils through various scenarios to compounds that contain C-C bonds in the gasoline + diesel range

Tt-O. Separations Efficiency

Two aspects: a) Staged thermal deconstruction that provides the primary separation. B) Solvent extractions and supercritical extractions using various alcohols, ethers, water and CO₂ with model pyrolysis oils and real streams.

5 – Future Work

- Continue improving catalysts and process conditions to optimize liquid yields and minimize deactivation
- With the large number of fractionation analysis data as well as catalytic reactions data, TEA and LCA studies become much more realistic and will guide the future experimental studies.
- Based on next TEA and LCA results, we will determine which scenarios are most promising and will focus on them. For example, recent analysis clearly indicate that, due to the preservation of C, acylation has a much greater impact than ketonization.
- With analysis like this, we reach decision points for Go/No-Go of different upgrading approaches that allow us to redirect efforts.

Summary

- The first results of this project show that by an effective fractionation strategy combined with catalytic upgrading it is possible to improve the yield of liquids with appropriate O content and molecular weight to incorporate in oil refineries.
- Separating vapors and liquids of different bio-oil fractions greatly enhances the effectiveness and utilization of catalysts used during the upgrading
- Life-cycle and techno-economic analyses help making process decisions on which ones are most promising routes.

Additional Slides

Analytical identification and quantification of most components present in bio-oil

compound	RT	compound	RT	compound	RT	compound	RT
light gas	7.101	pyran Isomer	25.898	unknown	40.719	Acetoguaiacone	52.2
furan	7.374	2,3-Dihydroxyhex-1-ene-4-one	26.011	unknown	40.849	Anhydrosugar: unknown	52.669
Propanal-2-one	8.055	gamma-Butyrolactone	26.866	unknown	40.922	Syringol, 4-vinyl-	53.753
Methyl furan	8.706	(5H)-Furan-2-one	27.343	1,4: 3,6-Dianhydro-glucopyranose	41.53	Guaiacylacetone	54.149
2,3-Butanedione	9.242	Lactone	28.041	unknown	42.442	Syringol, 4-allyl-	54.453
Unknown: similar to 3-Pentanone	9.534	2H-Pyran, 3,4-dihydro-2-methoxy-	28.245	Guaiacol, 4-vinyl-	42.686	unknown	54.817
Hydroxyacetaldehyde	10.213	2,5-Furandione, dihydro-3-methylene-	28.552	eugenol	43.727	Coniferyl alcohol	55.853
acetic acid	11.095	Methyl-dihydro-(2H)-pyran-2-one	29.351	5-Hydroxymethyl-2- fu raldehyde	44.272	Syringol, 4-propenyl- (trans)	56.345
acetol	12.453	3-Methyl-(5H)-furan-2-one	29.533	Syringol	44.898	unknown	57.107
2-Propenoic acid, methyl ester	15.504	Phenol	30.862	Unknown	45.261	Levoglucosan	58.011
3-Hydroxypropanal	16.475	Guaiacol	31.708	2-Hydroxy-butanedial	45.718	Syringol, 4-propenyl-	58.531
(3H)-Furan-2-one	17.092	Methyl-butylaldehyde derivative	33.834	Isoeugenol (trans)	46.03	Syringaldehyde	59.571
(2H)-Furan-2-one	17.702	unknown	34.841	unknown	46.522	unknown	60.292
unknown	17.987	Guaiacol, 3-methyl-	35.055	2-Hydroxymethyl-5-hydroxy-2.3-dihydro-(4H)-pyran-4-one	47.019	Homosyringaldehyde	61.127
2-Hydroxy-3-oxobutanal	18.448	gamma-Lactone derivative: unknown	35.277	1,5-Anhydro-fl-D-xylofuranose	47.946	Acetosyringone	61.939
furfural	19.219	Levoglucosenone	36.165	Isoeugenol	48.16	1,6-Anhydro-.alpha.-d-galactofuranose	62.82
2-Furfuryl alcohol	21.218	Guaiacol, 3-methyl-	36.499	Vanillic acid	48.651	Syringyl acetone	63.396
1-Acetyloxypropane-2-one	21.659	Anhydrosugar: unknown	36.569	Vanillin	49.022	Propiosyringone	64.471
2-Ethyl-butanal	22.021	3,5-Dihydroxy-2-methyl-(4H)-pyran-4-one	37.03	Catechol, 3-methyl-	50.749	Sinapyl alcohol	65.041
Dihydro-methyl-furanone	24.481	Guaiacol, 4-ethyl	40.219	Guaiacol, 4-propyl-	51.375	Dihydrosinapyl alcohol	67.497
Dihydro-methyl-furanone	25.434	2,4(3H,5H)-Furandione, 3-methyl-	40.373	Syringol, 4-ethyl-	51.546	Sinapaldehyde	71.56

Publications

With explicit acknowledgement to the BETO DoE Grant

- Felipe Anaya, Lu Zhang, Qiaohua Tan, Daniel E. Resasco, “Tuning the Acid-Metal Balance in Pd/ and Pt/Zeolite Catalysts for the Hydroalkylation of m-Cresol” *Journal of Catalysis* - doi:10.1016/j.cattod.2014.06.037, online **2015**
- Daniel E. Resasco, Steven P. Crossley “Implementation of concepts derived from model compound studies in the separation and conversion of bio-oil to fuel” *Catalysis Today*, In Press, online **2014**,
- Shaolong Wan, Christopher Waters, Adam Stevens, Abhishek Gumidyala, Rolf Jentoft, Lance Lobban, Daniel Resasco, Richard Mallinson, and Steven Crossley, “Decoupling HZSM-5 Catalyst Activity from Deactivation during Upgrading of Pyrolysis Oil Vapors” *ChemSusChem.*, DOI: 10.1002/cssc.201402861, online **2015**
- J. A. Herron, D. E. Resasco, C. T. Maravelias, “Process synthesis for biomass torrefaction,” AIChE Annual Meeting, Atlanta, GA, November **2014**.