

DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

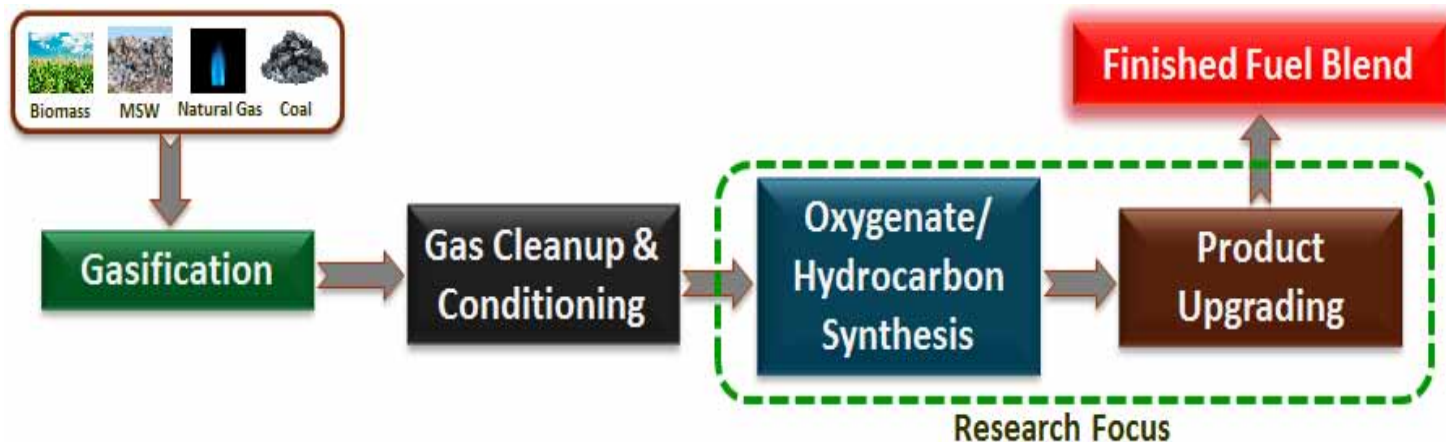
2.11.2.13 Liquid Fuels via Upgrading of Syngas Intermediates

March 26th, 2015
Indirect Liquefaction Technology Area Review

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Goal Statement

- **Problem:** Conventional synthetic fuel synthesis processes (e.g., FT, MTG, MTOGD) have drawbacks, specifically for the scale of biomass.
 - ❖ FT provides diesel blend but requires costly hydrocracking (waxes, etc.).
 - ❖ MTG provides gasoline range (aromatic rich), can be modified to produce a mixture of gasoline and distillates; capital intensive.
- **Goal:** Develop a catalytic upgrading technology enabling conversion of **syngas** and other **biologically-produced intermediates** to **gasoline, jet,** and/or **diesel** blend-stocks at a **scale** relevant for biomass and achieving BETO's targeted processing cost of **\$3/GGE** by **2022**.



Timeline

- Project start date: October 1, 2013
- Project end date: September 30, 2017
- Percent complete: 37%

Budget

	Total Costs FY 10 –FY 12*	FY 13 Costs*	FY 14 Costs	Total Planned Funding (FY 15-Project End Date)
DOE Funded	\$5.6M*	\$0.8M*	\$1.5M	\$5.6M
Project Cost Share (Comp.)				

*Prior mixed alcohol synthesis program.

Barriers

- Barriers addressed
 - ❖ Tt-I. Catalytic Upgrading of Gaseous Intermediates to Fuels and Chemicals.
 - ❖ Tt-N. Aqueous Phase Utilization and Wastewater Treatment.
 - ❖ Tt-K. Product Finishing.

Partners

- Washington State University – Experimental Catalysis.
- NREL – Techno-economic Analysis.
- Engaging with potential industrial partners.

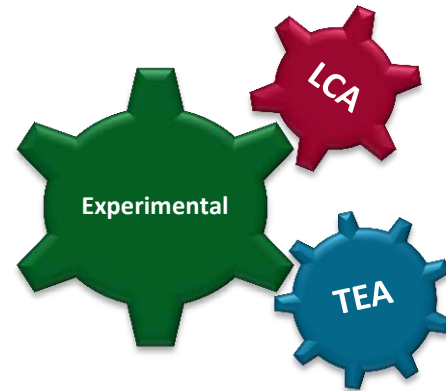
1- Project Overview

➤ Project History:

- ❖ Prior to FY14 PNNL activities in this platform were focused on **gasification**, **syngas cleanup**, **mixed alcohol**, and **oxygenate synthesis**.
- ❖ In FY14 PNNL began exploring **upgrading** technologies for the conversion of **mixed alcohols/oxygenates** to **fuels** and **chemicals**.

➤ Objectives of Project:

- ❖ Develop an **indirect liquefaction** (IDL) process amenable to an array of feedstocks (MSW, waste wood) suitable for the **scale** of biomass.
- ❖ Leverage interdisciplinary project teams to provide **experimental** data informing **techno-economic analyses** (TEA) and **life cycle analysis** (LCA) that provide regular feedback into the project plan.
- ❖ Process demonstration to meet the **BETO 2022 cost goals** for an (IDL) fuels pathway.



2- Approach (Technical)

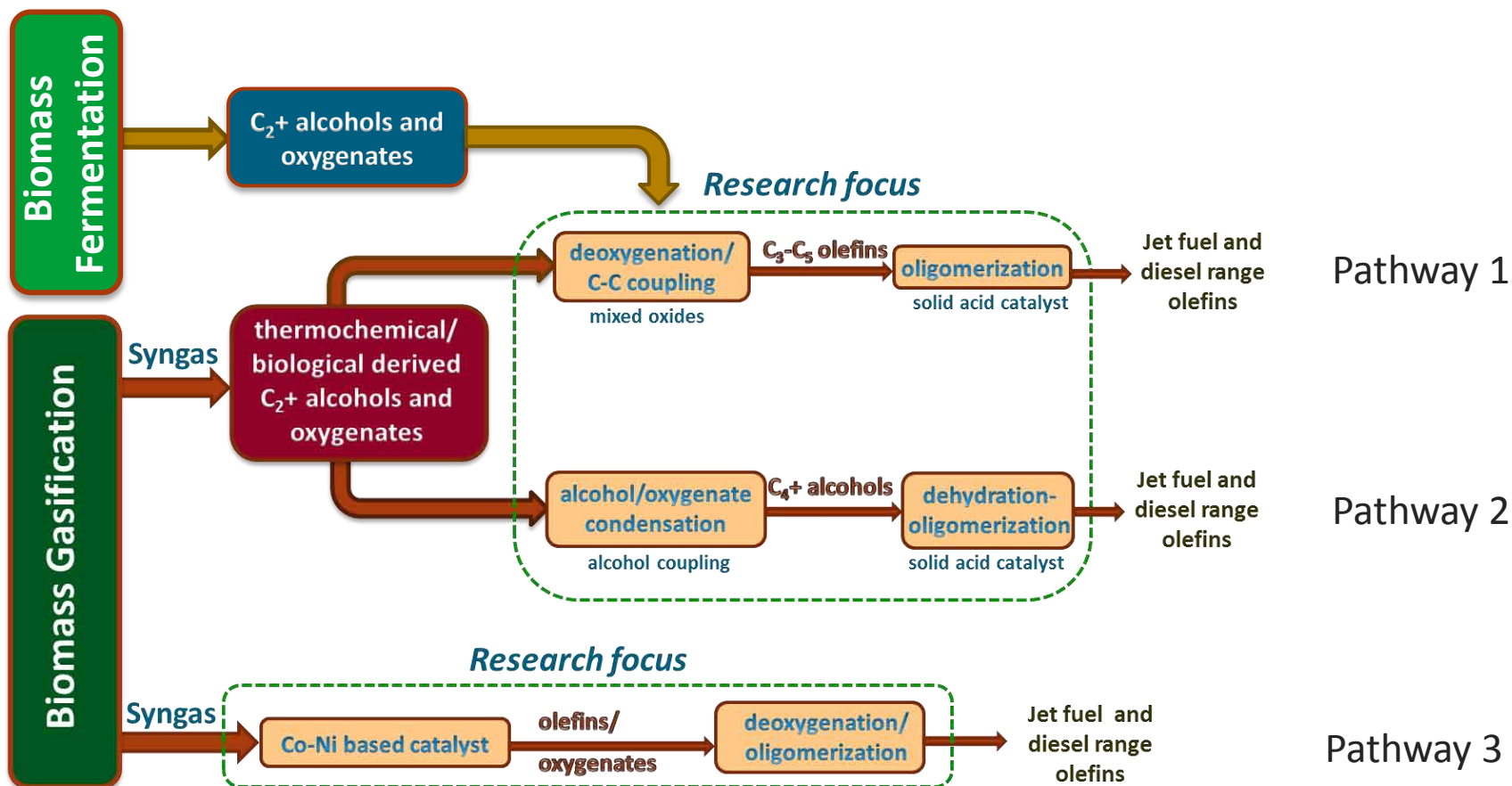
- **Leverage** recent **biomass research advances**, evaluate multiple, alternative pathways using combined experimental and techno-economic analyses.
 - ❖ Coordinate with NREL who is evaluating other pathways (e.g. through methanol intermediates).
- Critical success factors:
 - ❖ **High carbon and energy efficiency:** Benchmark against the conventional fuel synthesis processes.
 - ❖ **Feedstock flexibility:** MSW, flue gas, wood wastes, biologically-derived feedstocks, and other low cost feedstocks.
 - ❖ **High fuel quality:** Produce high quality jet and/or diesel blendstocks (composition, freeze points, boiling points, energy and volumetric density).
 - ❖ **Viable process economics:** Economically and environmentally sustainable.
- The challenges of this project are to develop a process that is selective towards a **jet** and/or **diesel** blend while maximizing carbon efficiency at a scale relevant for biomass.

2- Approach (Management)

- **Project Management Plan** (PMPs) in place indicating scope, budget and schedule.
- **Annual Operating Plans** (AOPs) with quarterly milestones prepared prior to each fiscal year.
- **Merit Review Proposal** in FY15.
- **Quarterly reporting** to BETO (written and regularly scheduled calls).
- **Monthly Project Team Meetings** engaging task managers and collaborators from Washington State University (Yong Wang's catalysis team).
- **Go/No-Go** pathway down select in mid-FY16.
- **Engage Industrial Partners** via site visits and technical discussions for future collaborations.

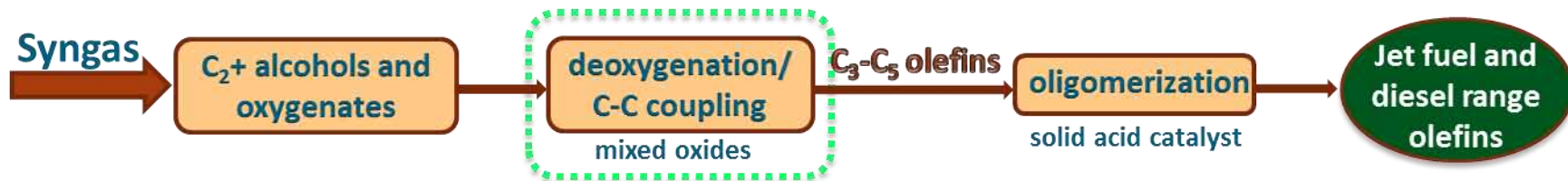
3- Technical Accomplishments

- Three synthesis pathways being evaluated:
 - ❖ Pathway 1: Mixed alcohol /oxygenate upgrading via **mixed oxides** catalysts.
 - ❖ Pathway 2: Mixed alcohol/oxygenate upgrading via **alcohol coupling**.
 - ❖ Pathway 3: **Direct syngas conversion** to olefin-rich intermediates and upgrading.



Pathway 1: Mixed Oxides to i-butene

Model compounds over Mixed Oxides ($Zn_xZr_yO_z$)



- Acetaldehyde, acetic acid and ethyl acetate lead to faster zeolite catalyst deactivation compared with ethanol, and also contribute significantly to aromatic hydrocarbon production.

Recent advance

Mixed oxide catalyst recently reported for ethanol conversion to isobutylene in a single catalytic process. J. Am. Chem. Soc., 2011, 133, 11096-11099



How we are using it...

Mixed oxide type catalyst exploited for the conversion of multiple oxygenates and mixtures thereof:

- ❖ Ethanol, Acetic Acid, Ethyl Acetate, Acetaldehyde.

Feed (wt%) ^a	Conv (%)	Selectivity (C mol %)								
		Olefins						C2-C5 Alkanes	Acetone	Other Oxygenates
		CH4	CO2	C2	C3	C4	C5			
20% Ethanol	100	6.8	32.2	1.7	5.4	42.4	0.0	0.0	11.1	0.5
10% Acetic Acid	100	13.8	39.0	0.0	0.0	37.6	0.0	0.0	9.6	0.0
10% Acetaldehyde	100	11.0	36.4	0.0	3.2	38.8	0.0	0.0	10.6	0.0
10% Ethyl Acetate	100	10.8	37.8	1.2	2.0	40.5	0.0	0.0	7.7	0.0

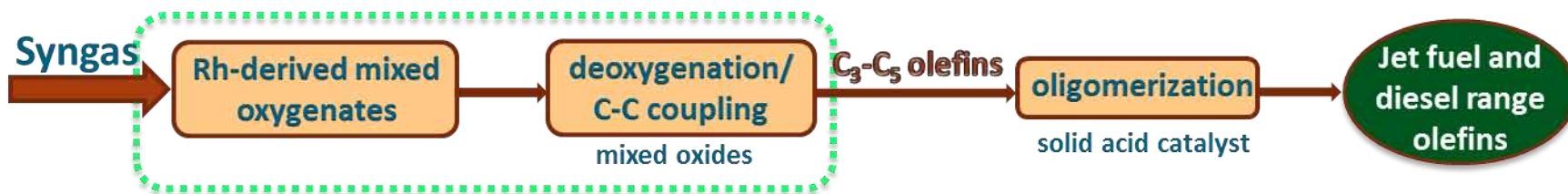
a. bal H₂O. Conditions: T=450°C, GHSV=5000 hr⁻¹, P_T=1 atm, P_{N₂}=0.5 atm

Accomplishment:

Developed unique catalytic pathway to convert **multi-functional oxygenated feedstocks** to **C₄-rich olefins**.

Pathway 1: Mixed Oxides to i-butene

Real Mixed Oxygenate Feed over Mixed Oxides

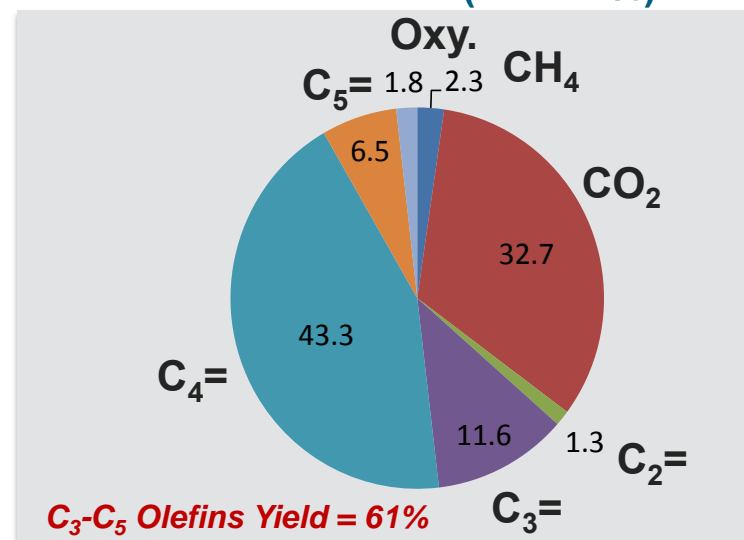


Rh-derived Mixed Oxygenates from Syngas (~80% C Selectivity)

Component	Concentration (wt%)
Methanol	0.8
Ethanol	20.5
1-propanol	0.8
1-butanol	0.8
1-pentanol	0.2
Acetic Acid	10
Acetaldehyde	10.5
Ethyl Acetate	9.9
Water	46.5
Sum	100

PNNL Report, 2013, PNNL-22786

Product Yield (mol C %)



- Provisional **patent** application filed on mixed oxides technology.

Accomplishment:

- Developed $Zn_xZr_yO_z$ mixed oxide catalyst with tailored acid and base sites to convert **syngas-derived oxygenated complex mixtures** to **C₃-C₅ olefins** and simultaneously produce H₂.

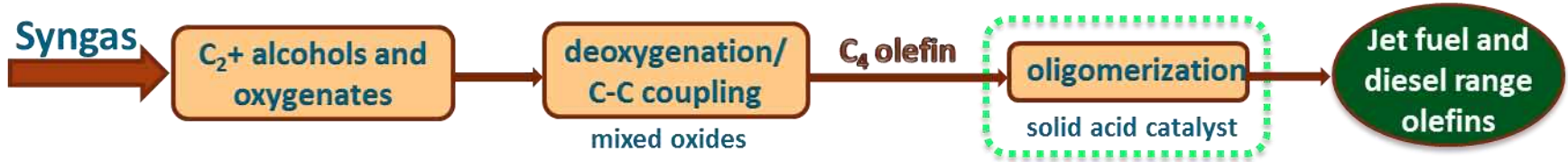
Pathway 1: Mixed Oxides to i-butene

i-Butene Oligomerization - Acid Catalysts



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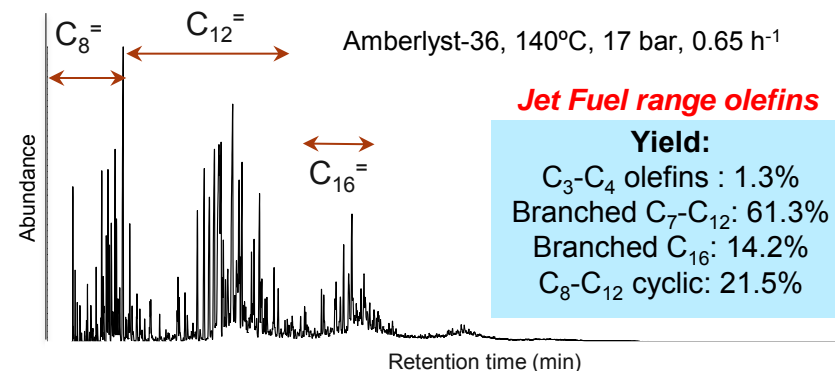


- Oligomerization of olefin intermediates can produce a range of hydrocarbons.
- Fuel flexibility (e.g., carbon ranges, branching) offered through choice of catalyst and process conditions.
- High yield to C_7^+ products in gasoline and jet fuel range.
 - ❖ Longer chain hydrocarbons (e.g., C_{16}) produced with Amberlyst-36.

Catalyst	HY	HZSM-5	Amberlyst
Reaction Temperature (°C)	250	250	140
Pressure (bar)	17	17	17
WHSV(h ⁻¹)/GHSV (h ⁻¹)	1.3/197	1.1/330	1.3/589
Time-on-Stream (hrs)	21	17	31
Conversion (%)	100	100	100
Selectivities (%):			
C_1 - C_6 olefins	13.4	4.7	0
C_1 - C_6 paraffins	6.4	20.9	0
C_7 - C_{12} olefins	67.9	26.9	49.9
C_7 - C_{12} paraffins	6.2	47.5	1.5
C_{16}^+ olefins	0	0	14.6
C_8 - C_{12} cyclic hydrocarbons	6.1	0	34.0
C_7^+ Yield (%)	80.2	74.4	98.4

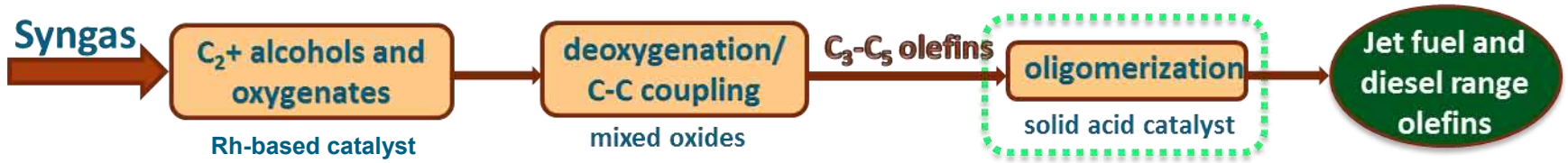
Accomplishment:

- Evaluated **i-butene oligomerization** over different **solid acid catalysts** to understand resulting fuel quality.



Pathway 1: Mixed Oxides to i-butene

Mixed Olefins Oligomerization - Amberlyst



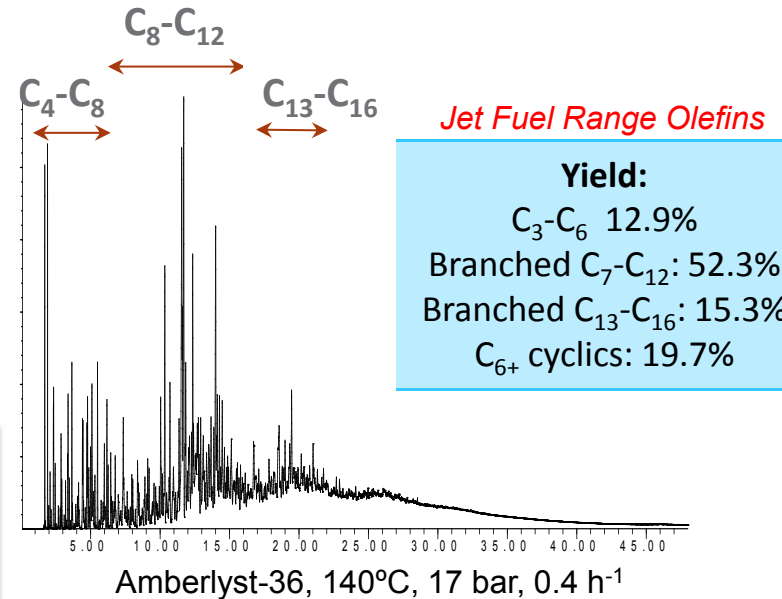
- Representative **olefin mixture** from **mixed oxides reactor** was used as a feed for the **oligomerization** reactor and produced a jet-range olefin.

Oligomerization Feed

11% Propylene
77% Butylene
12% Pentylene



Oligomerization Product



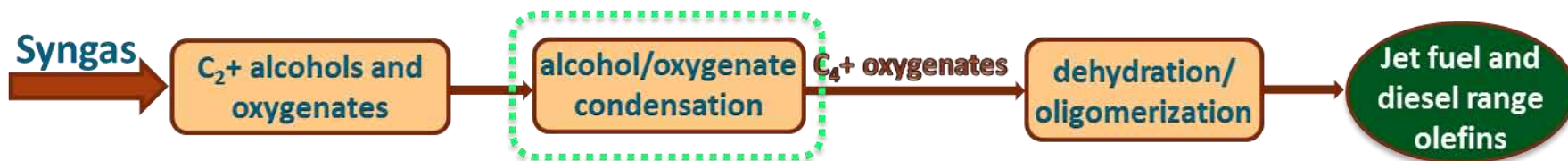
Accomplishment:

- Developed and demonstrated integrated new pathway from **syngas** to **jet fuel range** hydrocarbons.

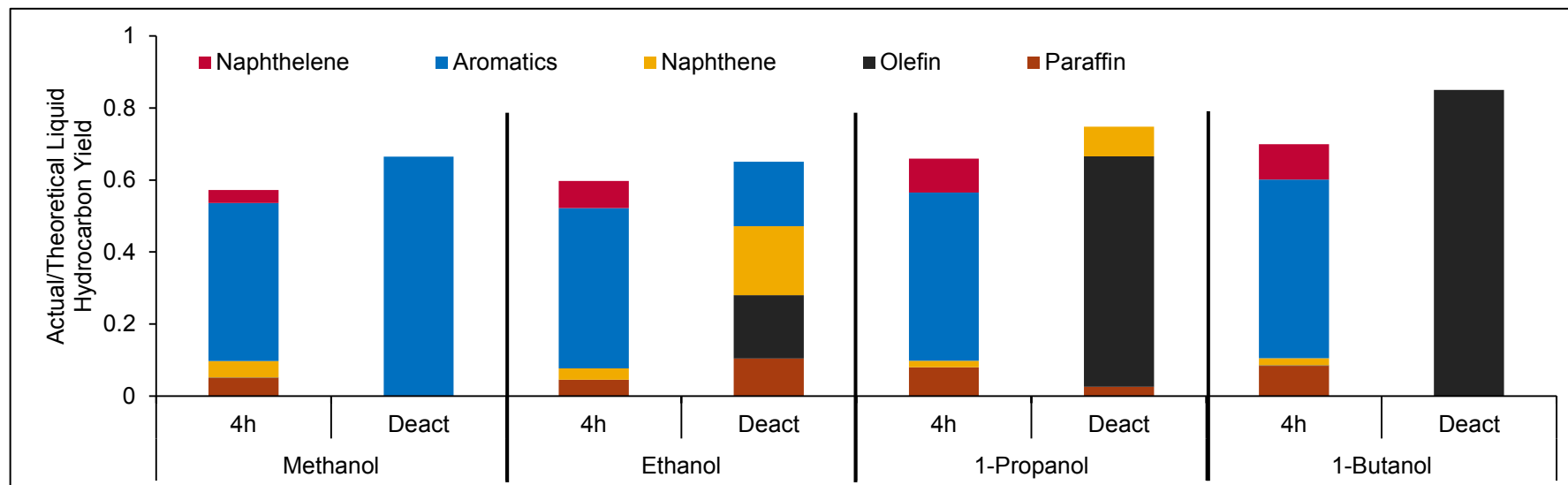
- **Challenges ahead:** Exploit mixed oxide technology for additional feedstocks and applications (other than Rh-derived mixed oxygenates). Explore co-production of fuels and products.

Pathway 2: Alcohol Coupling

Rationale for Alcohol Coupling Pathway



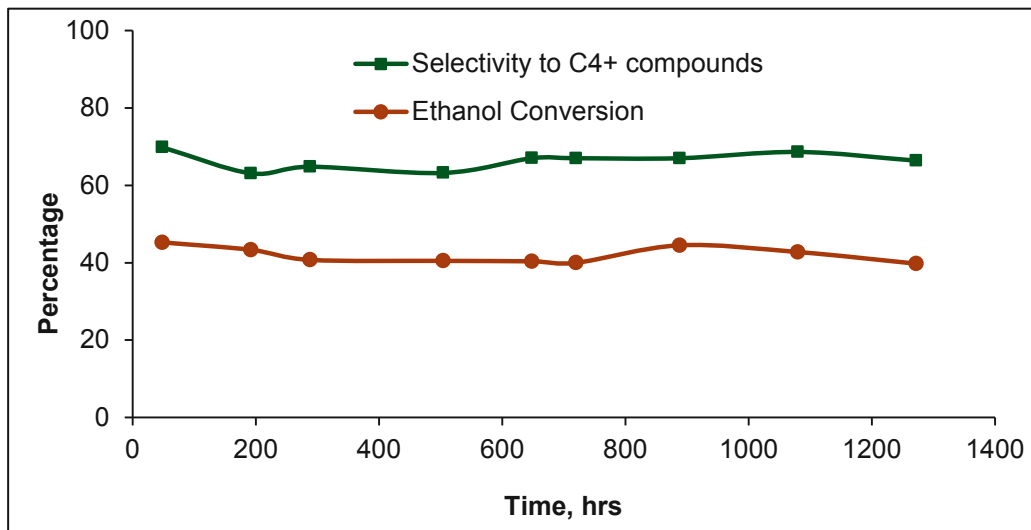
HZSM-5 Catalyzed Alcohol Conversion



Product class distribution of the liquid hydrocarbon sample different time on stream from the conversion of methanol, ethanol, 1-propanol and 1-butanol over HZSM-5 catalyst at 350°C. (Ramasamy et al., Journal of Energy Chemistry, 2013, 22, 65-71)

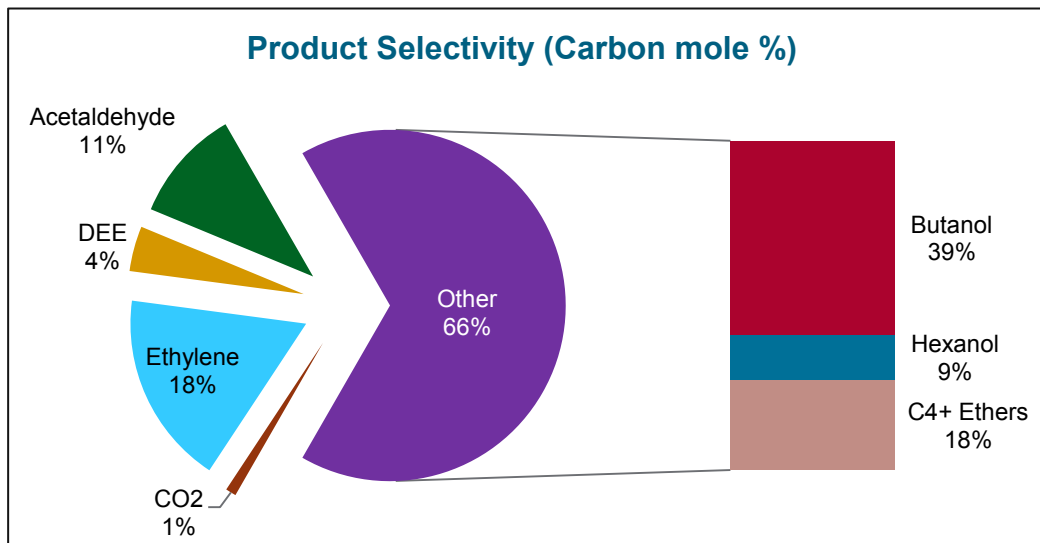
- Higher alcohols ($\geq C_3$) primarily generate **C₆+ olefin-rich** compounds over deactivated zeolite.
- Coupling of **low carbon chain alcohols** (e.g., ethanol) to **C₃+ alcohols** will readily dehydrate and oligomerize to a high-value jet fuel-range hydrocarbon.

Pathway 2: Alcohol Coupling Catalyst Stability and Product Composition



Ethanol condensation experiments were conducted on bifunctional acid-base catalysts at 350°C and atmospheric pressure.

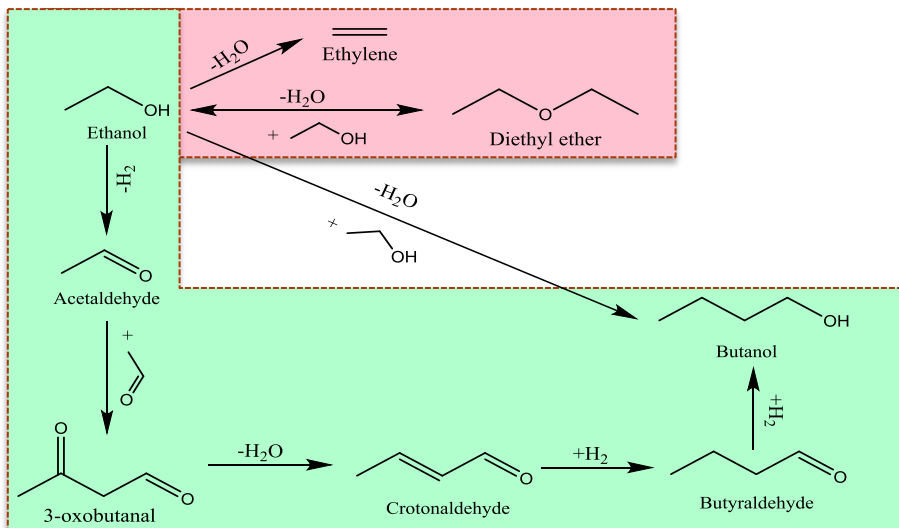
- **C₄+ compounds** can be converted to jet fuel range olefins in a single step process.
- **Other than CO₂** all of the products can be utilized in generating the jet fuel range compounds.
- ❖ **Acetaldehyde** and **DEE** (small quantities) can be **recycled** with unconverted ethanol.
- ❖ **Ethylene** (small quantities) along with **higher alcohols** can be sent to the downstream **dehydration/ oligomerization step**.



Accomplishments:

- For >1000 hours ~40 percent conversion was achieved showing **catalyst stability**.
- ~65 percent selectivity to **C₄+ compounds**.

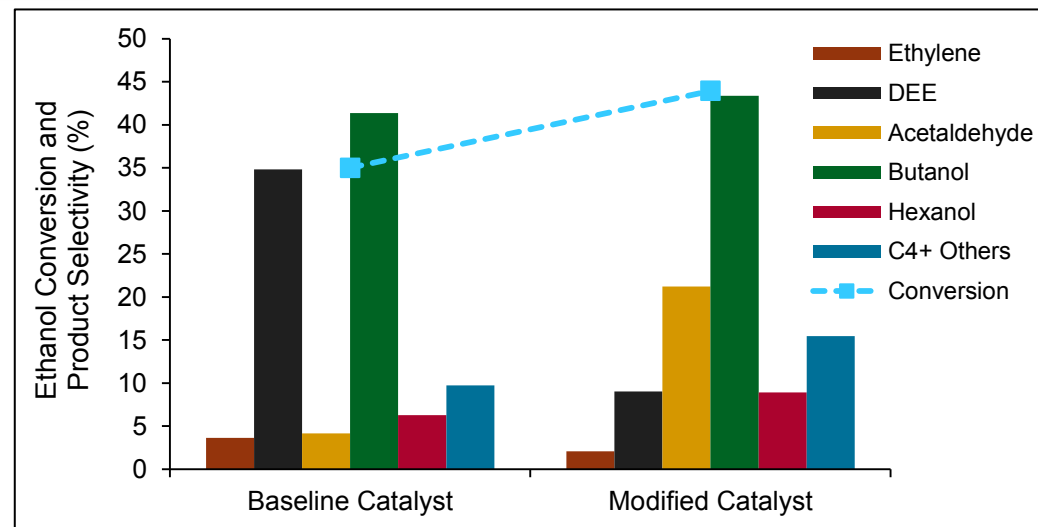
Pathway 2: Alcohol Coupling Catalyst Modification to Reduce Byproducts



- **Undesired byproducts** are **ethylene** and **DEE** via inter and intra molecular dehydration of ethanol.
- Small levels of **promoter** added to modify the sites responsible for the dehydration pathway and promote the dehydrogenation.

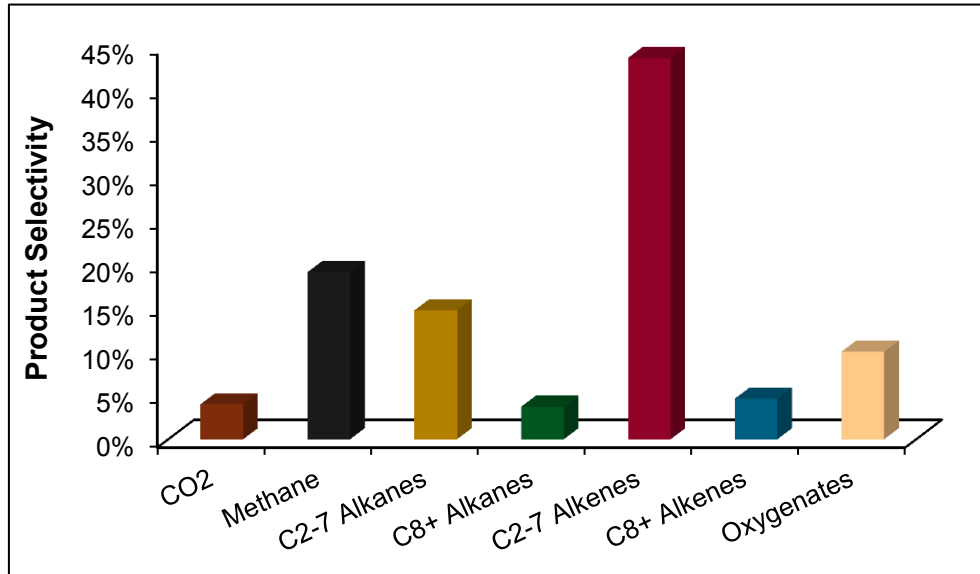
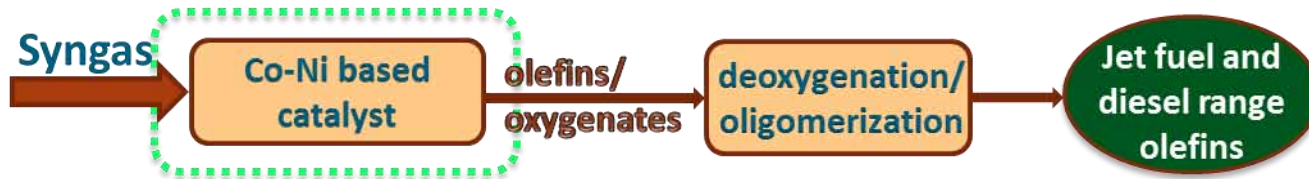
Accomplishments:

- Presence of promoter **reduced DEE** generation and **increased ethanol** conversion.
- Achieved 45 percent **ethanol** conversion.



- **Challenges ahead:** Develop efficient upgrading process of C_4+ alcohols and ethers to fuel-range hydrocarbons in a single dehydration/oligomerization step.

Pathway 3: Direct Syngas Conversion Syngas over Co-Ni Bimetallic Catalyst



Product selectivity for syngas hydrogenation over the Co-Ni bimetallic catalyst at 285°C, 1200psi, H₂/CO =2, and GHSV=12000 L/Kg/hr operating conditions. CO conversion ~ 20%.

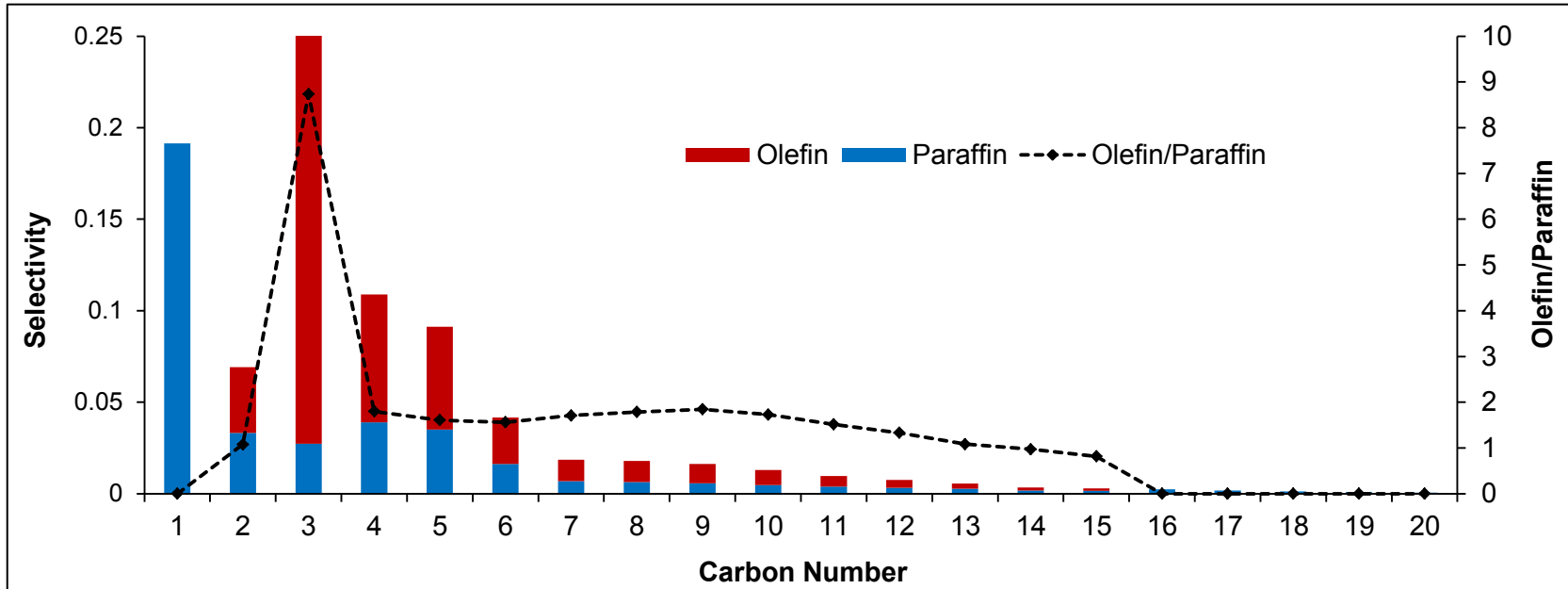
- Unique properties of **Co-Ni bimetallic catalyst** produces high levels of **light olefins** from syngas in one step, that can be oligomerized/alkylated to fuel-range hydrocarbons.
- Low **CO₂ selectivity** (unlike conventional Fe-based syngas to olefin catalysts).
- Low catalyst metal (total Co-Ni) loading (<10 wt.%).

Accomplishment:

- Achieved direct syngas conversion with **high olefin selectivity** (~50%).

Pathway 3: Direct Syngas Conversion

Olefin-to-Paraffin Ratio



Selectivity of paraffin, olefin, and the olefin to paraffin ratio generated from the CO hydrogenation experiment conducted over the Co-Ni catalyst at 300°C, H₂/CO=2, GHSV=12000 L/Kg/hr, and 1200psi operating conditions.

Accomplishments:

- **High olefin-to-paraffin ratio** (~8 for C₃ hydrocarbon).
- **No waxes produced** - even under relatively high temperature (for FT) of 300°C; relatively high GHSV (12,000 hr⁻¹).

- **Challenges ahead:** Minimize CH₄ formation; upgrading of olefin/paraffin products via oligomerization/alkylation to produce fuel-range hydrocarbons with high carbon efficiency.

4 - Relevance

- This project is developing an upgrading process enabling conversion of syngas and biologically-produced intermediates to **gasoline, jet, and/or diesel** blend-stocks at a **scale** relevant for biomass that will achieve BETO's targeted processing cost of **\$3/GGE** by **2022** by:
 - ❖ Leveraging **PNNL** and **WSU catalysis** and **chemical processing expertise**.
 - ❖ Ensuring targeted R&D by integrating **techno-economic** with **experimental** analyses.
 - ❖ Enabling emerging **bioenergy industry** with new, **innovative technology options**.
 - ❖ Facilitating **technology transfer** (1 patent application thus far, voluminous publications).
 - ❖ **Engaging industrial partners**.
- Addresses Thermochemical Conversion R&D Strategic Goal:

*“Develop commercially viable technologies for converting biomass into energy-dense, fungible, finished liquid fuels, such as renewable **gasoline, jet, and diesel**, as well as **biochemicals** and biopower.”*
- Addresses Thermochemical Conversion R&D Technical Challenge -

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

*“**New**, more durable technologies and processes are needed for converting biomass-derived syngas into **fuels** and **chemicals**... More robust processes and catalysts are needed for producing **mixed alcohols, olefins, and alkanes**...”*

5 - Future Work

- Mixed alcohol/oxygenate upgrading:
 - ❖ Assess the use of **mixed oxide** technology for additional feedstocks and applications.
 - ❖ Evaluate **upgrading** of **Guerbet condensation products** (dehydration/olig.) in order to understand back-end processing and resulting fuel quality.
 - ❖ Design **product production** strategies that enable **economically viable fuels** (co-production of fuels and products).
- Direct syngas conversion:
 - ❖ Evaluate **upgrading** of **Co-Ni** derived products via oligomerization and/or alkylation.
- Techno-economic evaluations of pathways being assessed:
 - ❖ Models with performance targets currently being developed in FY15.
 - ❖ State of technology for pathways in FY16.
- Down select to preferred pathway to fuels (project level).
 - ❖ Go/No-Go in mid-FY16.

5 - Future Work, continued

ML, DL, G/NG	Description	FY15		FY16	
		Q3	Q4	Q1	Q2
ML	Determine effects of impurities carried from front end oxygenate generation steps that can impact the conversion on the Guerbet process. These results will help to understand requirements needed in front end processes with respect to feed purity (Pathway 2).				
ML	Provide experimental bench scale data necessary (e.g., catalyst activity and selectivity, process conditions) to complete techno economic assessment for at least one (1) techno economic model for the indirect liquefaction of biomass.				
DL	Submit a manuscript to a peer reviewed journal detailing the fundamental aspects related to Co-Ni bi-metallic catalyst with respect to Syngas conversion to hydrocarbons and oxygenates (Pathway 3).				
ML	Develop and determine preferred catalyst choice based on favorable catalyst performance for the upgrading of at least one higher alcohols synthesis processing scheme that is NOT RhMn-based (Pathway 1).				
G/NG	Based on experimental results to date and techno economic analyses, determine preferred pathway for continued development; criteria based on cost and performance targets that hold promise in beating that of state of the art hydrocarbon synthesis routes (e.g., FT, MTG, and MOGD).[1]				

**Go/No-go
(mid-FY16)**



[1] Performance targets will be established by the thermochemical platform analysis team in FY15.

- Leveraging recent alcohol and oxygenate synthesis research advances, promising novel catalytic pathways to fuels and chemicals are being evaluated that offer:
 - ❖ **Feedstock flexibility** (e.g. MSW, wood waste, biologically-derived oxygenates).
 - ❖ **Desirable fuel compositions** (jet and/or diesel-range).
- Key enabling upgrading technologies evaluated since FY14:
 - ❖ **Mixed oxides catalysts** capable of converting aqueous mixtures of oxygenates to C₄-rich olefins in a single processing step; also demonstrating subsequent oligomerization to jet range olefins.
 - ❖ **Guerbet condensation catalysts** useful for coupling short chain alcohols, thus producing with high selectivity C₄+ oxygenates enabling facile dehydration and oligomerization.
 - ❖ **Direct syngas conversion** to olefin-rich intermediates useful for subsequent alkylation/oligomerization.
- With **techno-economic analyses** guiding **experimental** activities we aim to develop a biomass-based gaseous intermediate route to hydrocarbon fuels at a **scale** relevant for biomass:
 - ❖ BETO's targeted processing cost of **\$3/GGE** by **2022**.
 - ❖ Engaging **industrial partners**.
 - ❖ Will explore **co-production** of **fuels** and high value **products**.



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Additional Slides

2014 AOP Merit Review Comments and Responses

Feedback received from the FY14 AOP merit review was very positive. Some questions/criticisms from the reviewers comments are addressed here:

- 1. Comment:** “Each task appears to be highly exploratory in nature, and although reference is made to using TEA to guide the research there is no discussion of how this will take place. Particularly since all of the processes are complex, TEA should be used at the outset to establish critical parameters and specific targets for each step in the context of the end-to-end process which they support. The project would be more effective if experimental and theoretical work in Year 1 were directed at feasibility of meeting these targets, with a planned down select at 12 or 18 months to 1 or 2 processes.”

Response: The comments received from the merit review were very helpful and we have incorporated many of them into our management plan. For example, techno-economic analyses is now being performed earlier than originally proposed. Now, in the first year (FY15) of the then-proposed three-year effort (FY15-FY17) we are working to establish models in order to understand the current state of technology for the pathways under development. Concurrently, we are also establishing goal cases, given certain technological advances. Thus, techno-economic analysis is serving to guide the research early on, while simultaneously benchmarking the pathways under development to conventional synthetic fuel processes (e.g., FT, MTG). We also plan to have a pathway down select in mid-FY16 to then focus our resources.

- 2. Comment:** “Why is methanol not considered as the starting point of the upgrading effort? Easy to produce, transportable, dehydrates readily to DME.”

Response: This is a valid point. It was not adequately highlighted in our original proposal that PNNL is performing complimentary activities in coordination with NREL in this platform. NREL is investigating routes through methanol intermediates. PNNL has identified different, alternative pathways to evaluate that involve the upgrading of other oxygenated intermediates. Leveraging recent advances in biomass we are striving to unlock new potential pathways to fuels and chemicals that are only recently possible. Benchmarking these novel pathways to more conventional synthetic fuel processes is also critically important.

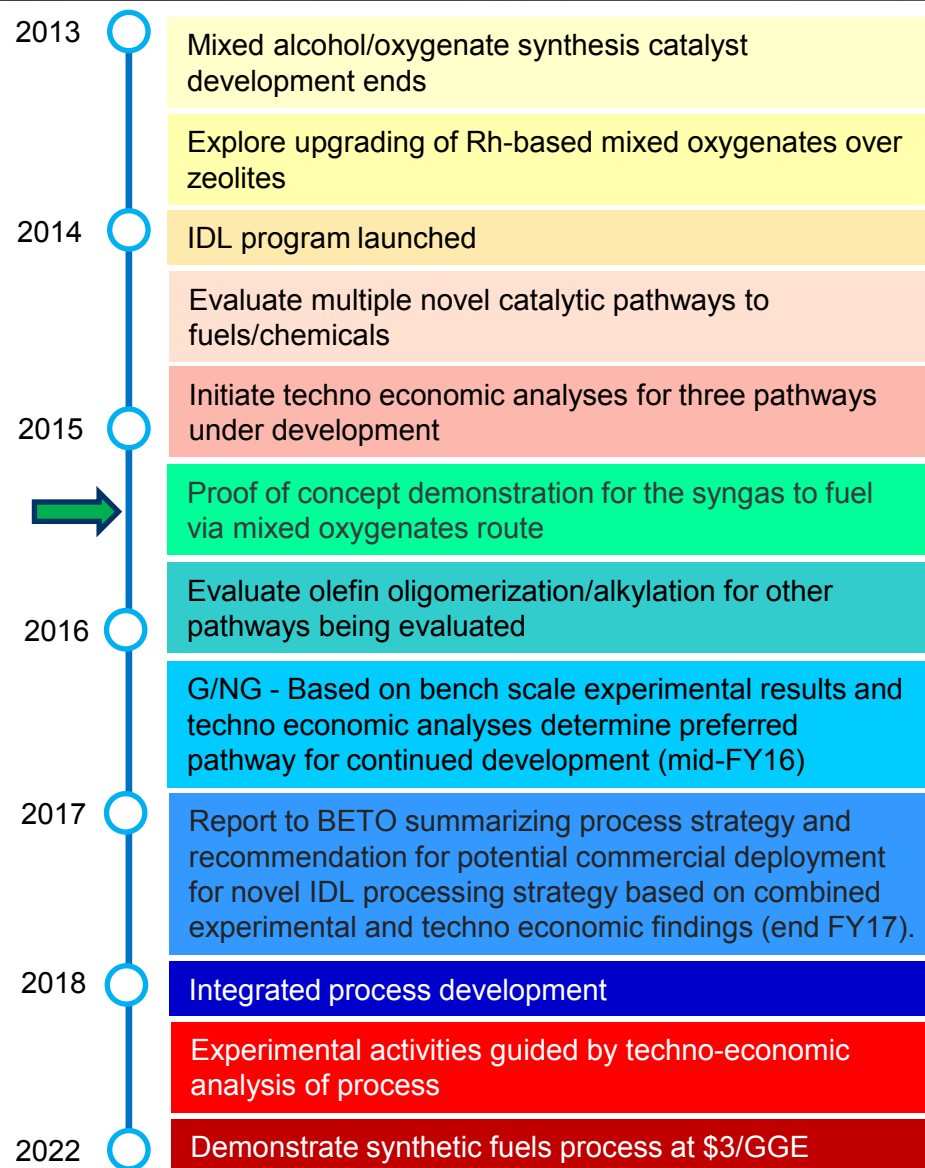
- 1) Robert Dagle, Colin Smith, Vanessa Lebarbier Dagle, Karthikyeen K. Ramasamy, Michel Gray, Matthew Flake, Libor Kovarik, Junming Sun, and Yong Wang. "Conversion of C₂+ Mixed Oxygenates to C₃-C₅ Olefins over Zn_xZr_yO_z Mixed Oxide Catalysts". To be submitted to ACS Catalysis upon IP review.
- 2) Karthikyeen K. Ramasamy, Colin Smith, Michael A. Lilga, Michel Gray, Heather Job, Yong Wang, "Ethanol condensation reaction on hydrotalcite and the effect of temperature on the reaction Mechanism" Submitted to Catalysis Science and Technology.
- 3) Karthikeyan K. Ramasamy, Michel Gray, Heather Job, Yong Wang, "Direct Syngas Hydrogenation over a Co-Ni Bimetallic Catalyst: Process Parameter Optimization" Submitted to Chemical Engineering Science.
- 4) Karthikeyan K. Ramasamy, Yong Wang, "Ethanol Conversion to Hydrocarbon on HZSM-5: Effect of Reaction Conditions and Si/Al Ratio on the Product Distributions" Catalysis Today, 2014. DOI: 10.1016/j.cattod.2014.02.044.
- 5) Karthikeyan K. Ramasamy, Junming Sun, He Zhang, Yong Wang, "Performance of Hierarchical HZSM-5 for the Conversion of Ethanol to Hydrocarbon" Catalysis Today, 2014. DOI: 10.1016/j.cattod.2014.01.037.
- 6) Donghai Mei, Vassiliki-Alexandra Glezakou, Vanessa Lebarbier, Libor Kovarik, Haiying Wan, Karl O. Albrecht, Mark Gerber, Roger Rousseau, Robert A. Dagle. "Highly active and stable MgAl₂O₄-supported Rh and Ir catalysts for methane steam reforming." Journal of Catalysis, 2014, 316, 11-23.
- 7) Karthikeyan K. Ramasamy, Mark A. Gerber, Matthew Flake, He Zhang, Yong Wang, "Conversion of Biomass-Derived Small Oxygenates over HZSM-5 and its Deactivation Mechanism" Green Chemistry, 2014. DOI: 10.1039/C3GC41369A. 2014.
- 8) Lebarbier VMC, RA Dagle, J Li, CA Deshmane, CE Taylor, X Bao, and Y Wang. 2014. "Direct Conversion of Syngas-to-Hydrocarbons over Higher Alcohols Synthesis Catalysts Mixed with HZSM-5." Industrial and Engineering Chemistry Research 53(36):13928-13934. doi:10.1021/ie502425d
- 9) Karthikeyan K. Ramasamy, Yong Wang, "Catalyst Activity Comparison of Alcohols over Zeolites" Journal of Energy Chemistry, 22, 65-71, 2013.
- 10) Karthikeyan K. Ramasamy, Yong Wang, in: Bin Zhang, Yong Wang (Eds.), "Thermochemical Conversion of Fermentation-derived Oxygenates to Fuels", Biomass Processing, Conversion and Biorefinery, Nova Science Publishers, Inc. New York, 2013, pp. 289–300.
- 11) Donghai Mei, Vanessa M. Lebarbier, Roger Rousseau, Vassiliki-Alexandra Glezakou, Karl O. Albrecht, Libor Kovarik, Matt Flakem and Robert A. Dagle. "Comparative investigation of benzene steam reforming over spinel supported Rh and Ir catalysts." ACS Catalysis, 2013, 3, 1133-1143.
- 12) Christopher J. Howard, Robert A. Dagle, Vanessa M. Lebarbier, James E. Rainbolt, Liyu Li, and Dave L. King. "Progress toward Biomass and Coal-Derived Syngas Warm Cleanup: Proof-of-Concept Process Demonstration of Multicontaminant Removal for Biomass Application." Ind. Eng. Chem. Res., 2013, 52, 8125-8138.

Presentations

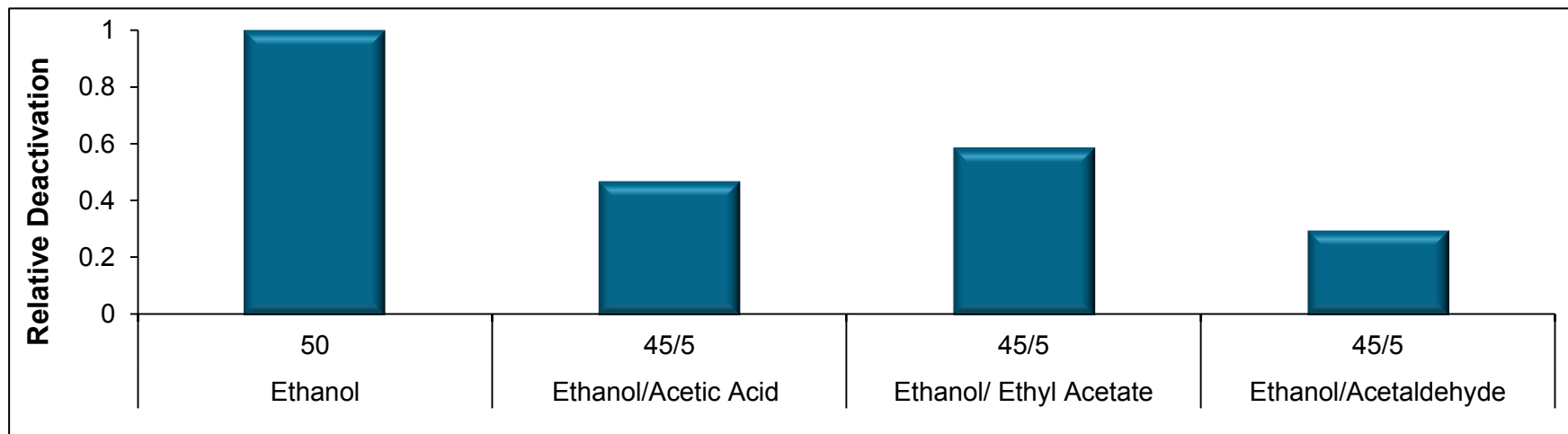
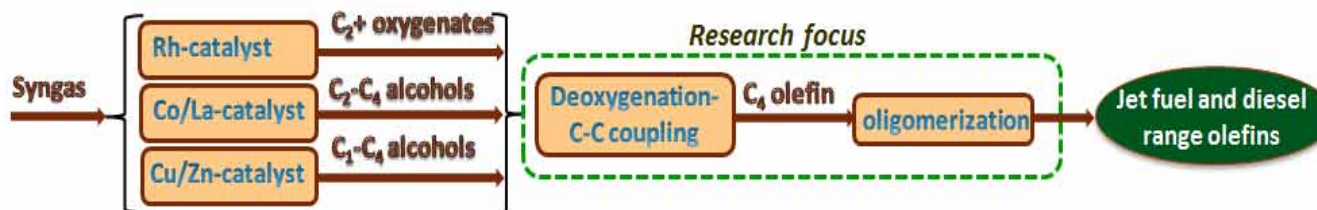
- 1) Karthikeyan K. Ramasamy, Colin Smith, Michel Gray, Heather Job and Yong Wang "Ethanol Condensation over Mixed Oxides to Generate High Value Oxygenates" Submitted to 24th NAM, Pittsburg, 2015.
- 2) Karthikeyan K. Ramasamy, Michel Gray, Heather Job and Yong Wang "Calcination Temperature Effect of Co-Ni Bimetallic Catalyst on the Syngas Conversion to Hydrocarbons" Submitted to 24th NAM, Pittsburg, 2015.
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- 6) Michel J. Gray, Mark A. Gerber, Becky L. Thompson, Karthikeyan K. Ramasamy, "Syngas Conversion to Mixed Alcohol over Rhodium Based Catalyst: Catalyst Lifetime Study" TCS 2014, Denver, 2014.
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- 12) Karthikeyan K. Ramasamy, Yong Wang, "Conversion of Methanol, Ethanol and 1- Propanol over HZSM-5" NAM, Louisville, 2013.
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- 14) Karthikeyan K. Ramasamy, Mark A. Gerber, Michael A. Lilga, Matthew Flake, "Deactivation Mechanism of Mixed Oxygenates Over HZSM-5" ACS Spring National Meeting, New Orleans, 2013.
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2- Approach (Management)

- Risk mitigation by evaluating multiple synthesis strategies in order to best identify favorable pathway opportunities.
- Coordination with NREL who is evaluating other pathways (e.g., through methanol intermediates).
- Bench-scale experimental data informs modeling activities (e.g., TEA, LCA).
- Quarterly milestones and annual reporting deliverables.
- Down select to preferred pathway in mid-FY16 (**Go/No-Go**).
- Process demonstration at \$3/GGE in FY22.



Mixed Oxide Catalyst- Rationale



Relative deactivation normalized to ethanol calculated based on the amount of feed converted between the start of the experiment and the time at which ethylene concentration in the exit gas stream reached 5 vol%. (HZSM-5 with a Si/Al:15 at 360°C and 300psig).

- Over HZSM-5 Presence of acetaldehyde, acetic acid and ethyl acetate deactivate the catalyst faster compared to ethanol.
- The product composition was primarily composed of aromatics.

Techno-economic analysis pathway comparison methodology

	RhMn Oxygenates + i-Butene	Ni/Co Hydrocarbons	MoS Alcohols + Guerbet + Dehydration	UOP Methanol to Olefins
MFSP				
Yield, gal/dry ton				
Carbon Efficiency				
# of Steps after Syngas				
Syngas Intermediate	Mixed Oxygenates	Range of Paraffins/Olefins, w small amt of oxygenates	Mixed Alcohols	Methanol
Challenges & Benefits				
Syngas to Intermediate: Oxygenate or paraffin/olefin mix	<ul style="list-style-type: none"> High C efficiency BETO investment Rh catalyst expensive; validate goal case assumptions (85% selectivity, catalyst life 4 years) 	C2+ paraffins, C2+olefins w some in desired range, many too light <ul style="list-style-type: none"> validate CO₂/CH₄ recycle & projected improvements oxygenates removal TBD 	<ul style="list-style-type: none"> BETO investment MoS alcohols process is expensive Need to keep catalyst sulfided 	Commercial process
Oxygenate to olefins	Olefin type: i-butene <ul style="list-style-type: none"> Low C efficiency: 33% C loss to CO₂ CO₂ and H₂ dilution affect conversion-need to separate 	N/A	Olefin type: mostly butene <ul style="list-style-type: none"> Guerbet step and extra reactor Higher alcohols dehydration TBD Separation & recycle 	Olefin type: ethylene & propylene Commercial process
Alkylation	N/A	<ul style="list-style-type: none"> Mixed olefin performance TBD, coke formation, high olefin to paraffin ratio; Unknown reactor design, product distribution, catalyst cost and lifetime 	N/A	N/A
Oligomerization	i-butene relatively easy, but requires separation and recycle if conversion not 100%	<ul style="list-style-type: none"> no catalyst data for mixed olefins Paraffins inert? Separation & recycle 	<ul style="list-style-type: none"> Butene relatively easy no catalyst data for mixed olefins Paraffins inert? Separation & recycle 	<ul style="list-style-type: none"> no catalyst data for mixed olefins Separation & recycle
Hydrogenation	<ul style="list-style-type: none"> Required No issues expected 	<ul style="list-style-type: none"> Required No issues expected 	<ul style="list-style-type: none"> Required No issues expected 	<ul style="list-style-type: none"> Required No issues expected