



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

# 2015 Project Peer Review

March 26, 2015

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

Liquid Fuels via Upgrading of Syngas Intermediates  
2.3.1.305/2.3.1.306

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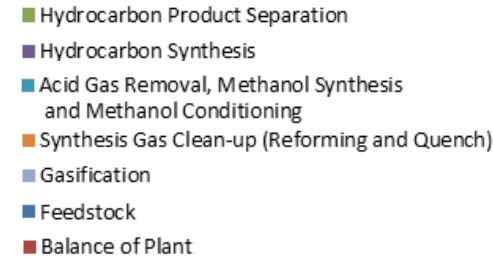
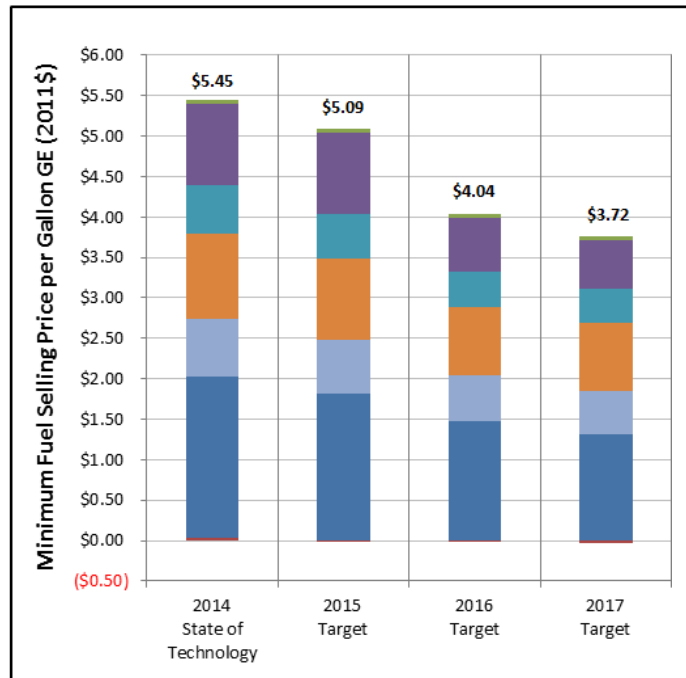
# Goal Statement

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**Project Goal** – To develop and demonstrate catalyst technologies that convert biomass-derived synthesis gas to drop-in hydrocarbon fuels and to reduce total cost from the FY14 SOT of \$5.45/gge to \$3.72/gge by FY17 and \$3.41/gge by FY22

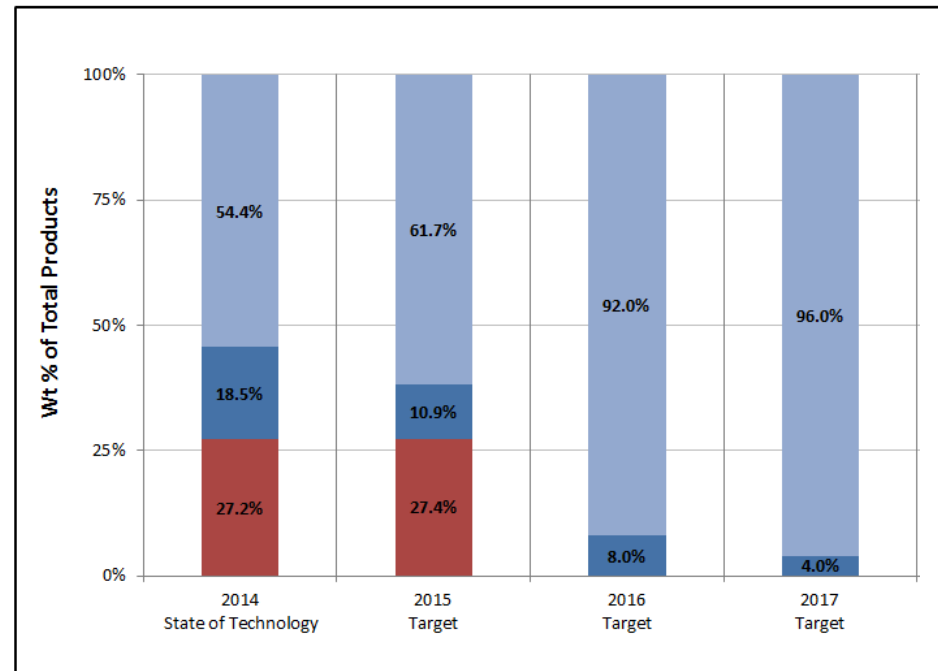
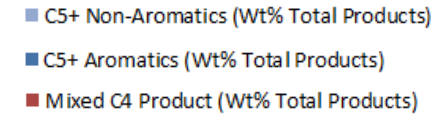
- **Focus on high yield and efficiency** to more completely utilize the United States' biomass resources and to reduce net production costs
  - Achieve a yield of 65 gallons high octane gasoline per ton biomass with  $\leq 4\%$  aromatic content by 2017 (FY14 SOT is 40 gallons/ton with 25% aromatics + 18 gallons/ton LPG)
  - Improve fuel value by further reducing aromatics to  $\leq 0.5\%$  and converting a portion of the gasoline product to premium jet or diesel by 2022
- **Improve and validate** the performance of catalysts that transform syngas intermediates to premium fuels and chemicals
- **Optimize processes** that are suited *to the scale of biomass conversion*

# Cost and Quality Targets Through 2017



← **Cost**

**Quality** ↓



- Data & assumptions for gasification, reforming, and gas cleanup based on previous BETO investment (thermochemical ethanol 2007-2012)
- Catalyst improvements for reduced hydrocarbon synthesis costs
- Increased process intensity for lower parasitic losses and reduced costs at other unit operations

# Quad Chart Overview

## Timeline

- Project start: 10/1/2010<sup>†</sup>
- Project end: 9/30/2017<sup>‡</sup>
- Percent complete: 69%

## Budget

	Total Costs FY 10 – FY 12 <sup>†</sup>	FY 13 Costs	FY 14 Costs*	Total Planned Funding (FY 15-Project End Date
DOE Funded	\$4030 k	\$559 k	\$1276 k	\$8548 k

<sup>†</sup> scope of project changed from demonstration of syngas derived ethanol to development of syngas derived hydrocarbon fuels in FY13

<sup>‡</sup> a design report has been developed (FY14) with technical targets through FY22

\* ~ \$383k additionally encumbered in FY14 but not costed until FY15; appears within FY15+ plan

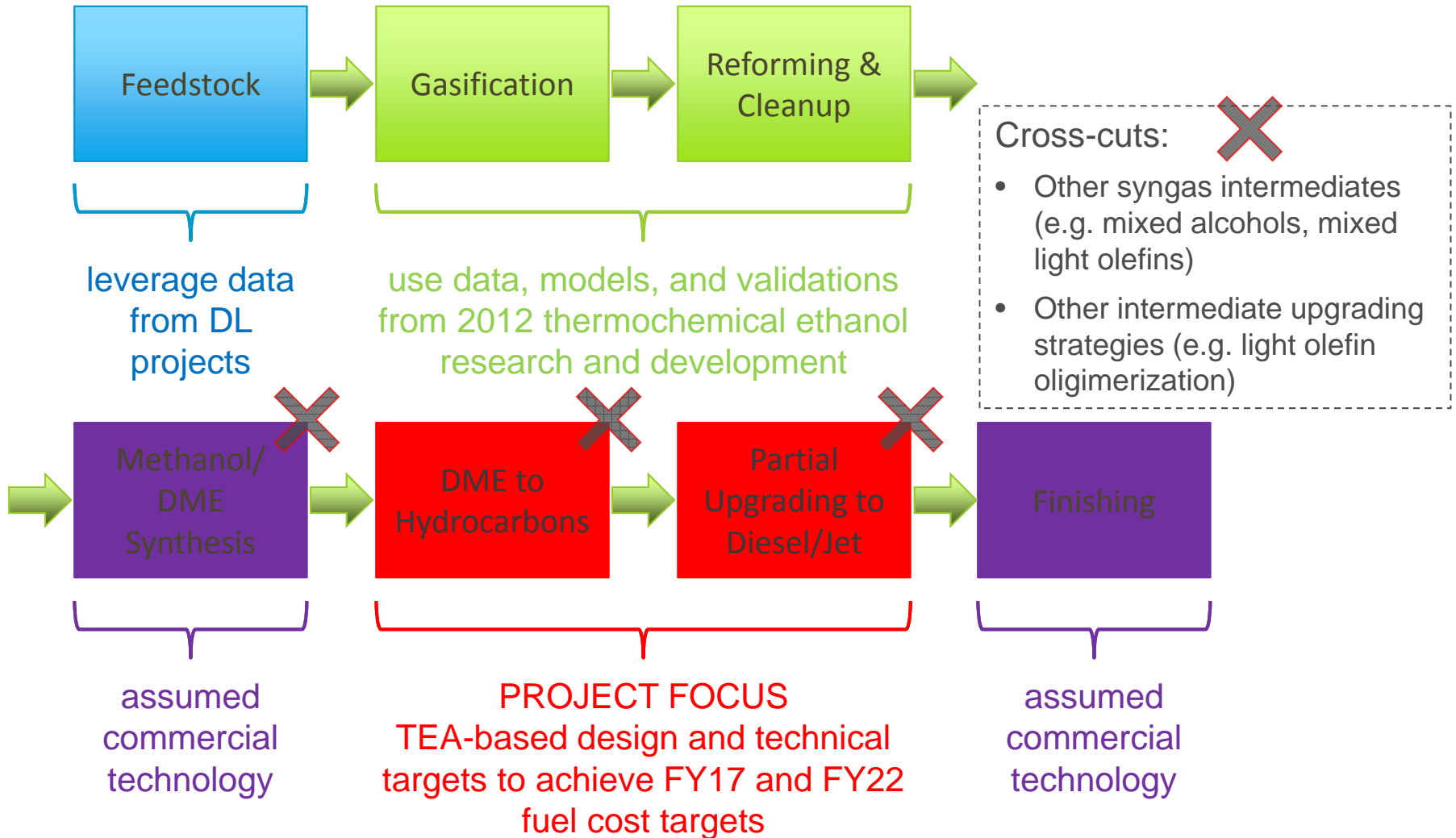
## Barriers

- Tt-I – catalytic upgrading of gaseous intermediates to fuels and chemicals  
 “Significant efforts are needed to develop and improve processes and catalysts that can produce hydrocarbon fuels and chemicals and meet reasonable performance targets and commercially viable capital and operating costs.”
- Tt-L – knowledge gaps in chemical processes  
 “Understanding the fundamental chemical processes that occur during intermediate upgrading can inform technology breakthroughs and drive optimization.”
- Tt-R – process integration (upcoming efforts)

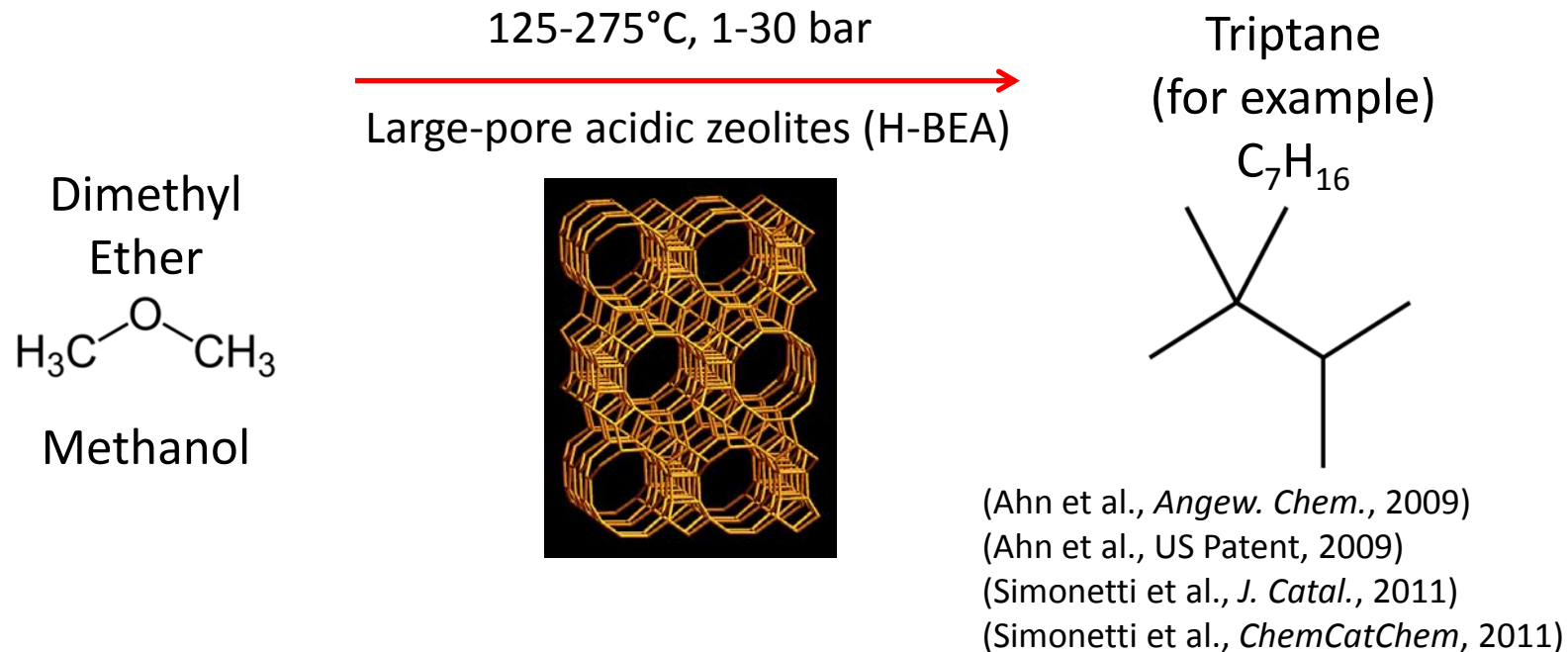
## Partners

- National Labs
  - NREL (79%, FY13/14)
  - ANL (21%, FY13/14)
- Colorado School of Mines (SUB)
- University of Kansas (MOU)

# Overview: Biomass Gasification for Fuels



# Overview: Proposed DME to Gasoline Process



## Key Points on SOT:

- DME and methanol can be synthesized selectively from biomass synthesis gas
- Research octane number of triptane is 112 (gasoline: ~ 92)
- Selectivity to  $\text{C}_7$  is ~20-30%
  - selectivity to triptyls (triptane and triptene) within  $\text{C}_7$ : >70%
- Process selectivity is tunable via operating conditions

# Overview: Research Challenges

## Hydrogen Deficiency



$$4n \text{ H} \quad (4n+2) \text{ H}$$

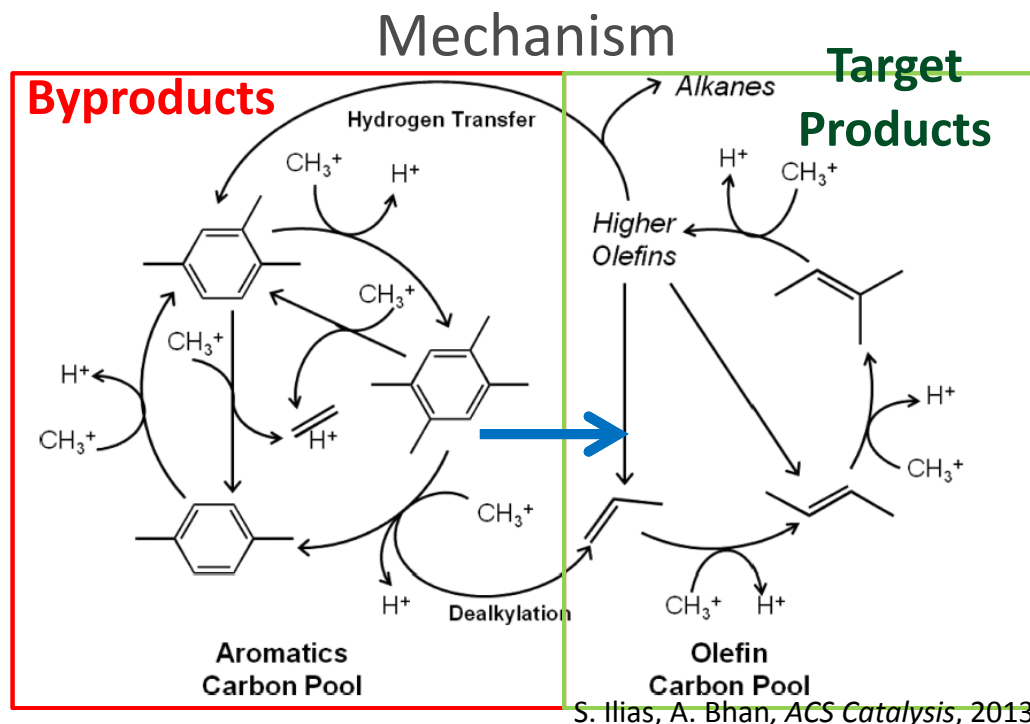
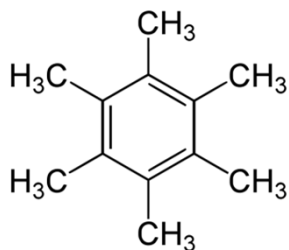


$$6n \text{ H} \quad (6n+2) \text{ H}$$

Need an additional 2H per alkane produced

## Yield Loss

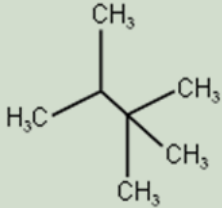

Leads to formation of heavy unsaturated hydrocarbons



## Hypotheses:

1. Through catalyst modification,  $\text{H}_2$  can be activated and participate in the reaction mechanism to reduce aromatic formation while maintaining selectivity to  $\text{C}_{5+}$
2. Through catalyst modification,  $\text{C}_4$  paraffins can be reactivated and reenter the catalytic cycle (recycle to extinction)

# Overview: How this Project Differs from 'MTG'

Process Attribute	High-Octane Gasoline Pathway Target	Methanol to Gasoline (MTG) Pathway	Impact on Techno-Economic Analysis
Molecular structures favored in synthesis reactions	Branched paraffins 	Aromatics 	High octane product rich in branched paraffins, similar to a refinery alkylate. H-saturation decreases density, increasing product volume.
Example Compound Specific Gravity	Triptane 0.70	Toluene 0.87	
Hydrocarbon synthesis catalyst	Beta-Zeolite (12-membered rings)	ZSM-5 (10-membered rings)	Different pore sizes and structures result in different compound selectivities.
Octane number of gasoline-range product	RON: 95+ MON: 90+	RON: 92 MON: 83	Octane number increases value of product as a finished fuel blendstock.
Selectivity of C <sub>5</sub> +product	C <sub>5</sub> + product only (~65 Gal / Ton)	~ 85% C <sub>5</sub> + (~55 Gal / Ton)	High selectivity to primary (premium quality) product maximizes overall product value.
Severity of synthesis operating conditions	350 – 450 Deg. F 130 PSIA	650 – 950 Deg. F 315 PSIA	The lower severity operating conditions result in lower capital and operating costs relative to MTG.
Coke formation	Coke formation is minimized by hydrogen addition and selectivity to branched paraffins rather than aromatics.	High propensity for coke formation due to aromatic coke pre-cursors.	Minimizing coke formation helps to maximize product yield / carbon efficiency and maximizes catalyst regeneration and replacement cycles.

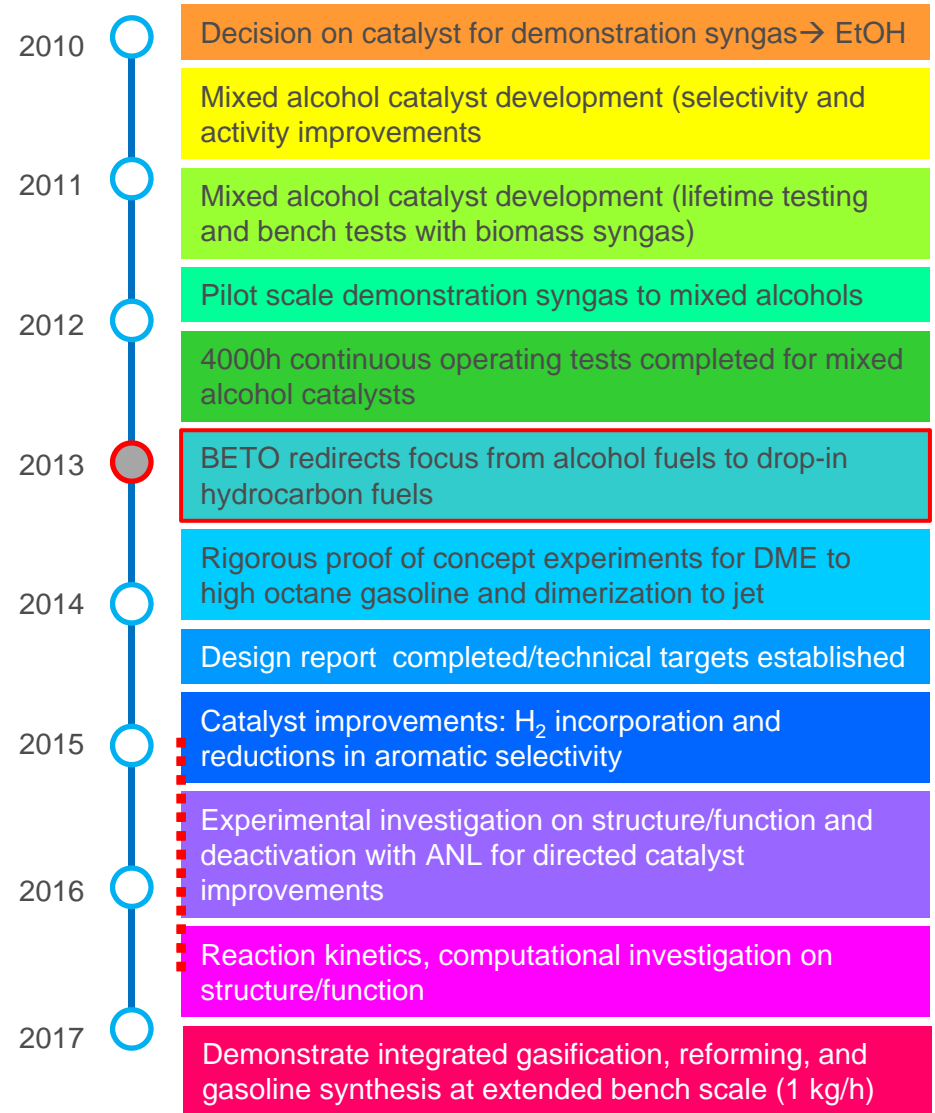
**Note:** Yield values have been estimated for both processes using an identical 'front end' in an analysis project: 2.1.0.302



# Project Objectives & Timeline

## Objectives

- **Rigorously develop** catalysts that convert DME to high octane gasoline and jet with high yield and low aromatic content
- **Identify and consider** other technologies that can convert syngas to drop-in hydrocarbon fuels *at the scale of biomass*
- **Provide** performance **information** for techno-economic modeling of thermochemical biomass to gasoline/jet
- **Validate** catalyst performance using real biomass derived syngas



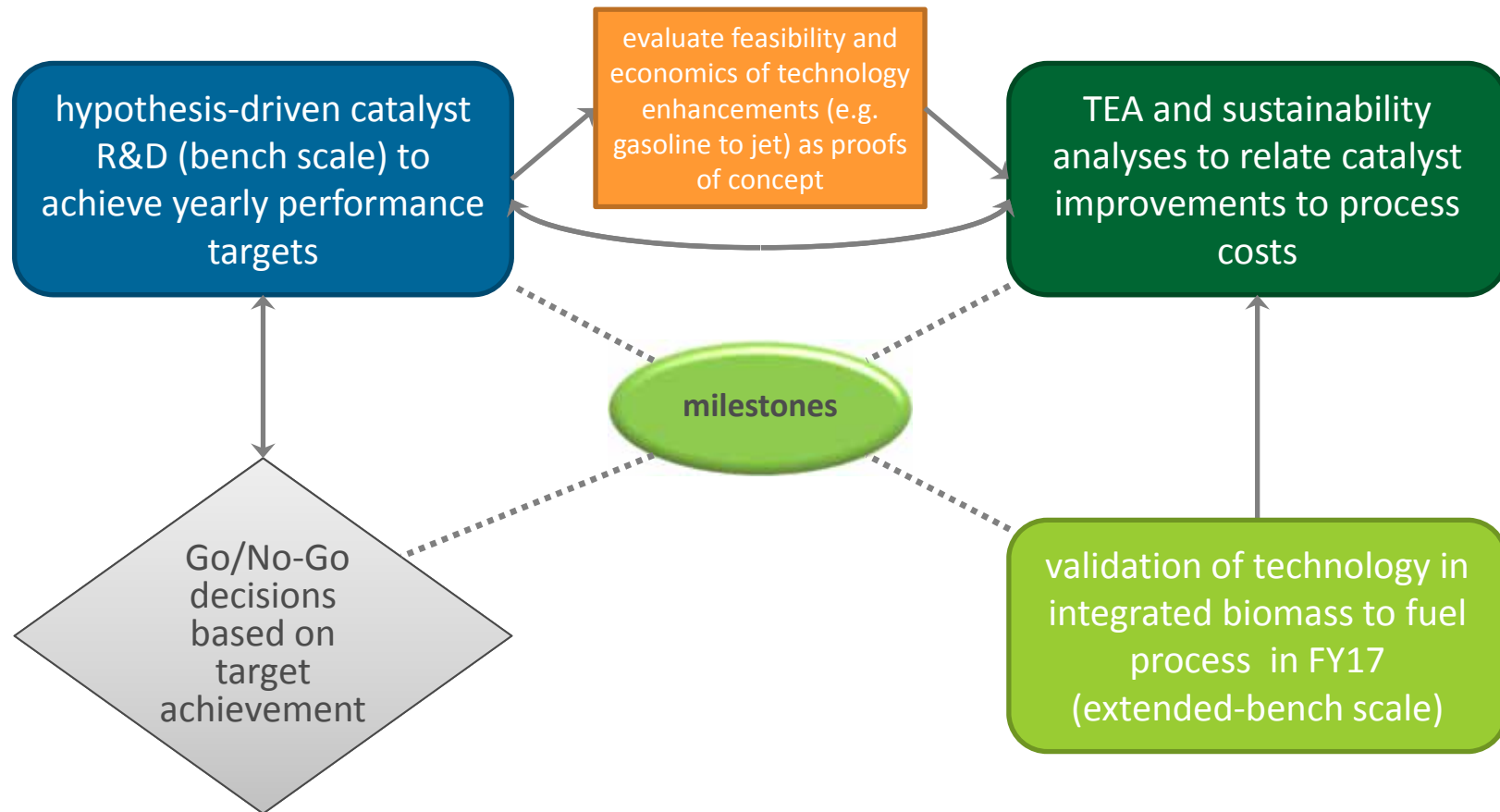
# Success Factors

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- Catalysts:
  - Improve the **yield** of premium gasoline products over the current SOT of 40 gallons per ton biomass to 64 gallons/ton by 2017
    - Reduce net aromatic production and maximize paraffin **selectivity**
    - Convert low carbon products (e.g. butanes) to larger molecules
  - Maintain catalyst lifetimes at or above the SOT of 2 years
  - Minimize increases in catalyst price by using lower-cost metals
- Process:
  - Minimize capital and operating costs by using catalyst systems that operate under **less-severe conditions** and convert intermediates in **fewer process steps**
  - Develop integrated processes that minimize separation duties
  - Utilize byproducts as **recycle** streams to produce additional higher-value product instead of lower-value side products

# Management Approach

2017 target: modeled MFSP of \$3.72/gge



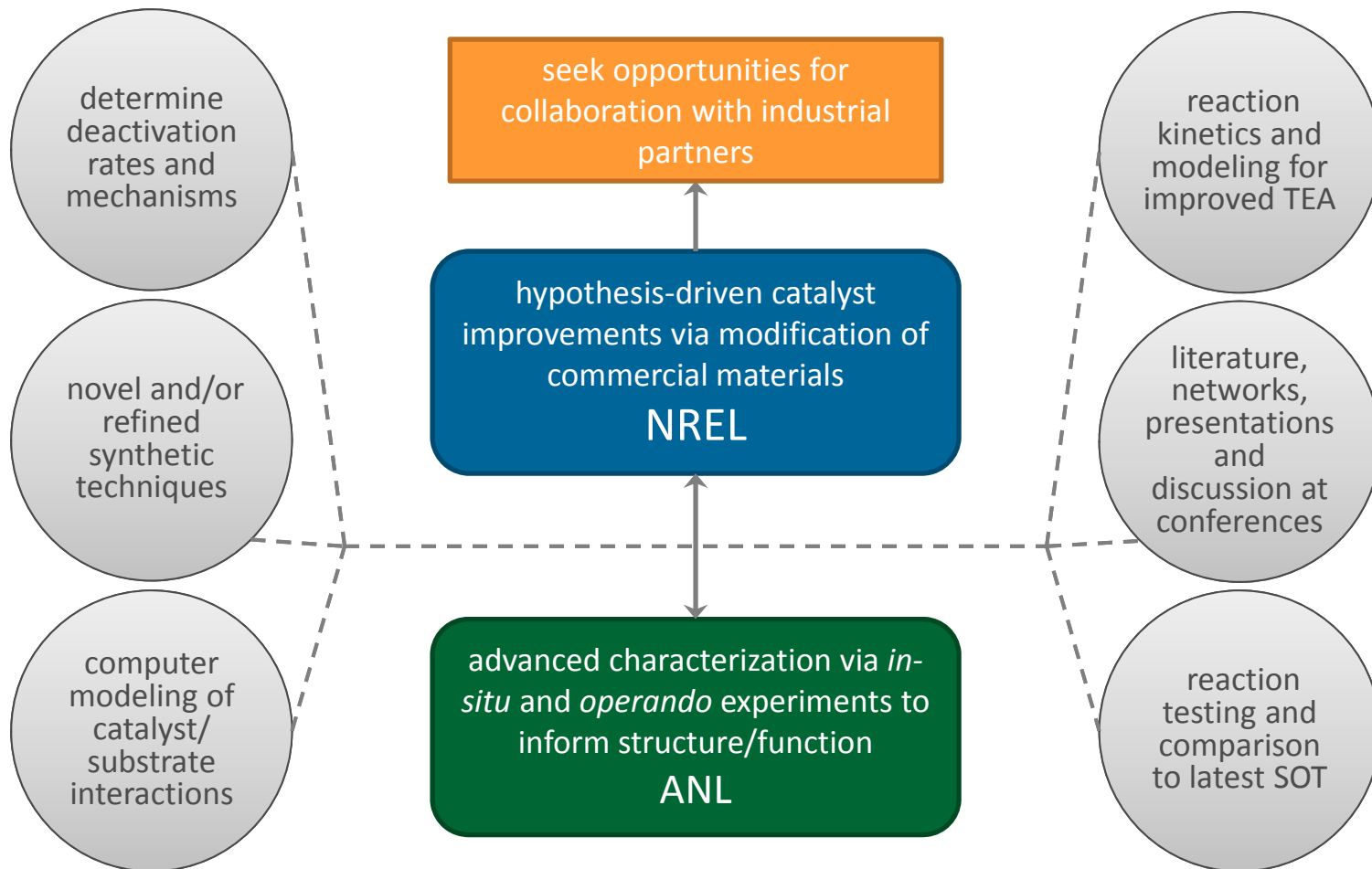
**Management Approach:** DOE-approved Project Management Plans detail schedules/milestones/risk abatement

- AOPs target catalyst improvements as directed by TEA <BETO reviewed in advance of work>
- Go/No-Go criteria established in peer-reviewed 3-year AOP

# Technical Approach

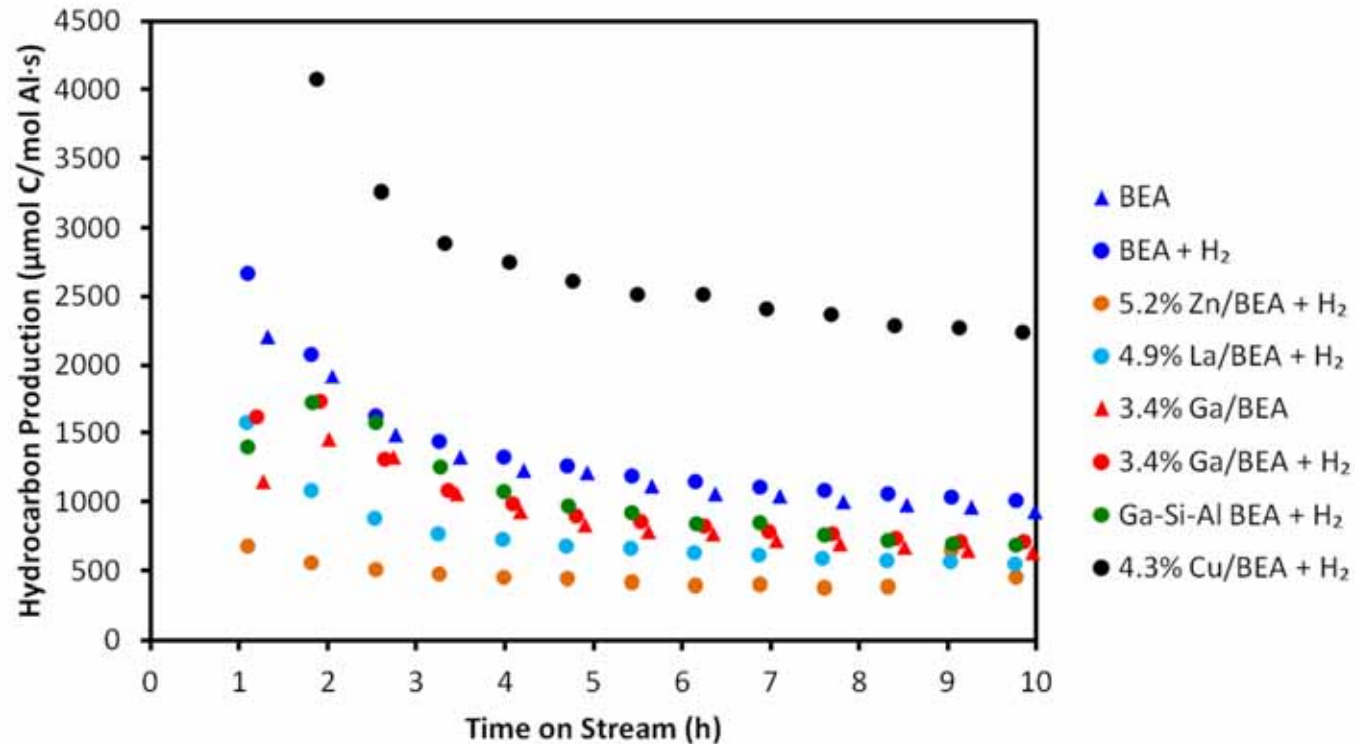
## 2017 targets

- Incorporate H<sub>2</sub> to reduce aromatic yield from 27% to 4%
- Use recycle and catalyst modification to reduce LPG product yield from 27% to nil
- Determine the feasibility of dimerization of a portion of the gasoline product to diesel/jet



# Research Progress

Hypothesis: the addition of Lewis acidic materials to the SOT catalyst (HBEA) will render  $H_2$  reactive via hydride formation and reduce aromatic production



- The addition of metals altered production rates of non-aromatic hydrocarbons
- Copper increased productivity 2x
- All other metals decreased productivity slightly

# Research Progress

Hypothesis: the addition of Lewis acidic materials to the SOT catalyst (HBEA) will render  $H_2$  reactive via hydride formation and reduce aromatic production

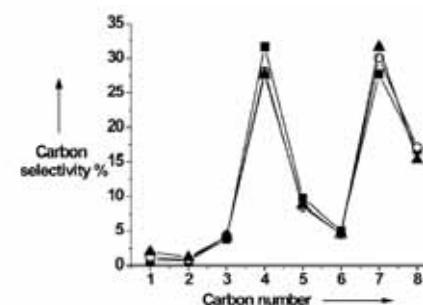
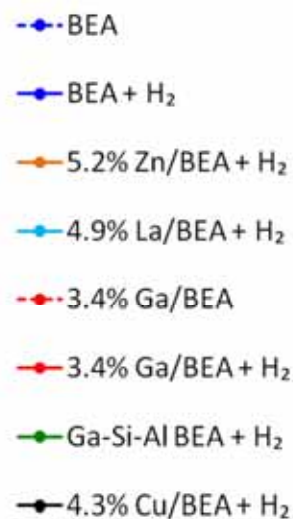
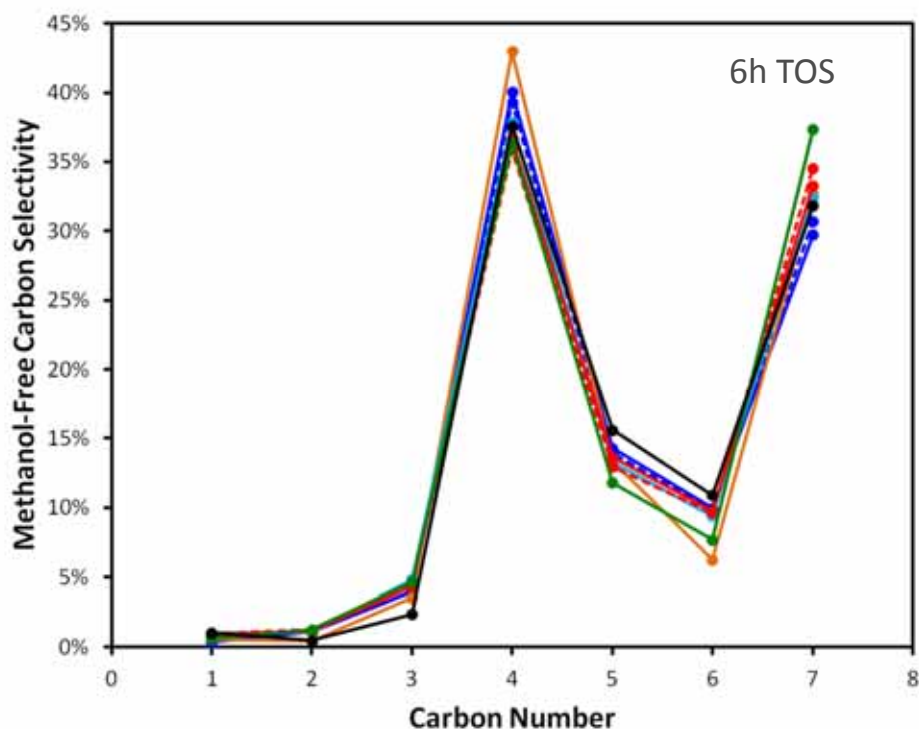


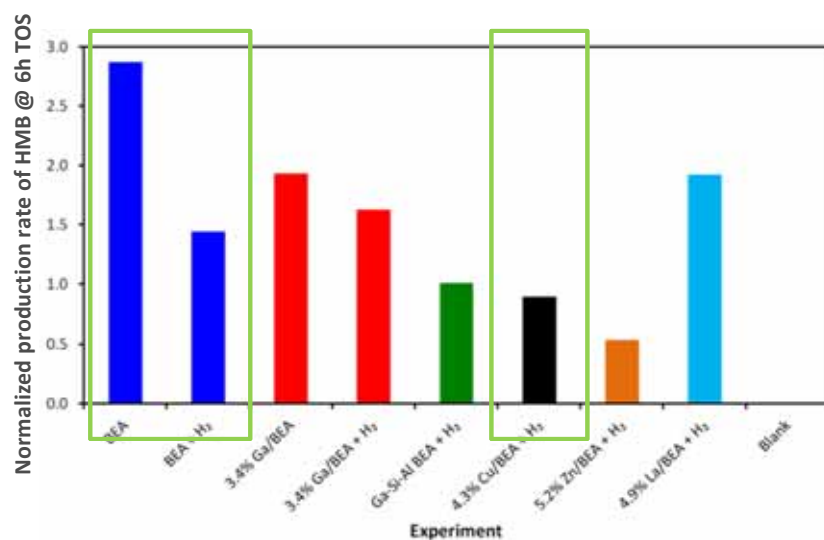
Figure 1. DME pressure effects (60 kPa (■), 125 kPa (○), and 250 kPa (▲)) on chain size of the hydrocarbon products (473 K, 0.4 g H-BEA; Si/Al = 12.5, 0.28 cm<sup>3</sup> s<sup>-1</sup> total flow rate, at DME conversion rates of 380 μmol carbon (s mol Al)<sup>-1</sup>)

(Ahn et al., *Angew. Chem.*, 2009)

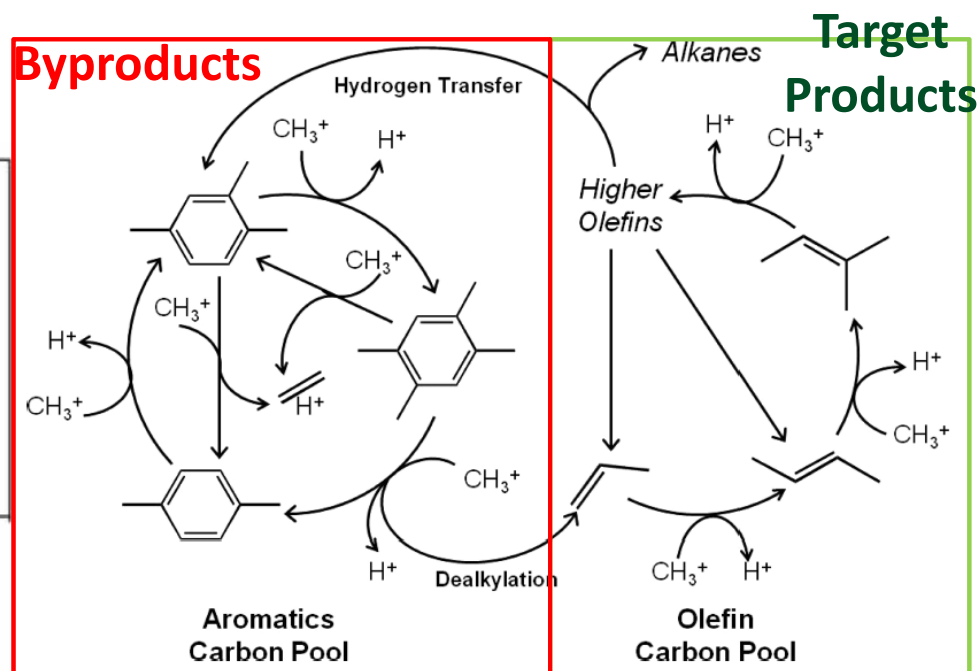
- Carbon selectivity for the SOT material matched literature data closely
- The addition of metals did not impact selectivity appreciably

# Research Progress

Hypothesis: the addition of Lewis acidic materials to the SOT catalyst (HBEA) will render H<sub>2</sub> reactive via hydride formation and reduce aromatic production



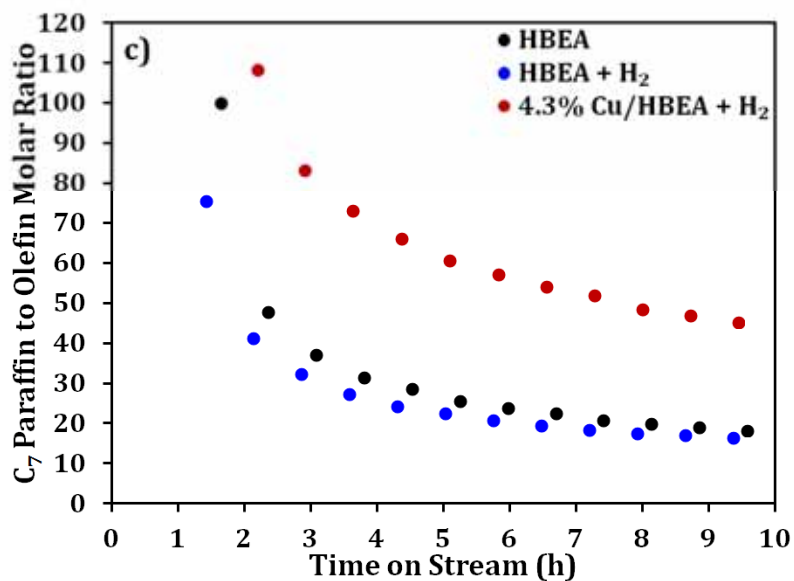
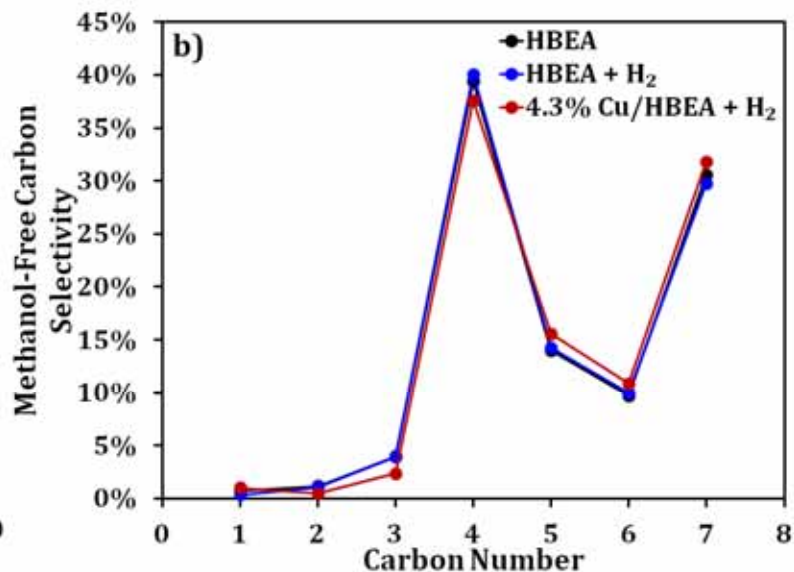
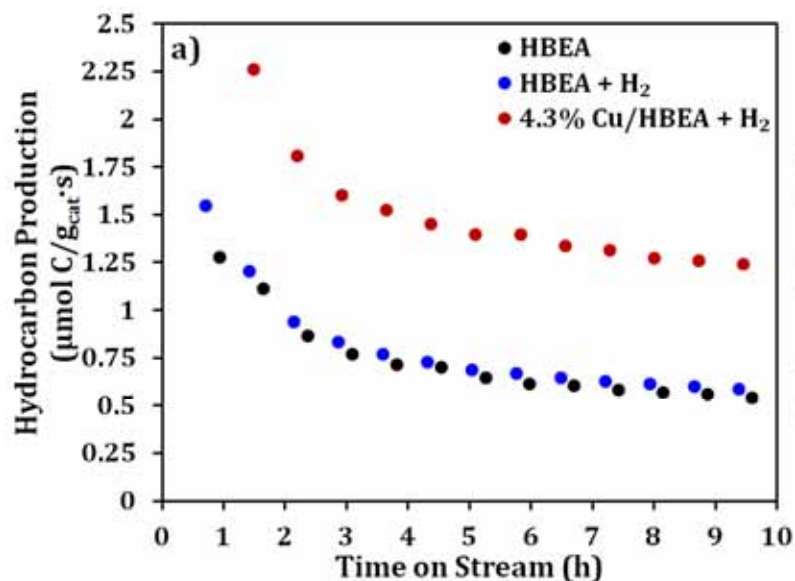
**aromatic production was reduced to 1/3 of SOT value** when Cu added to catalyst and H<sub>2</sub> cofed



	Aromatic cycle	Olefin Cycle	% C as HMB
HBEA	23%	77%	13%
HBEA + H <sub>2</sub>	21%	79%	
Cu/HBEA + H <sub>2</sub>	<b>8%</b>	<b>92%</b>	<b>4%</b>

- The addition of metal impacts aromatic production
- The addition of H<sub>2</sub> impacts aromatic production

# Research Progress – Cu/HBEA



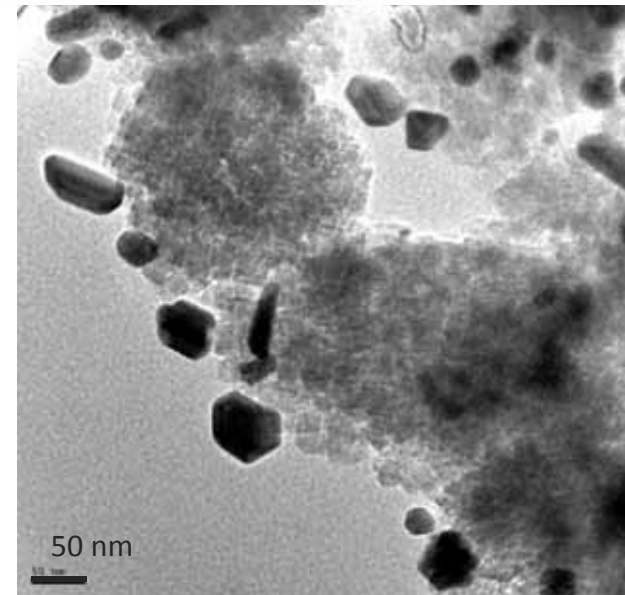
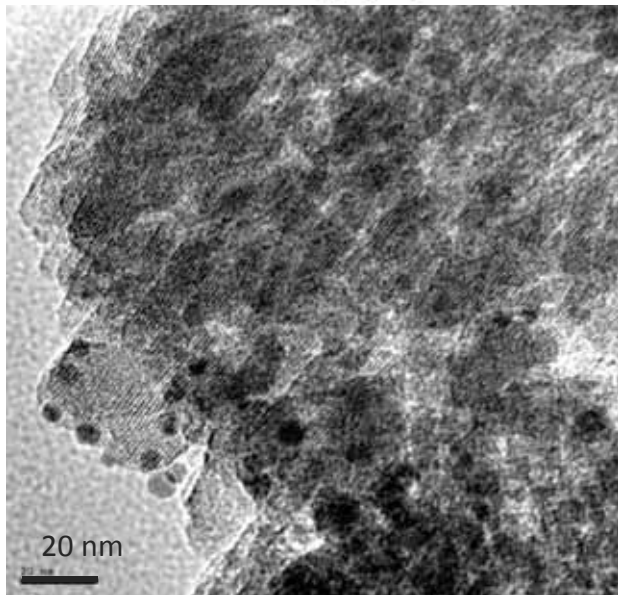
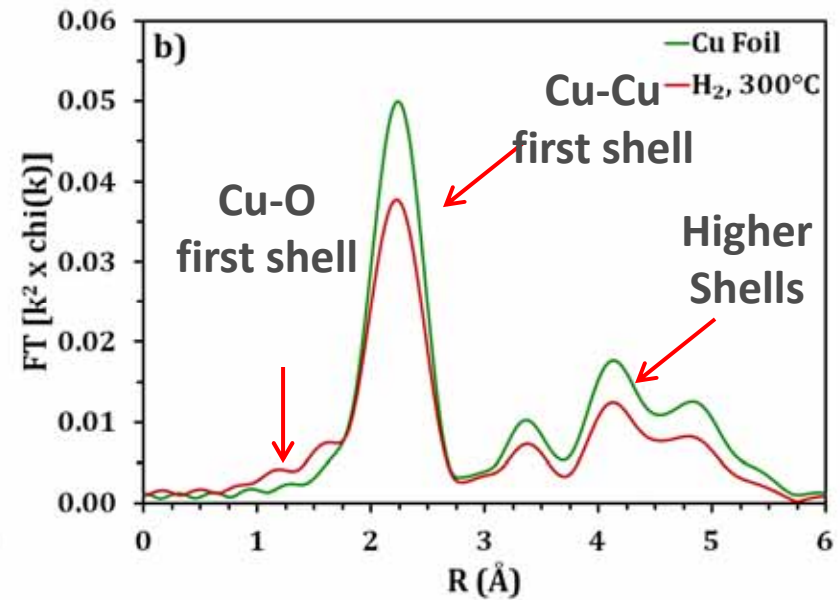
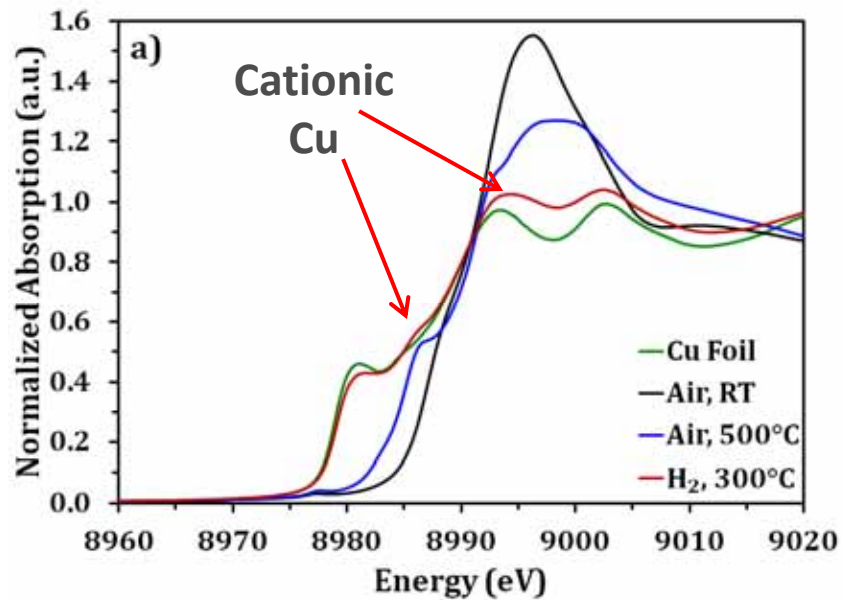
2x improvement in hydrocarbon production rate using Cu/HBEA + H<sub>2</sub>

2-3x increase in paraffin to olefin ratio (higher value product)

Schaidle, J.; Ruddy, D.; Habas, S.; Pan, M.; Zhang, G.; Miller, J.; Hensley, J. **2015** *ACS Catal*, DOI: 10.1021/cs501876w

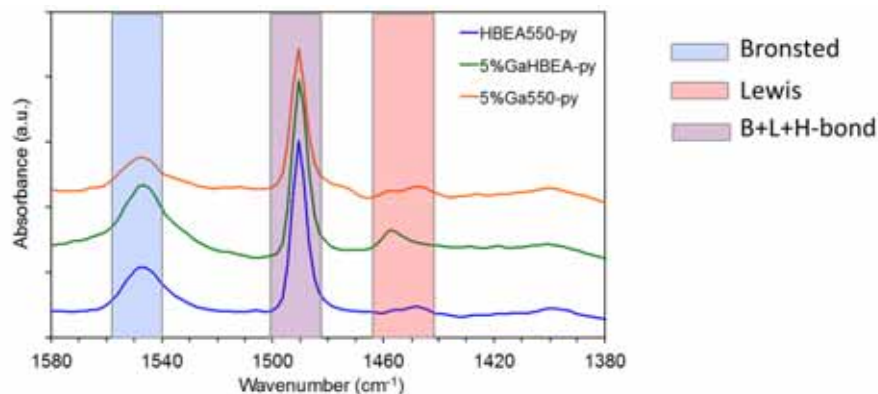


# Research Progress – Structure/Function



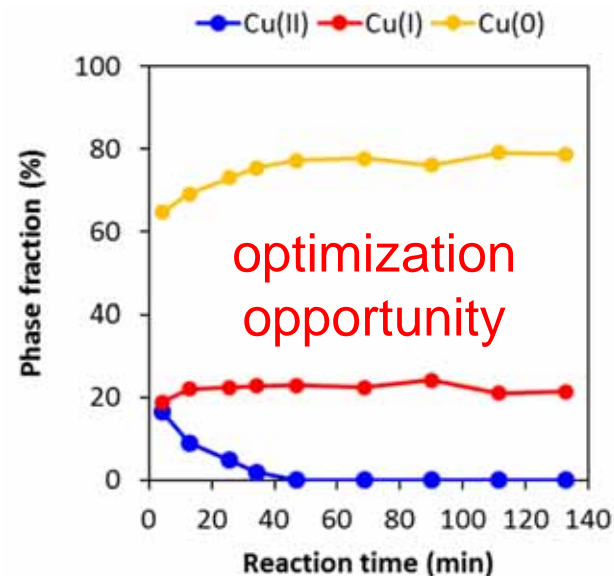
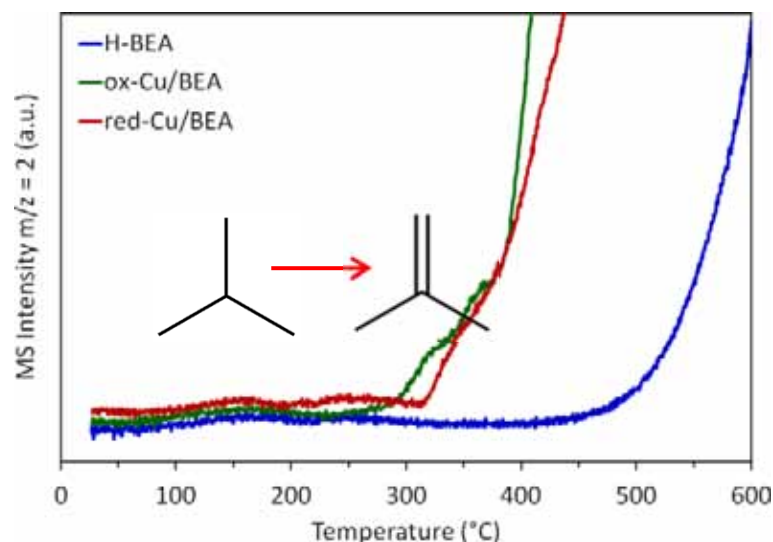
# Research Progress – Structure/Function

Reincorporation of isobutane into the reaction cycle is CRITICAL to improving gasoline yield and meeting FY16 and FY17 technical targets



A combination of advanced techniques has been used to show:

- Lewis-acidic metals change the local environment within the zeolite catalyst pore
- Ionic metals are capable of dehydrogenating isobutane at much lower temperatures than the SOT catalyst



Schaidle, J.; Ruddy, D.; Habas, S.; Pan, M.; Zhang, G.; Miller, J.; Hensley, J. 2015 *ACS Catal*, DOI: 10.1021/cs501876w

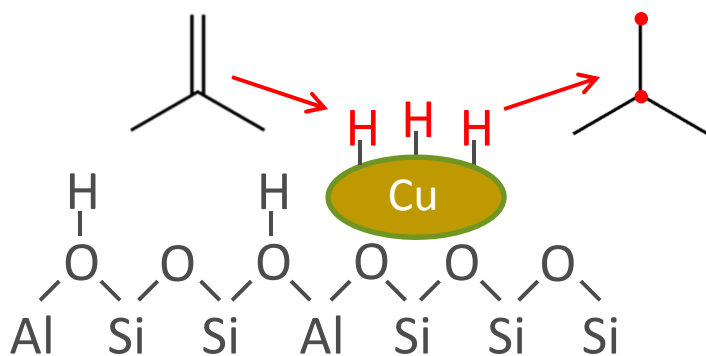
# Research Progress – Structure/Function

Results of advanced characterization show that:

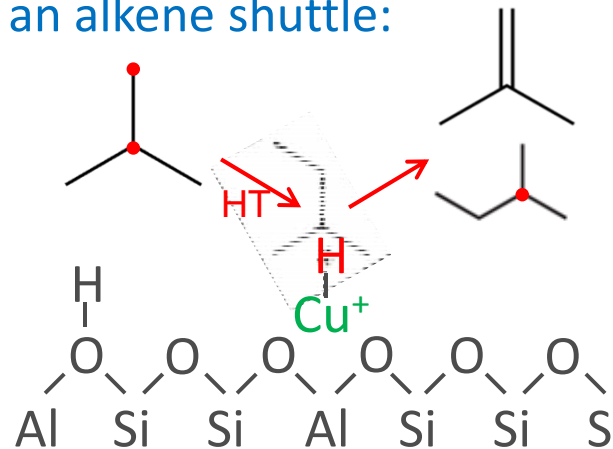
- Cu exists *on the working catalyst* as *both* metal and ion
- Other metals (data not shown) are only ionic
- Metallic domains are too large to exist in catalyst pores

Allows for accelerated hypothesis testing and advancement to new ideas and testing—an efficient and synergistic relationship

Follow-on hypothesis for why Cu works – it acts as an alkene shuttle:

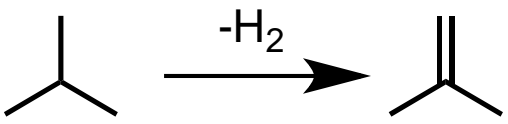


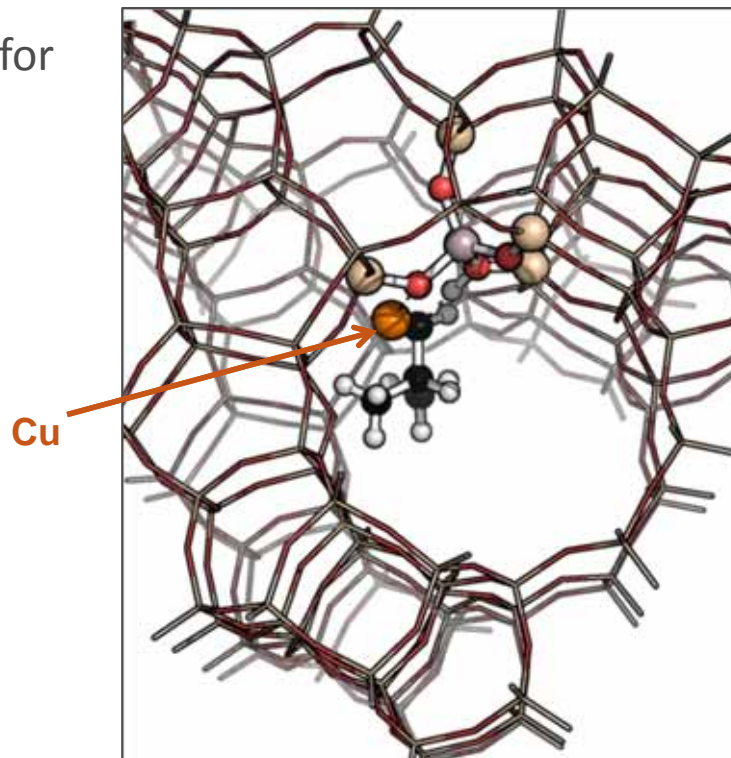
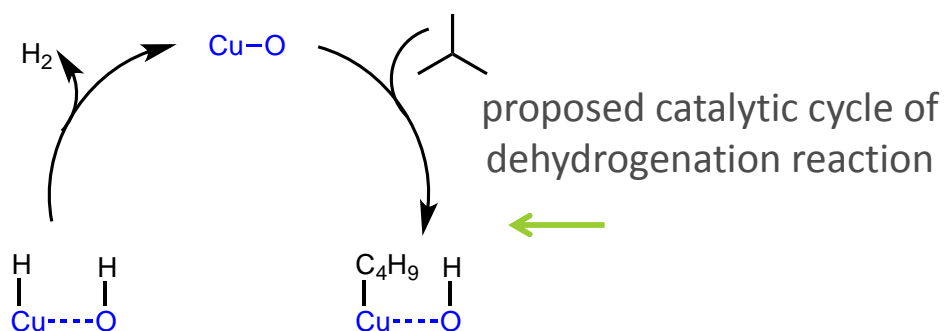
**Metallic Cu  
function**



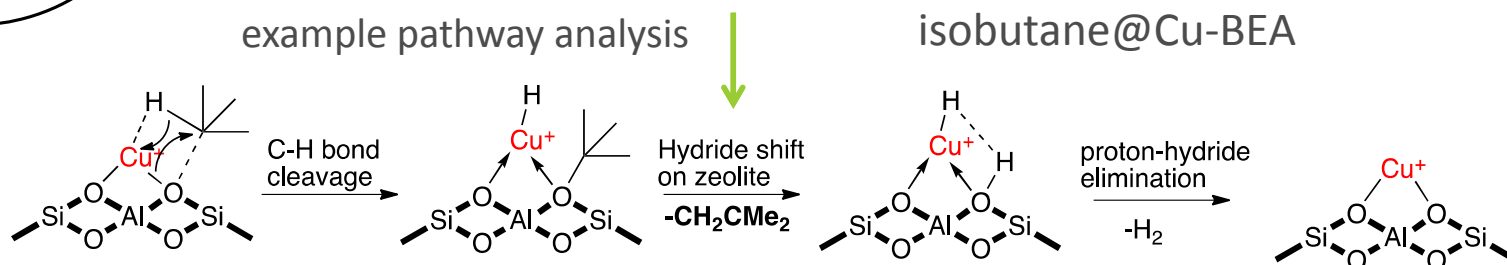
**Promoted by Lewis Acidic Cationic  
Cu**

# Research Progress – Computational Modeling

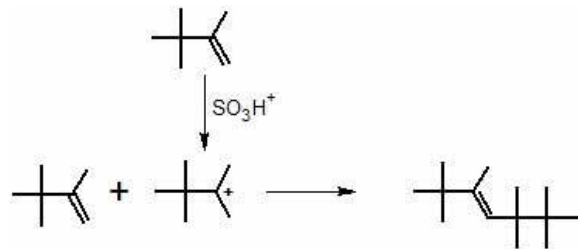
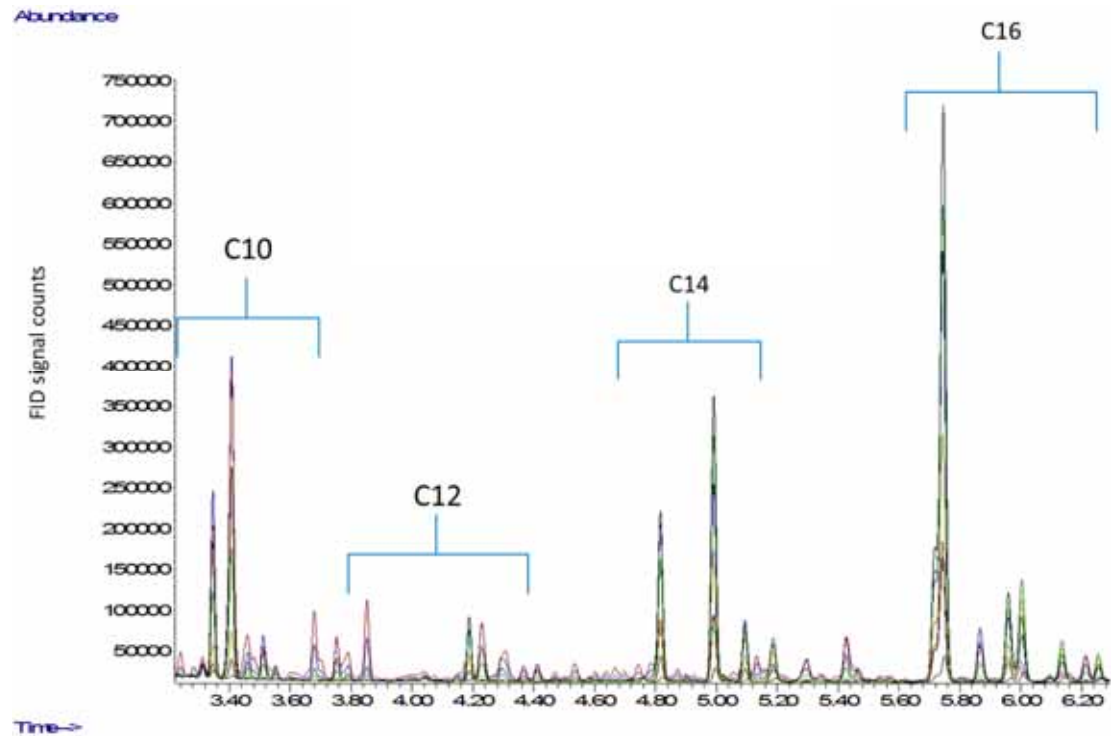
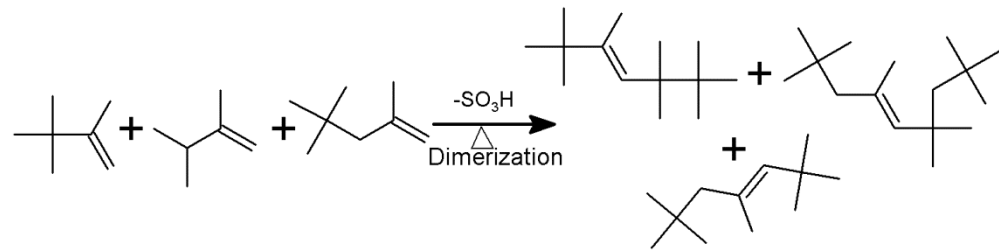
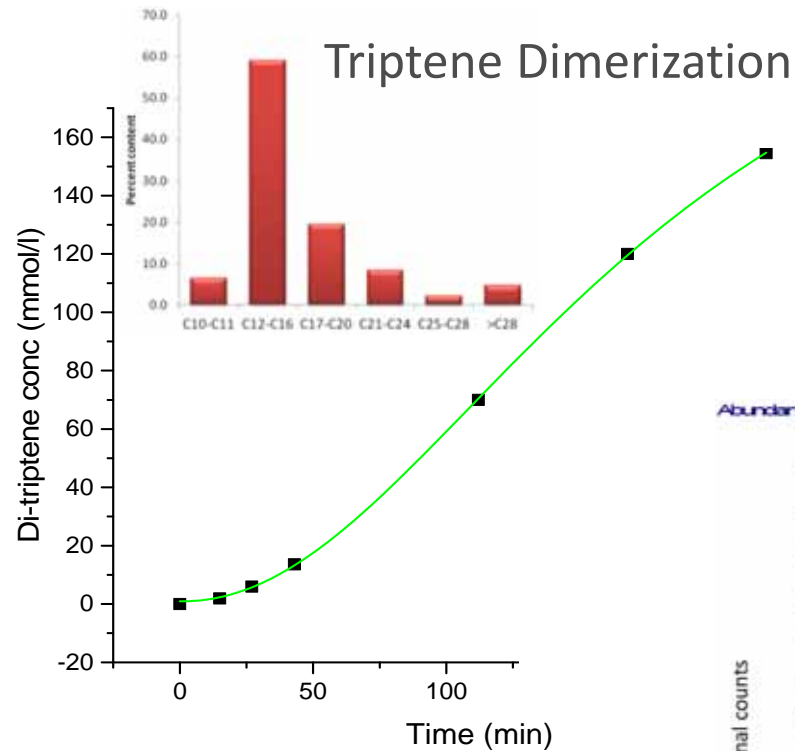
- DFT-calculated relative deprotonation energies for multiple T sites in BEA
- Target reaction: 
- Substituting framework/extraframework metals (Ga, Cu, Zn, Fe)



Optimized transition state of isobutane@Cu-BEA



# Research Progress – Moving Toward Distillates



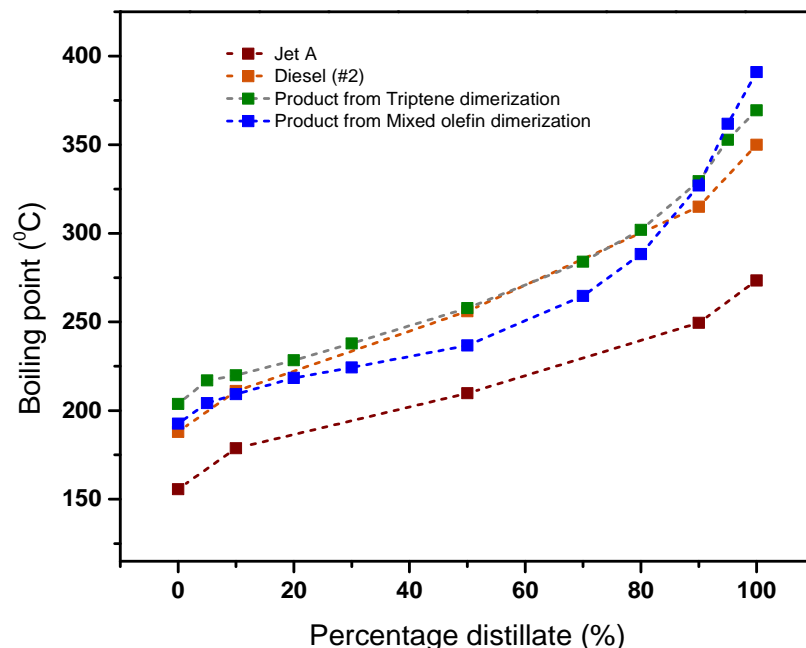
# Research Progress – Moving Toward Distillates

Have confirmed that C<sub>5</sub>-C<sub>8</sub> olefinic product can be dimerized over a commercial catalyst (Amberlyst)

- Product has MWs and boiling points within distillate range
- **Properties appear most attractive for jet** (low FP, low CP, correct boiling range)
- Dimerized product highly branched, lower cetane values
- Evaluating for inclusion into design report

Fuel properties	Known values for typical fuels*		As-measured values	
	Commercial fuels		Synthetic fuel from triptene	Synthetic fuel from mixed olefin feed
Cloud point	-48 °C (Jet-A)		-81 °C (ASTM 5773)	< -65 °C
LHV (MJ/kg)	42.8 (Jet-A)		42.87 (ASTM D240)	42.64 (ASTM D240)
BP range (°C)	Diesel(#2)    Jet-A		ASTM-D2887	ASTM-D2887
	IBP	180    156	204	193
	T10	211    180	220	209
	T90	315    251	329	327
	FBP	350    274	369	391
Flash point (°C)	≥52	≥38	62.9 ‡	

\* Kook, S.; Pickett, L. M. *SAE Int. J. Fuels Lubr.* 2012 5(2), 647-664  
 ‡ ( for pure di-triptene C<sub>14</sub>H<sub>28</sub>)



Behl, M.; Schaidle, J.A.; Christensen, E.; Hensley, J.E. submitted to *Energy & Fuels* for peer review

# Relevance

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- Addresses BETO's strategic goal for conversion R&D:  
*"develop commercially viable technologies for converting biomass feedstocks into energy-dense, fungible, liquid transportation fuels"*
  - **TEA-informed technical targets** for the economic production of hydrocarbon fuels from biomass syngas
  - Research and development by national lab *partners* with expertise in **applied (NREL) and fundamental (ANL) science and engineering**
  - Research **leverages previous investment by BETO** in biomass gasification and syngas cleanup
- Project addresses MYPP pathways for conversion of agricultural residues, energy crops, forest resources, and waste:
  - Syngas to non-ethanol fuels
- Project accomplishments in FY13 and FY14 helped BETO to reach its strategic goals:
  - Proof of concept data and catalyst development **contributed to the completion of a design report**: "Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbons via Indirect Liquefaction: Thermochemical Pathway to High-Octane Gasoline Blendstock through Methanol/Dimethyl Ether Intermediates" {W.B.S. 2.1.0.302}
  - **Demonstrated improvements in catalyst performance which lead to achievement of technical targets**
- A successful project has market potential beyond biomass gasification
  - DME to hydrocarbon fuel technology 'syngas agnostic'
  - Applicable to conversion of butanes to higher-value fuel products

# Future Work

- **Reduce the aromatic content** in C<sub>5+</sub> product from 25% (SOT) to 15% by FY15 (achieved), 8% by FY16, and 4% by FY17
- **Reduce the yield of LPG** from 27% (SOT) to 0% by FY16 by:
  - Recycling C<sub>4</sub> to the reactor and reactivating it through catalytic dehydrogenation\*
  - Recycling C<sub>3-</sub> to the reformer†
- Obtain target catalyst performances at single pass DME conversions of 20% by FY16 and 30% by FY17 as compared to the SOT value of 15%
- **Increase the productivity** of the catalyst from 0.02 (SOT) to 0.03 by FY15 (achieved), 0.04 by FY16 (achieved), and 0.05 kg/kg-cat/h by FY17
- **Demonstrate the regenerability** of the modified catalyst(s) (similar to that of the SOT material) through successive oxidation/reduction/operation cycles
- **Optimize a catalyst formulation** for kinetic studies, process scaleup, and integrated validation by end of FY16
  - Promoter metal
  - Metal loading
  - Synthesis procedure
  - Operating ranges
- **Demonstrate integrated biomass gasification, tar reforming, methanol/DME synthesis, and gasoline production with the above optimized catalyst at the extended bench scale (1 kg biomass/h) in FY17**

\*simulated in FY15/16

†assumed, not investigated



# Summary

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- This project shifted focus in FY13
  - FY10-FY12 objective: catalytic conversion of syngas to ethanol; demonstration in integrated pilot process
  - FY13-FY17 objective: catalytic conversion of a syngas intermediate to drop-in hydrocarbon fuels; demonstration in integrated bench process
- In FY13/14 a technical pathway and goals were established
  - Focus on **conversion of DME** (a commercial syngas product) **to gasoline and diesel/jet**
    - Lower intensity process than ‘MTG’
    - **Targeting higher yields, higher product value compared to ‘MTG’**
  - Achieve MFSP of \$3.72/gge by FY17 through
    - Catalyst improvements and validation
    - Process intensification and validation
    - Feedstock cost reductions borrowed from those achieved in DL projects
  - **R&D results in FY13/14 suggest that this project is on track to meet technical targets set for FY15-17**
    - Exceeded targets in FY13/14
    - **Published results in a top catalysis journal, *submitted patent application* for materials**

# Acknowledgements

## NREL

*Jason Bates (I)*

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*Susan Habas*

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*I – DOE Office of Science Intern*

*TT – Transportation Technologies*

*Group, NREL*

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*Dan Ruddy*

*Josh Schaidle*

*Mike Talmadge*

*Eric Tan*

*Jason Thibodeaux*

*Matt Yung*

## ANL

*Jennifer Dunn*

*James Gallagher*

*Jeff Miller*

*Guanghui Zhang*



**DOE BeTO**



# Questions

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# Additional Slides for Q&A Session

# Glossary of Terms

<b>AKI</b>	anti-knock index - the average of RON and MON and the commonly listed 'octane' rating at the gas pump	<b>IDL</b>	indirect liquefaction (gasification followed by gas to liquids conversion)
<b>Al</b>	aluminum, incorporated as oxide	<b>La</b>	lanthanum, ionic
<b>ANL</b>	Argonne National Laboratory	<b>LHV</b>	lower heating value - energy released to yield carbon dioxide and steam
<b>AOP</b>	annual operating plan	<b>LPG</b>	liquefied petroleum gas
<b>BETO</b>	Bioenergy Technology Office	<b>MFSP</b>	minimum fuel selling price, based on economic assumptions in BETO-sponsored design reports
<b>C4</b>	for example, a C followed by a number indicates a hydrocarbon with the indicated number of carbons per molecule	<b>MON</b>	motor octane number
<b>CP</b>	cloud point	<b>MOU</b>	memorandum of understanding--parties work together but there is no exchange of funds or personnel
<b>Cu</b>	copper, metallic or ionic or incorporated as oxide	<b>MTG</b>	methanol to gasoline, specifically the process developed by Mobil in the 1970s to convert methanol or dimethyl ether to an aromatic-rich gasoline range hydrocarbon liquid
<b>DFT</b>	density functional theory	<b>MYPP</b>	Multi-Year Program Plan
<b>DL</b>	direct liquefaction (fast pyrolysis followed by quench to recover condensable vapors)	<b>NREL</b>	National Renewable Energy Laboratory
<b>DME</b>	dimethyl ether	<b>ox</b>	oxidized
<b>DOE</b>	Department of Energy	<b>R&amp;D</b>	research and development
<b>EtOH</b>	shorthand for ethanol	<b>red</b>	reduced
<b>FBP</b>	final boiling point	<b>RON</b>	research octane number
<b>Fe</b>	iron, ionic	<b>Si</b>	silicon, incorporated as oxide
<b>FT</b>	flash point	<b>SOT</b>	state of technology, always relative to an indicated date
<b>FY</b>	fiscal year	<b>SUB</b>	subcontractor
<b>Ga</b>	gallium, ionic	<b>TEA</b>	technoeconomic analysis - includes a process design and associated economics based on economic assumptions in BETO-sponsored design reports
<b>gge</b>	gallons of gasoline equivalent	<b>TOS</b>	time on stream
<b>HBEA</b>	shorthand for zeolite beta in its proton form	<b>triptane</b>	shorthand for 2,2,3-trimethylbutane
<b>HC/HCs</b>	hydrocarbons	<b>triptene</b>	shorthand for 2,2,3-trimethylbutene
<b>HMB</b>	hexamethylbenzene	<b>Zn</b>	zinc, ionic
<b>IBP</b>	initial boiling point	<b>ZSM-5</b>	shorthand for Zeolite Socony Mobil-5

# X-ray Absorption Spectroscopy as a Tool for Improving Catalyst Performance

**Objective:** Employ X-ray absorption spectroscopy to define the structural and chemical properties that determine catalyst performance.

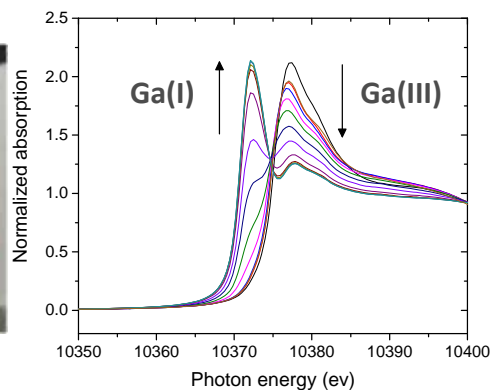
- **X-ray Absorption Near Edge Spectroscopy (XANES)** - used to determine metal oxidation state, fraction of metallic and oxidized species, formation of alloys, surface coverage
- **Extended X-ray Absorption Fine Structure (EXAFS)** - used to determine short-range structure, number of neighbors, type of neighbors, and distance between atoms

**In situ studies** – for evaluating the effect of catalyst pretreatment and oxidative ( $O_2$ ) or reductive ( $H_2$ ) environments on catalyst oxidation state.

**Operando studies** – for monitoring changes in both the oxidation state and the local structure of the catalyst under actual process conditions.



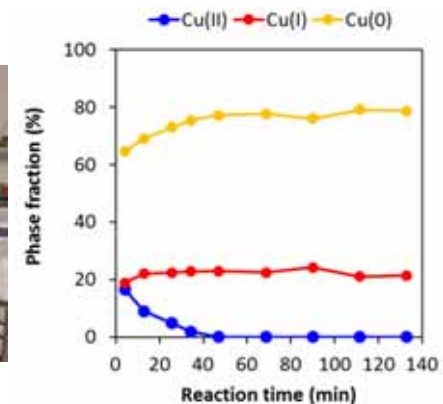
Multiple sample system for conducting *in situ* studies.



XANES spectra of Ga/H-BEA showing reduction of Ga(III) to Ga(I) upon heating under  $H_2$  140°C to 500°C.



Plug reactor system for conducting *operando* studies.



Change in Cu oxidation state of Cu/H-BEA catalyst with time for reaction of DME+ $H_2$  at 200°C.

# Specific Experiments Conducted at ANL FY13/14

Year	Significant Accomplishments
FY13	<ul style="list-style-type: none"> <li>Redox properties of 4 different (Ga, Zn, Fe, La)/BEA catalysts were investigated under H<sub>2</sub> or O<sub>2</sub></li> <li>First known observation of Ga(III) → Ga(I) redox</li> </ul>
FY14	<ul style="list-style-type: none"> <li>Completed construction of a reactor for <i>operando</i> studies</li> <li>Conducted <i>in-situ</i> and <i>operando</i> studies on Cu, Ga, and Cu-Ga/BEA catalysts</li> <li>Showed that Ga in Ga/BEA prepared by ion-exchange undergoes Ga(III) → Ga(I) redox but Ga in framework Ga/BEA is not reducible</li> <li>Determined that Ga is stable under triptane reaction conditions and does not contribute to the observed catalyst deactivation</li> <li>Tested for and observed no evidence interaction between Cu and Ga in Cu-Ga/BEA catalyst</li> </ul>
FY15	<ul style="list-style-type: none"> <li>Determined the change in Cu oxidation state and growth in Cu particle size with time on stream under triptane reaction conditions</li> <li>Investigating the changes in Cu oxidation state and growth in Cu particle size as a result of repeated oxidation/reduction cycles (presently underway)</li> </ul>

# Detailed Milestones for FY13, FY14

Due Date	Milestone Type	Milestone Title	Comments
12/21/2012	E	<u>Evaluate mixed alcohol catalyst performance with complete byproduct recycle:</u> A catalyst within the syngas to mixed alcohol to hydrocarbon fuel process will be operated for 100h with a liquid recycle stream comprising 50% of the methanol in actual product along with minor components as predicted by AspenPlus simulation.	Completed – used as a proof of concept to determine feasibility of a mixed alcohol intermediate
03/29/2013	D	<u>Process intensification for triptane synthesis:</u> Triptane will be produced from a zeolite catalyst using methanol that is produced in situ from syngas. Performance will be compared to triptane synthesis from methanol feed.	Completed
06/28/2013	D	<u>Extended operation of fuel synthesis catalyst:</u> A syngas-to-mixed alcohol-intermediates catalyst will be operated for 3000h at the bench scale and performance documented as a function of time to determine practical catalyst lifetime to support the FY14 design report on syngas to hydrocarbons via mixed oxygenates.	Completed – used as a proof of concept to determine feasibility of a mixed alcohol intermediate
09/27/2013	D	<u>Catalyst Characterization:</u> Characterize structure-function relationships for one fuel synthesis catalyst using in-situ techniques.	Completed
12/20/2013	E	<u>Demonstrate alkylation of mixed alcohols using acid catalysis:</u> A solid acid catalyst will be used to demonstrate alkylation of mixed alcohols in two (2) scenarios: i) feed composition typical of crude mixed alcohol product and ii) feed composition typical of refined mixed alcohol product with methanol substantially removed.	Completed – used as a proof of concept to determine feasibility of a mixed alcohol intermediate
03/31/2014	D	<u>Production of mixed olefins:</u> at least two (2) surrogate mixed alcohol streams similar to those used in the Q1 milestone will be dehydrated to olefins at a conversion greater than 60% using a commercial or in-house synthesized catalyst.	Completed
06/30/2014	D	<u>Dimerization of olefins:</u> Demonstrate synthesis of a dimerized olefin product on at least one (1) commercial or in-house synthesized catalyst. The composition of the olefin feed stream will be informed from results of dimethyl ether to triptane experiments and results will be presented in terms of conversion and selectivity to dimers and byproducts.	Completed
09/30/2014	D	<u>Catalyst Characterization :</u> Characterize structure-function relationships for one (1) fuel synthesis catalyst using in-situ techniques and prepare one (1) summary report on FY14 fundamental catalyst development in conjunction with task 2.11.2.15.	Completed



# Detailed Milestones for FY15

Due Date	Milestone Type	Milestone Title	Comments
12/31/2014	regular	<u>Productivity and Selectivity Improvements for Dimethyl Ether Conversion to Branched Hydrocarbons:</u> Increase the volumetric hydrocarbon productivity at 6h on stream (pseudo-steady-state) from 500 $\mu\text{molC}/\text{molsites}/\text{s}$ to at least 600 $\mu\text{molC}/\text{molsites}/\text{s}$ (20% increase) and decrease the selectivity to hexamethylbenzene defined as C in HMB divided by C in other HC from 0.12 to 0.1 (17% reduction) for the conversion of dimethyl ether to branched hydrocarbons	Completed
3/31/2015	progress	<u>Catalyst Screening for Mixed Alcohol Dehydration:</u> Evaluate the performance of Zr-KIT-6 compared to three (3) commercial catalysts for the dehydration of a surrogate mixed alcohol stream at two (2) different reaction temperatures.	Complete – submission pending
3/31/2015	Go/No-Go	<u>Evaluation of Go/No-Go for the gasification to high octane gasoline synthesis route:</u> Working with the TC Analysis task, an evaluation will be made, using Design Reports and SOT reports, to determine whether the pathway of gasification followed by methanol synthesis and high octane gasoline synthesis is on an appropriate trajectory to validate cost-competitive hydrocarbon fuels by 2017.	Pending
06/30/2015	progress	<u>Commercial Catalyst Screening for Branched Olefin Dimerization:</u> Evaluate the performance of Amberlyst-35 dry and two (2) other commercial catalysts for the dimerization of triptene and one (1) mixture of C5-C7 olefins representative of the product distribution from methanol/dimethyl ether conversion to branched olefins and paraffins. This will be used in the FY15 SOT report to determine whether this route to jet fuel represents an economically-feasible pathway and adjust FY16 work accordingly.	In progress
09/30/2015	progress	<u>Demonstrate Ethylene Oligimerization over an In-house Catalyst:</u> Demonstrate the oligomerization of ethylene and at least one (1) mixture of olefins over at least one (1) in-house synthesized catalyst and one (1) commercial catalyst.	In progress
09/29/2015	Regular	<u>100% IDL integrated process design - finalized process design and construction schedule:</u> Prepare one (1) complete project management binder to include final ES&H-approved process drawings, punch lists of required equipment modifications and connections, equipment specifications and ratings, equipment to procure, tag lists and wiring diagrams, a detailed schedule for construction and assembly of the integrated system, and a detailed schedule for system shake down and commissioning in FY16.	In progress

# Timeline: Integrated Bench Scale Demonstration



## Design Stage

FY15

### Activities

- identification of useable existing equipment
- process design
- HAZOPs
- drawings, equipment specifications, tag lists, construction schedule, and procurement lists

## Fabrication Stage

Q3 FY15 to Q1 FY17

### Activities

- plumbing and wiring
- continuity and I/O checks
- assembly of new equipment
- modifications to existing equipment

## Commissioning Stage

Q2 FY16 to Q2 FY17

### Activities

- cold and hot flow testing, interlock validation
- integrated gasification, reforming, and gas cleanup
- integrated syngas to DME and hydrocarbon demonstration
- recycle system testing and troubleshooting
- preliminary data collection

## Demonstration Stage

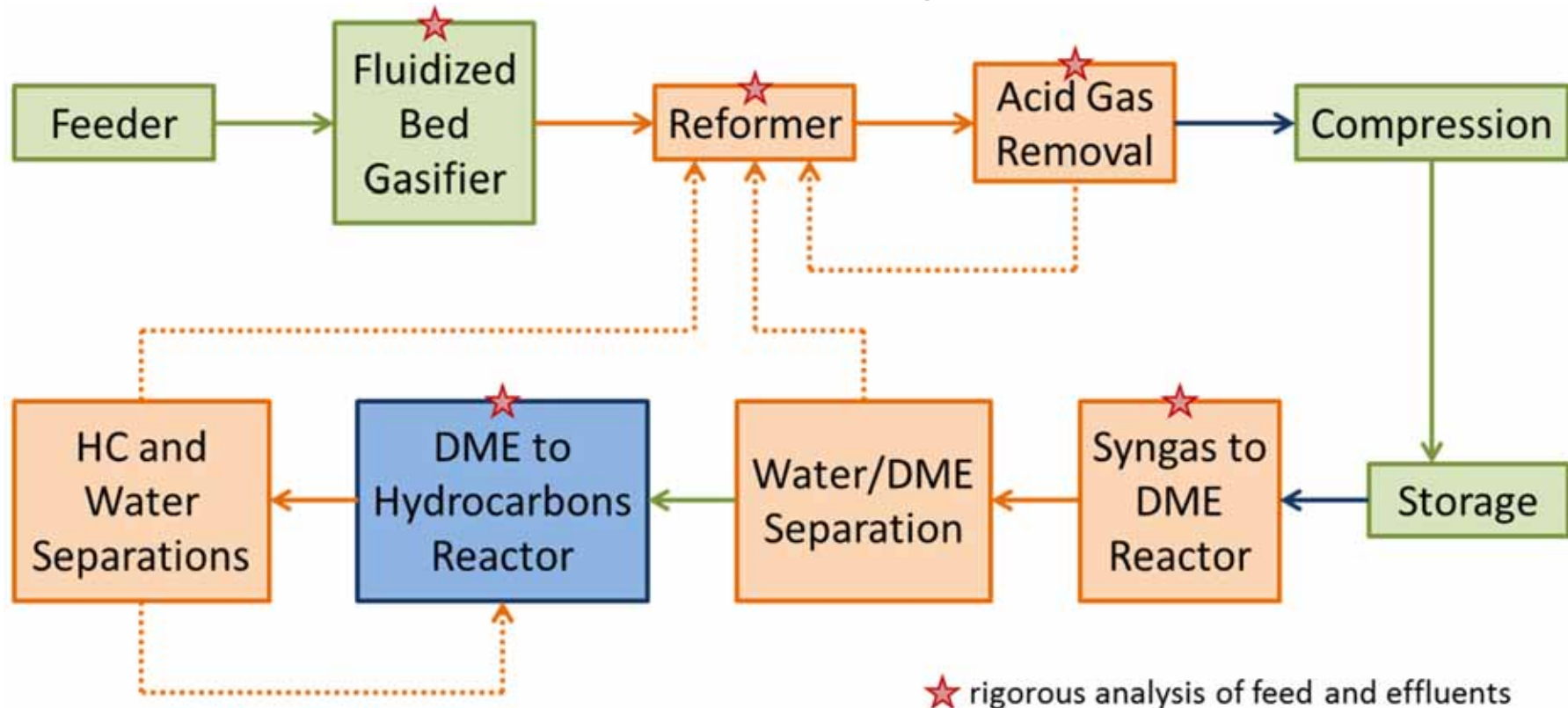
Q2 to Q4 FY17

### Activities

- integrated and continuous equipment operation
- evaluation of different feedstocks
- detailed material balances and performance calculations
- determination of needs for additional scaleup

# Process Flow: Integrated Bench Scale Demonstration

Scale: 20-40 kg/d



**Green:** equipment already in place

**Blue:** existing equipment to be modified for this project

**Orange:** to be assembled for this project of catalog parts

# Design Case Economic Summary (from 2.1.0.302)

Description of Economic Parameter	Current Value
Minimum Fuel Selling Price	\$3.41 / Gal GE
Minimum Fuel Selling Price	\$3.25 / Gallon
Feedstock Costs	\$1.23 / Gallon
Operating Costs & Credits	\$0.55 / Gallon
Capital Charges & Taxes	\$1.47 / Gallon
Gasoline Blendstock Production	47.0 MM Gallons / Year
Gasoline Blendstock Product Yield	64.9 Gallons / US Dry Ton
Delivered Feedstock Cost	\$80.00 / US dry ton
Total Purchase Equipment Cost (TPEC)	\$122.2 MM
Installation Factor / Total Installed Cost (TIC)	x 2.06 Factor = \$251.2 MM
Total Fixed Capital	\$415.2 MM
Working Capital / Land Costs	\$20.1 MM / \$1.6 MM
Total Capital Investment	\$437.5 MM
Lang Factor (TCI / TPEC)	3.58
TCI Lang Factor (TCI / ISBL TPEC)	4.54

2022

# Design Case Economic Summary (from 2.1.0.302)

## comparison to thermochemical ethanol

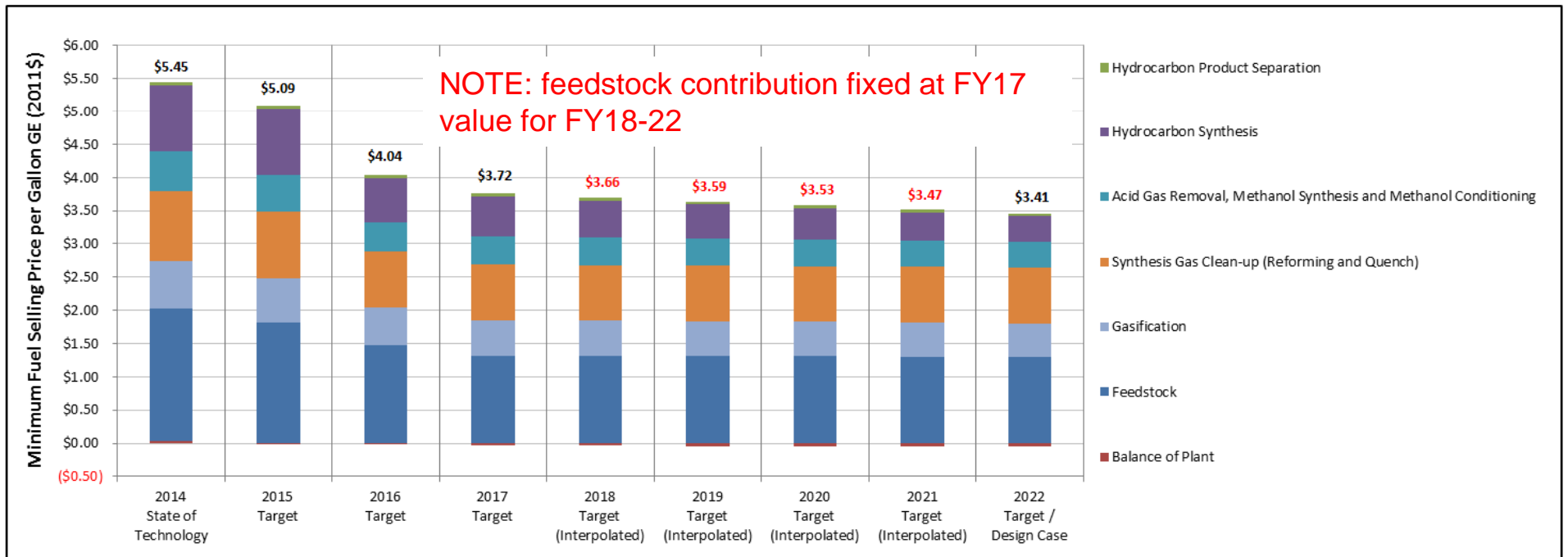
Description of Economic Parameter	Current Value	TC-MAS Demo
Minimum Fuel Selling Price	\$3.41 / Gal GE	\$3.80 / Gal GE
Minimum Fuel Selling Price	\$3.25 / Gallon	
Feedstock Costs	\$1.23 / Gallon	
Operating Costs & Credits	\$0.55 / Gallon	
Capital Charges & Taxes	\$1.47 / Gallon	
Gasoline Blendstock Production	47.0 MM Gallons / Year	47.0 MM GGE
Gasoline Blendstock Product Yield	64.9 Gallons / US Dry Ton	64.9 GGE
Delivered Feedstock Cost	\$80.00 / US dry ton	
Total Purchase Equipment Cost (TPEC)	\$122.2 MM	
Installation Factor / Total Installed Cost (TIC)	x 2.06 Factor = \$251.2 MM	
Total Fixed Capital	\$415.2 MM	\$527.5 MM
Working Capital / Land Costs	\$20.1 MM / \$1.6 MM	
Total Capital Investment	\$437.5 MM	\$553.9 MM
Lang Factor (TCI / TPEC)	3.58	3.45
TCI Lang Factor (TCI / ISBL TPEC)	4.54	4.31

# Technical Targets Summary (from 2.1.0.302)

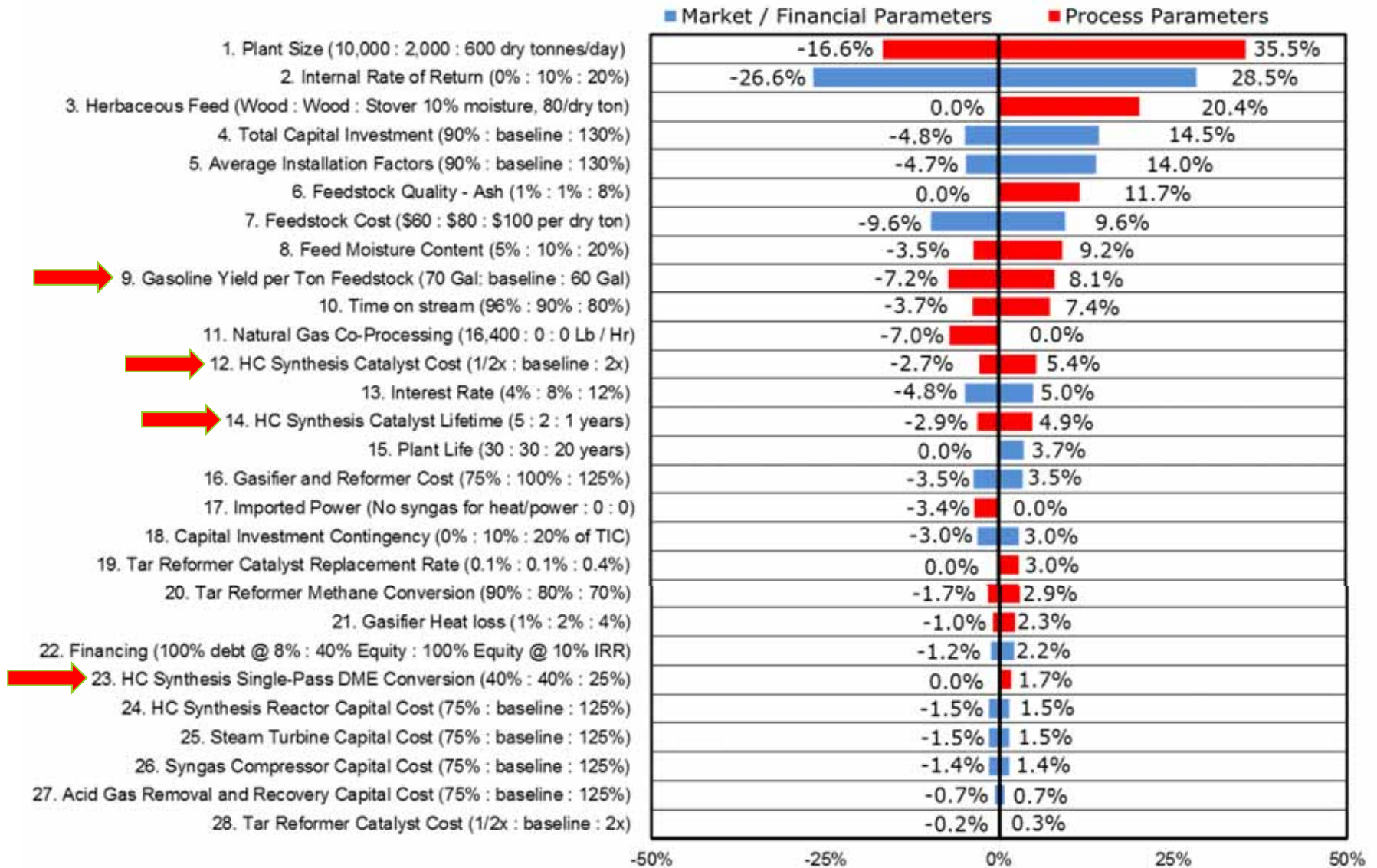
Process Parameter	2014 SOT	2015 Target	2016 Target	2017 Target	2022 Target / Design Case
Hydrocarbon Synthesis Catalyst	Commercially available beta-zeolite		Beta-zeolite modified with copper (Cu) and gallium (Ga) for performance improvement		
H <sub>2</sub> Addition to HC Synthesis	No	Yes			
C <sub>4</sub> Co-Product (Function of Recycle)	Yes (No Recycle of C <sub>4</sub> s)		No (Recycle C <sub>4</sub> s)		
Single-Pass DME conversion	15%	15%	20%	30%	40%
Productivity of Hydrocarbon Synthesis Catalyst (kg/kg-cat/h)	0.02	0.03	0.04	0.05	0.10
Carbon Selectivity to C <sub>5</sub> + Product	46.2%	50.8%	86.1%	89.9%	93.1%
Carbon Selectivity to Aromatics (HMB represents coke / pre-cursors)	25% Aromatics (10% HMB)	15% Aromatics (7% HMB)	8% Aromatics (4% HMB)	4% Aromatics (2% HMB)	0.5% as HMB
Dimerization of C <sub>4</sub> -C <sub>8</sub> Olefins to Jet	No	Consider in SOT cases as sensitivity or modify target case			
C <sub>5</sub> + Product Yield (Gallons / Ton)	39.7	40.4	61.8	64.2	64.9
Carbon Efficiency to C <sub>5</sub> + Product	20.7%	21.1%	29.9%	31.0%	31.2%
C <sub>4</sub> Product Yield (Gallons / Ton)	17.9	18.1	0.0	0.0	0.0
Carbon Efficiency to C <sub>4</sub> Product	7.5%	7.6%	0.0%	0.0%	0.0%
Minimum Fuel Selling Price (\$ / GGE)	\$5.45	\$5.09	\$4.04	\$3.72	\$3.41

# Process Economics Summary (from 2.1.0.302)

Minimum Fuel Selling Price (MFSP) Breakdown (\$ / Gallon of Gasoline Equivalent)	2014 State of Technology	2015 Target	2016 Target	2017 Target	2018 Target (Interpolated)	2019 Target (Interpolated)	2020 Target (Interpolated)	2021 Target (Interpolated)	2022 Target / Design Case
Feedstock	\$ 1.99	\$ 1.82	\$ 1.48	\$ 1.32	\$ 1.31	\$ 1.31	\$ 1.31	\$ 1.31	\$ 1.30
Gasification	\$ 0.70	\$ 0.67	\$ 0.56	\$ 0.54	\$ 0.53	\$ 0.52	\$ 0.52	\$ 0.51	\$ 0.50
Synthesis Gas Clean-up (Reforming and Quench)	\$ 1.06	\$ 1.00	\$ 0.84	\$ 0.84	\$ 0.84	\$ 0.84	\$ 0.84	\$ 0.84	\$ 0.84
Acid Gas Removal, Methanol Synthesis and Methanol Conditioning	\$ 0.59	\$ 0.55	\$ 0.44	\$ 0.42	\$ 0.42	\$ 0.41	\$ 0.41	\$ 0.40	\$ 0.39
Hydrocarbon Synthesis	\$ 1.01	\$ 1.01	\$ 0.67	\$ 0.60	\$ 0.55	\$ 0.51	\$ 0.47	\$ 0.42	\$ 0.38
Hydrocarbon Product Separation	\$ 0.05	\$ 0.05	\$ 0.05	\$ 0.04	\$ 0.04	\$ 0.04	\$ 0.04	\$ 0.04	\$ 0.04
Balance of Plant	\$ 0.04	\$ (0.00)	\$ (0.00)	\$ (0.04)	\$ (0.04)	\$ (0.04)	\$ (0.05)	\$ (0.05)	\$ (0.05)
<b>Minimum Fuel Selling Price (MFSP)</b>	<b>\$ 5.45</b>	<b>\$ 5.09</b>	<b>\$ 4.04</b>	<b>\$ 3.72</b>	<b>\$ 3.66</b>	<b>\$ 3.59</b>	<b>\$ 3.53</b>	<b>\$ 3.47</b>	<b>\$ 3.41</b>



# Process Economics Sensitivities (from 2.1.0.302)

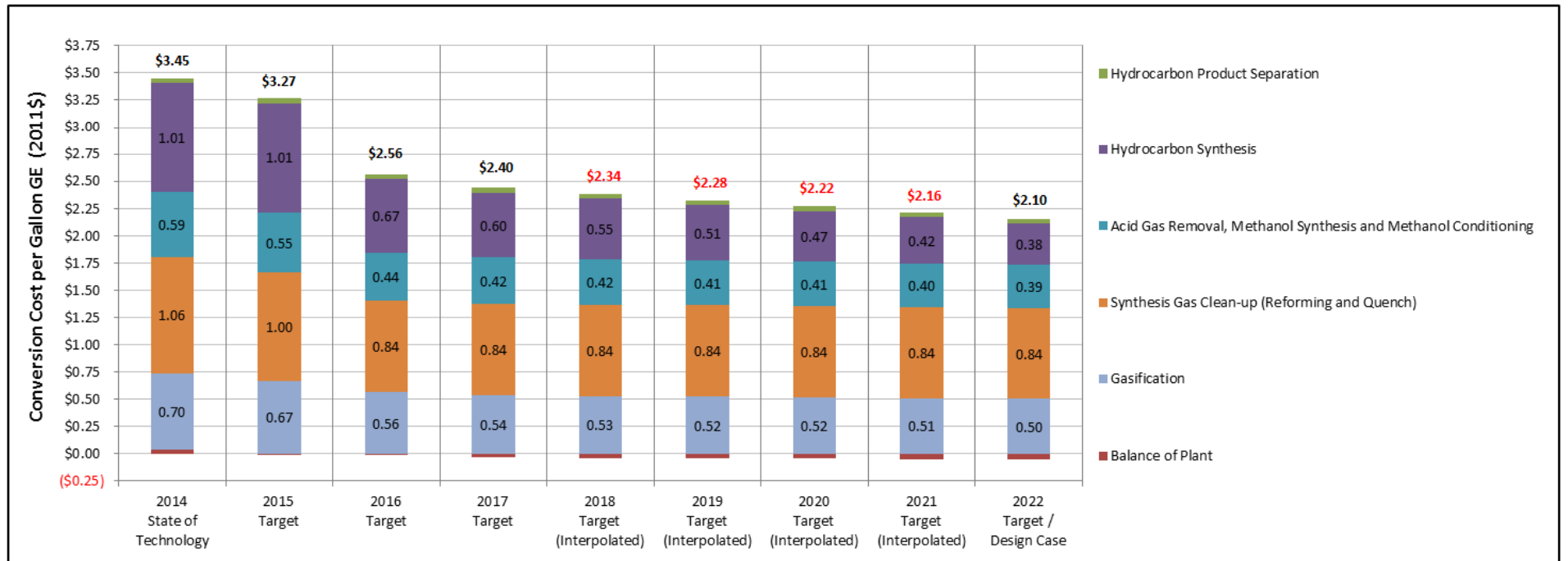




# Process Economics Summary (from 2.1.0.302)

## Excluding feedstock costs

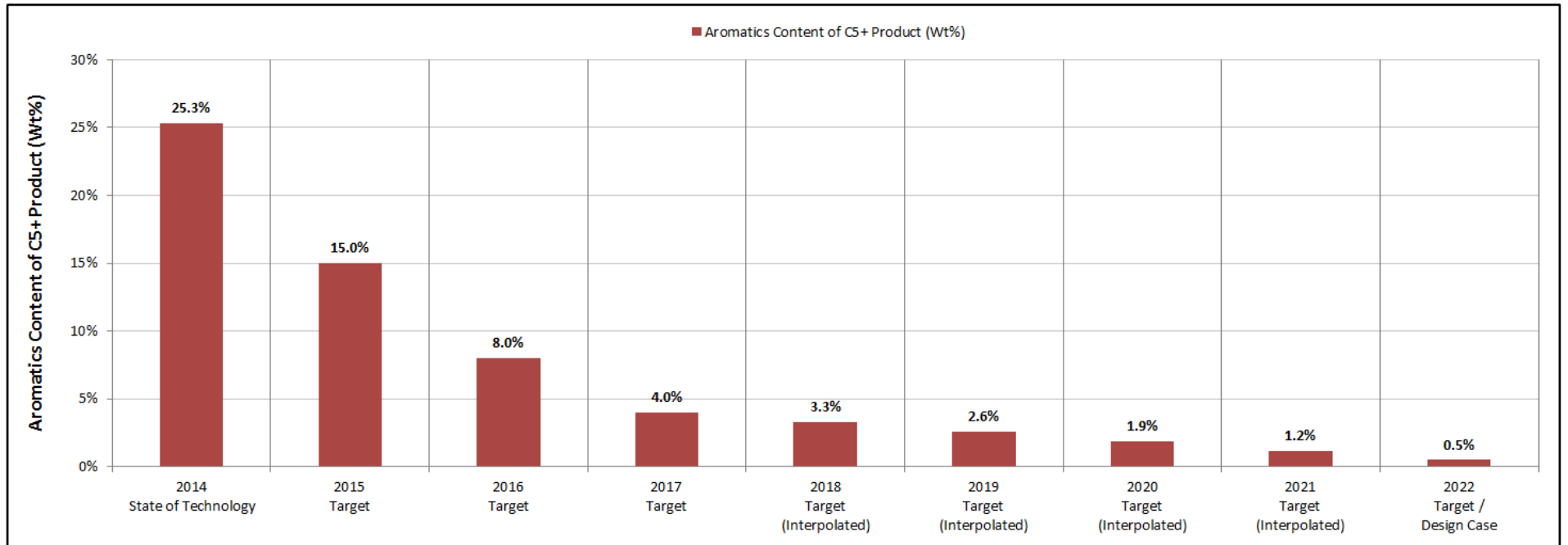
Conversion Cost Breakdown (\$ / Gallon of Gasoline Equivalent)	2014 State of Technology	2015 Target	2016 Target	2017 Target	2018 Target (Interpolated)	2019 Target (Interpolated)	2020 Target (Interpolated)	2021 Target (Interpolated)	2022 Target / Design Case
Gasification	\$ 0.70	\$ 0.67	\$ 0.56	\$ 0.54	\$ 0.53	\$ 0.52	\$ 0.52	\$ 0.51	\$ 0.50
Synthesis Gas Clean-up (Reforming and Quench)	\$ 1.06	\$ 1.00	\$ 0.84	\$ 0.84	\$ 0.84	\$ 0.84	\$ 0.84	\$ 0.84	\$ 0.84
Acid Gas Removal, Methanol Synthesis and Methanol Conditioning	\$ 0.59	\$ 0.55	\$ 0.44	\$ 0.42	\$ 0.42	\$ 0.41	\$ 0.41	\$ 0.40	\$ 0.39
Hydrocarbon Synthesis	\$ 1.01	\$ 1.01	\$ 0.67	\$ 0.60	\$ 0.55	\$ 0.51	\$ 0.47	\$ 0.42	\$ 0.38
Hydrocarbon Product Separation	\$ 0.05	\$ 0.05	\$ 0.05	\$ 0.04	\$ 0.04	\$ 0.04	\$ 0.04	\$ 0.04	\$ 0.04
Balance of Plant	\$ 0.04	\$ (0.00)	\$ (0.00)	\$ (0.04)	\$ (0.04)	\$ (0.04)	\$ (0.05)	\$ (0.05)	\$ (0.05)
<b>Minimum Fuel Selling Price (MFSP)</b>	<b>\$ 3.45</b>	<b>\$ 3.27</b>	<b>\$ 2.56</b>	<b>\$ 2.40</b>	<b>\$ 2.34</b>	<b>\$ 2.28</b>	<b>\$ 2.22</b>	<b>\$ 2.16</b>	<b>\$ 2.10</b>



# Product Quality Summary (from 2.1.0.302)

## Modeled product quality trends (1 of 3)

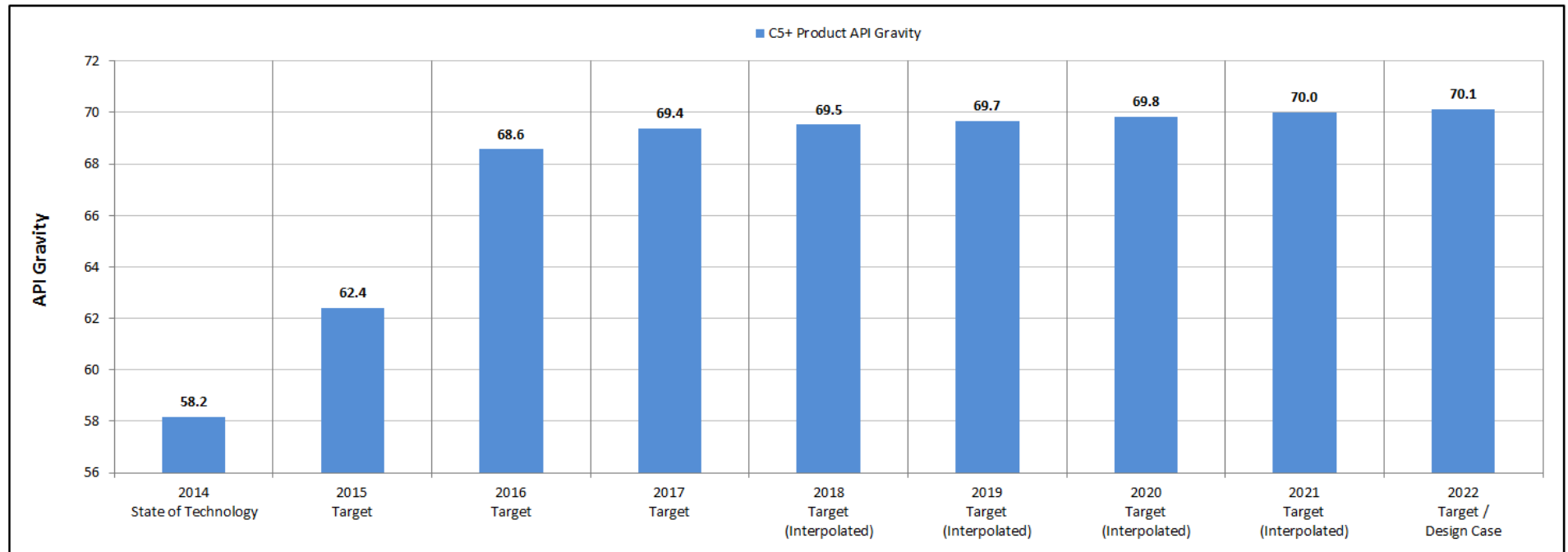
Product Quality Trends	2014 State of Technology	2015 Target	2016 Target	2017 Target	2018 Target (Interpolated)	2019 Target (Interpolated)	2020 Target (Interpolated)	2021 Target (Interpolated)	2022 Target / Design Case
Aromatics Content of C5+ Product (Wt%)	25.3%	15.0%	8.0%	4.0%	3.3%	2.6%	1.9%	1.2%	0.5%
C5+ Product Specific Gravity	0.75	0.73	0.71	0.70	0.70	0.70	0.70	0.70	0.70
C5+ Product API Gravity	58.17	62.41	68.57	69.37	69.52	69.68	69.83	69.98	70.14
Mixed C4 Product (Wt% Total Products)	27.2%	27.4%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
C5+ Aromatics (Wt% Total Products)	18.5%	10.9%	8.0%	4.0%	3.3%	2.6%	1.9%	1.2%	0.5%
C5+ Non-Aromatics (Wt% Total Products)	54.4%	61.7%	92.0%	96.0%	96.7%	97.4%	98.1%	98.8%	99.5%



# Product Quality Summary (from 2.1.0.302)

## Modeled product quality trends (2 of 3)

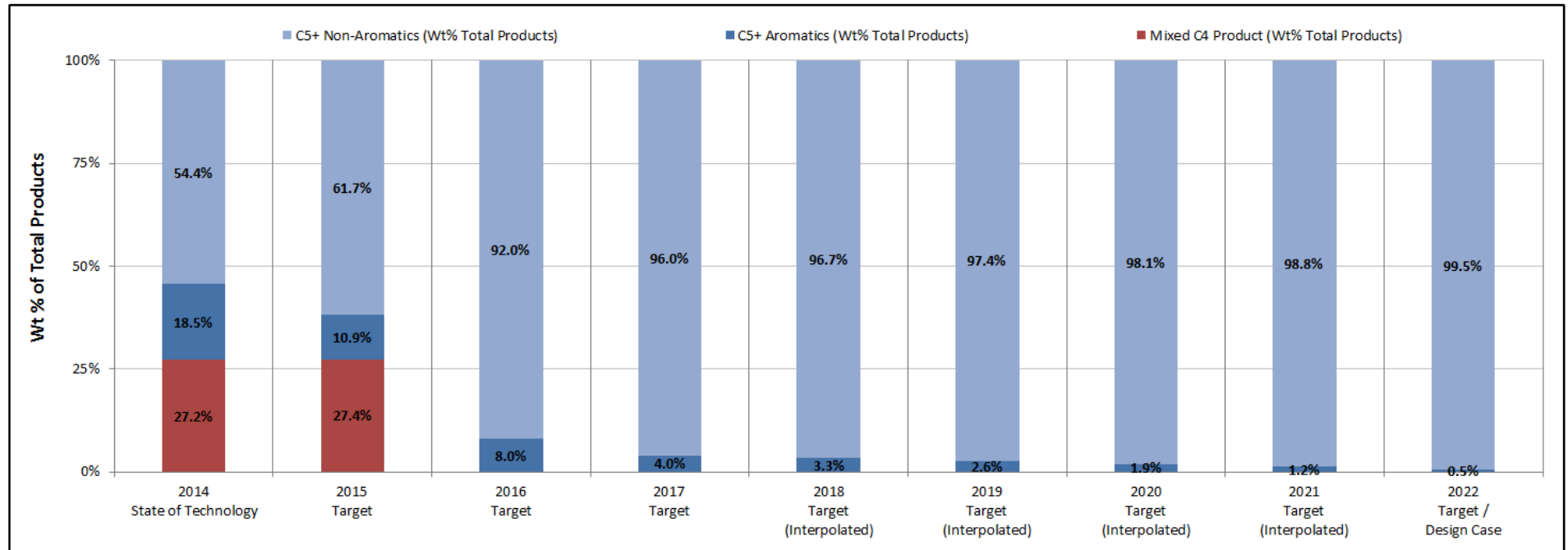
Product Quality Trends	2014 State of Technology	2015 Target	2016 Target	2017 Target	2018 Target (Interpolated)	2019 Target (Interpolated)	2020 Target (Interpolated)	2021 Target (Interpolated)	2022 Target / Design Case
Aromatics Content of C5+ Product (Wt%)	25.3%	15.0%	8.0%	4.0%	3.3%	2.6%	1.9%	1.2%	0.5%
C5+ Product Specific Gravity	0.75	0.73	0.71	0.70	0.70	0.70	0.70	0.70	0.70
C5+ Product API Gravity	58.17	62.41	68.57	69.37	69.52	69.68	69.83	69.98	70.14
Mixed C4 Product (Wt% Total Products)	27.2%	27.4%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
C5+ Aromatics (Wt% Total Products)	18.5%	10.9%	8.0%	4.0%	3.3%	2.6%	1.9%	1.2%	0.5%
C5+ Non-Aromatics (Wt% Total Products)	54.4%	61.7%	92.0%	96.0%	96.7%	97.4%	98.1%	98.8%	99.5%



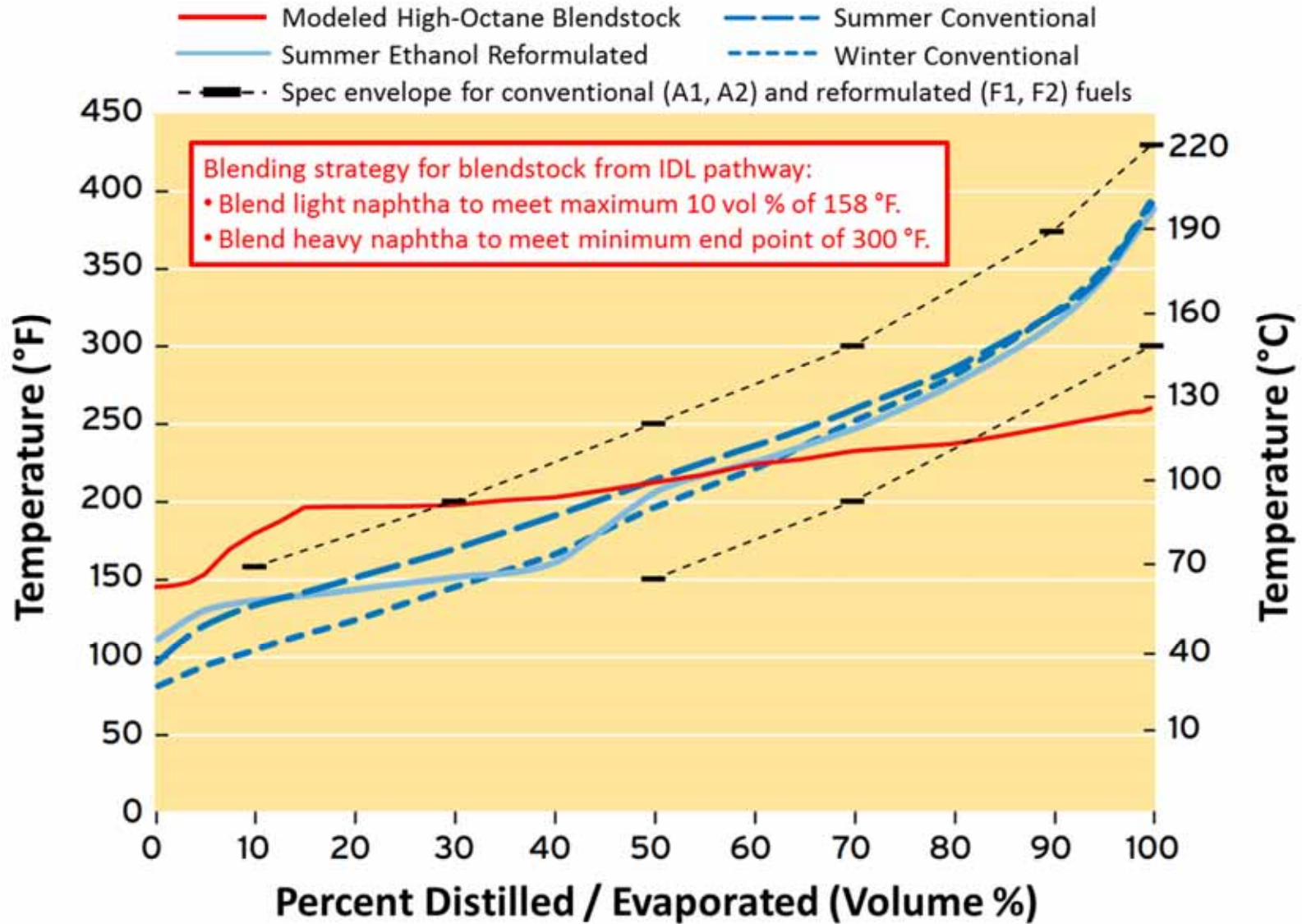
# Product Quality Summary (from 2.1.0.302)

## Modeled product quality trends (3 of 3)

Product Quality Trends	2014 State of Technology	2015 Target	2016 Target	2017 Target	2018 Target (Interpolated)	2019 Target (Interpolated)	2020 Target (Interpolated)	2021 Target (Interpolated)	2022 Target / Design Case
Aromatics Content of C5+ Product (Wt%)	25.3%	15.0%	8.0%	4.0%	3.3%	2.6%	1.9%	1.2%	0.5%
C5+ Product Specific Gravity	0.75	0.73	0.71	0.70	0.70	0.70	0.70	0.70	0.70
C5+ Product API Gravity	58.17	62.41	68.57	69.37	69.52	69.68	69.83	69.98	70.14
Mixed C4 Product (Wt% Total Products)	27.2%	27.4%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
C5+ Aromatics (Wt% Total Products)	18.5%	10.9%	8.0%	4.0%	3.3%	2.6%	1.9%	1.2%	0.5%
C5+ Non-Aromatics (Wt% Total Products)	54.4%	61.7%	92.0%	96.0%	96.7%	97.4%	98.1%	98.8%	99.5%

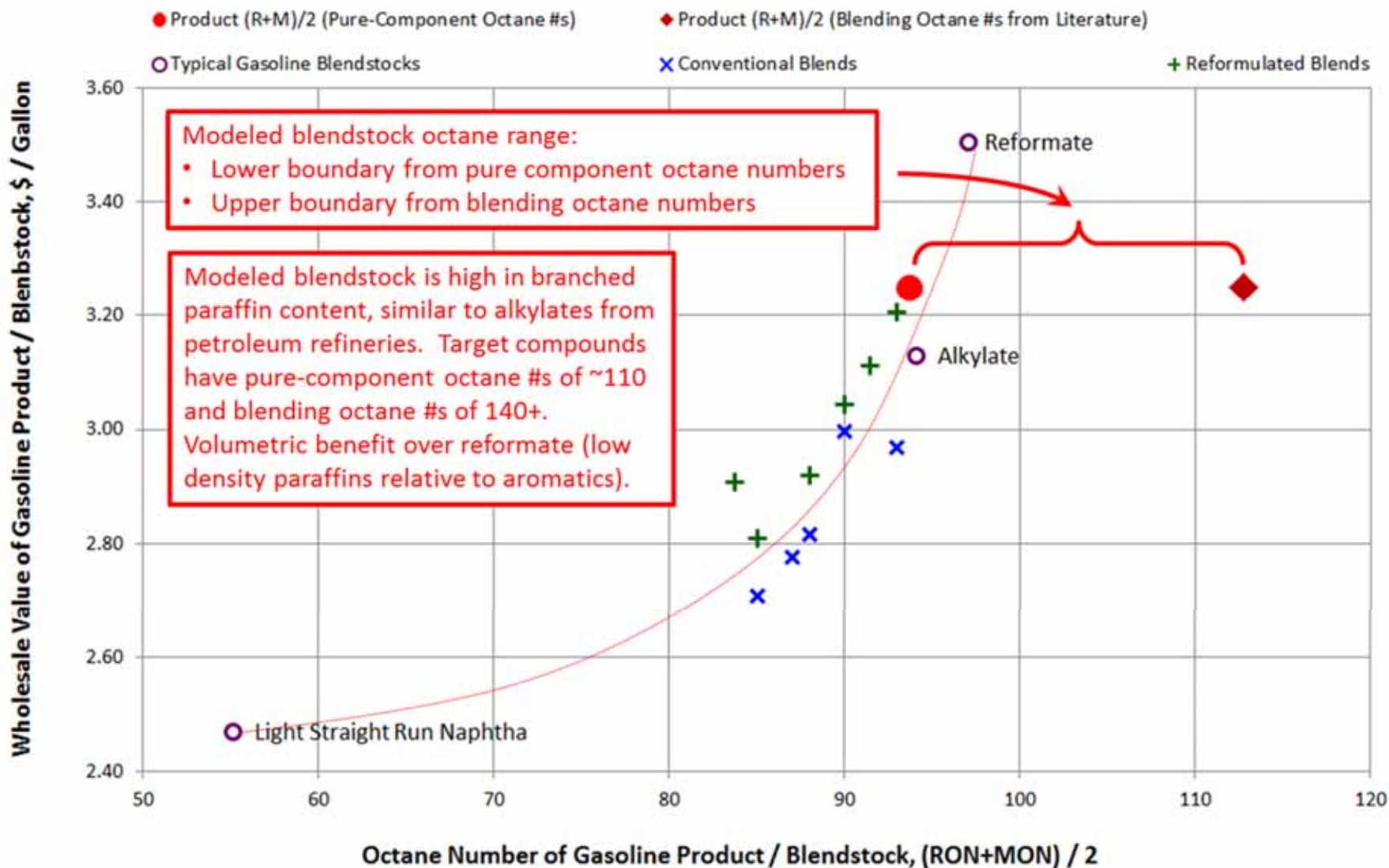


# Product Blending Potential (from 2.1.0.302)



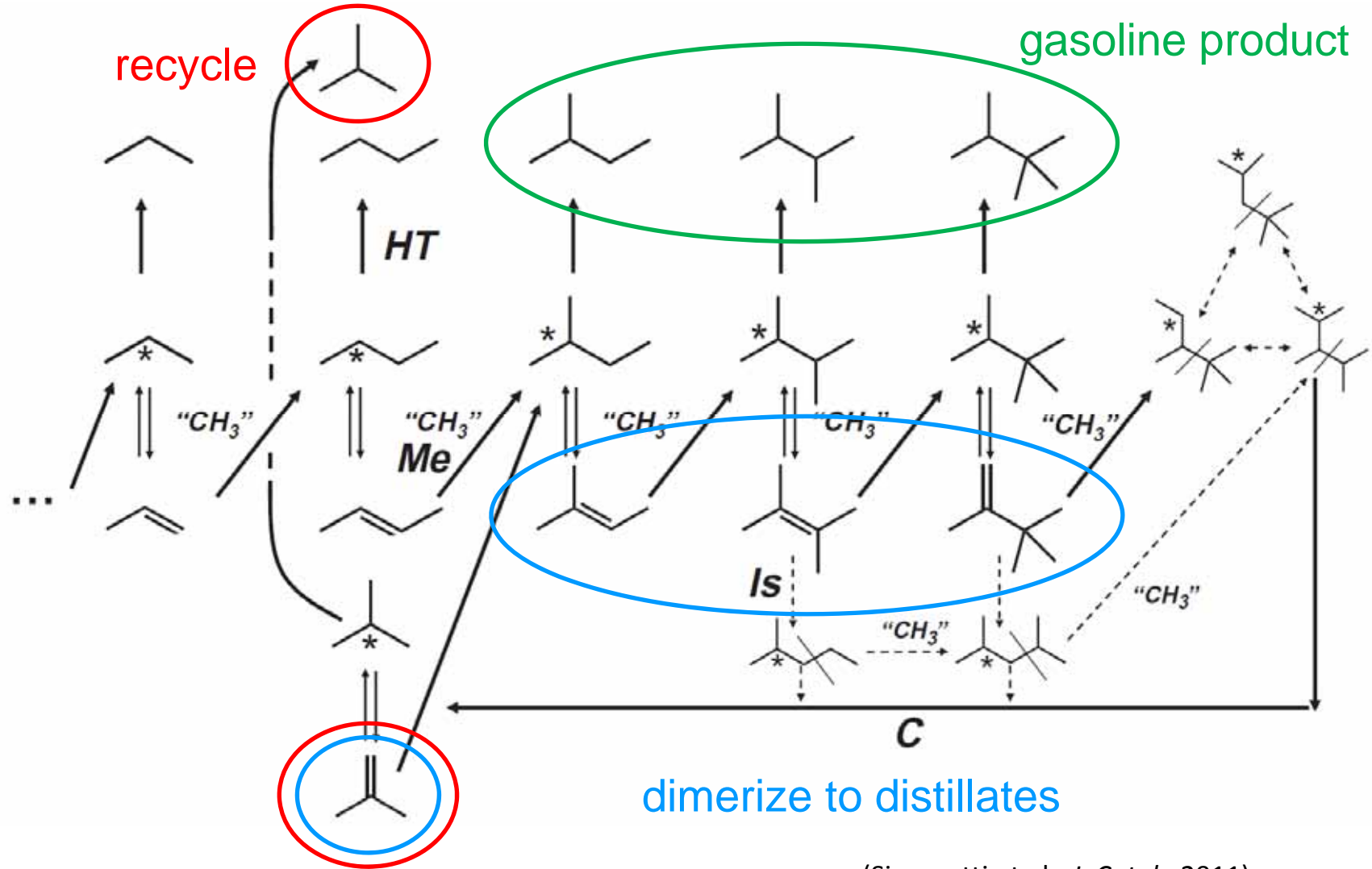
Sources: (1) Colonial Pipeline Company Product Codes and Specifications, (2) Chevron Motor Gasolines Technical Review

# Product Blending Potential (from 2.1.0.302)



Sources: (1) May 2014 Spot Prices from EIA, (2) Platts Oilgram Price Report - July 11, 2013, (3) Modern Petroleum Technology; 5th Edition Part II; Edited by G.D Hobson, Wiley 1984.

# Mechanism of HC formation from DME on SOT material



(Simonetti et al., *J. Catal.*, 2011)

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# Additional Required Slides for Peer Evaluation



# Responses to Previous Reviewers' Comments

**Comment – On project approach:** “The goal of producing mixed alcohols rather than ethanol is questionable.”

**Response –** We suspect that our discussion on the production of mixed alcohols versus ethanol may not have been clear. The project objective in FY11/12 was to make ethanol and ethanol only, and with a thermochemical process other byproducts (like alcohols and other oxygenates) are produced regardless of conversion technology. The TEA and design were still focused on separating ethanol from a mixed alcohol stream. However, we wanted to highlight the potential upside of NOT separating the ethanol as well as the challenges in doing so, mostly for those interested in using our data for ongoing work or commercialization.

**Comment – On technical progress:** “Efforts made, if any to minimize or eliminate unwanted hydrocarbons (by modifying the sulfide catalyst), such as aldehydes, were not discussed.”

**Response –** It was perhaps not clear enough in the presentation that we made efforts (and progress) in reducing hydrocarbon selectivity on the sulfide and RhMn catalysts. While not in the slides, we recall the discussion with reviewers on hydrocarbons and aldehydes and our explanation was that the aldehydes are necessary reaction intermediates at equilibrium with their corresponding alcohols and cannot be eliminated. The hydrocarbons are an unfortunate product but the pathway to making alcohols renders reaction intermediates susceptible to hydrogenation to form hydrocarbons. Thus, a different catalyst (unknown to us) would be required to address these issues, and we're confident that we're not the only ones who have looked for such a catalyst!

**Comment – On technical progress:** “Rh catalyst makes significant number of byproducts; downstream separations likely to be very expensive. MoS catalyst may be better, but performance extrapolated from P(CO) 400 psi to 1000 psi. Seems odd that critical test point could not be attained. A key aspect of the program is benchmarking against commercial alternatives.”

**Response –** As discussed in the presentation, the so-called critical test point could not be met due to process limitations from the gasifier/reformer. We did show that we could cover this critical test point in the bench reactors and provided the data. For the Rh materials, as with the sulfide materials, we agree that downstream separations are not simple. It is probably not yet appropriate to discount the Rh process route without performing separation studies, however, which was not in the scope of this project.

# Responses to Previous Reviewers' Comments

**Comment – On technical progress:** “Questionable components to this work include extrapolation of powdered catalyst performance to pelletized catalyst performance, and the presence of esters and other oxygenates in the product.”

**Response –** We disagree with the comment that we extrapolated powdered catalyst performance to pelletized catalyst performance. We measured (and showed) data for both. Byproducts are inevitable with these catalyst technologies and shouldn't be regarded as a negative for this project. Indeed, these are very minor components and you'll find in the literature that many researchers don't look for (or quantify and report) their presence and concentrations. Since this technology is moving toward commercialization, we feel there is an obligation to provide the research and industrial communities with the best facts we can.

**Comment – On critical success factors:** “Avoiding the formation of esters and aldehydes and methods to deal with dimethyl sulfur compounds were not addressed. Despite progress, a concern is that other programs (like Celenase) may have eclipsed these results. Product has many azeotropes, can't distill off and get a good ethanol product if you have to remove the impurities. Product would be a mixed stream that would have to be tested in car engines to determine suitability as a fuel. I wish they had done some of that testing.”

**Response –** Please see our response in the Technical Progress, Accomplishments, and Plans section on esters and aldehydes. We do not believe that a process that makes ethanol directly from syngas can be free of byproduct pathways. Because we were not in competition with or working with Celenase, we are OK with the prospect of their technology eclipsing ours. Indeed it would probably be inappropriate for BeTO to duplicate this technology and we've simply provided other options with associated pros and cons. It is true that we found many azeotropes and we hope that this can be regarded as beneficial information as it was not in the original scope of the project but added significant insight. Engine testing was not in the scope of the project.

**Comment – On technology transfer and collaboration:** “The project has produced several report and publications of interest, however, there has been little industrial collaboration apart from Dow. More collaboration should be sought, so that this work can continue in the industrial sector.”

**Response –** The information we've generated is now or will become public through technical reports, manuscripts, and milestone reports. We would certainly welcome more industrial collaboration with other catalyst developers. It has been our experience, however, that for this type of work, industry prefers to keep their technology development in-house. We will continue to engage industry.

# Responses to Previous Reviewers' Comments

**Comment – On overall impressions:** “The project performers seem to have a good handle on these tradeoffs, and have addressed many of these technical challenges, however, industry has shown little interest in these catalysts to date. Part of the issue may be related to the synthesis focus on mixed alcohols rather than ethanol.” and “Although a well thought out plan to develop EtOH synthesis catalysts, it does not appear that any effort was made to revisit procedures for catalyst synthesis to prevent the production of undesirable oxygenates such as esters and aldehydes. Attention was not paid to the fate of sulfur addition to the MoS catalyst during EtOH synthesis. The unwanted oxygenates and the dimethyl sulfur contaminant in the raw product raises questions about its acceptance as transportation fuel.”

**Response –** Please see our response in the Technical Progress, Accomplishments, and Plans section on esters and aldehydes. It was not mentioned in the presentation (due to time constraints) but was discussed in the Q&A: we have rigorously evaluated the fate of added sulfur to the catalyst and have found that H<sub>2</sub>S is converted (net) to organic sulfides like dimethyl sulfide. We will also defend ourselves here with respect to addressing fuel specifications and catalyst criteria from the start. This was done, and as we explained in our presentation, a rigorous effort was made at project outset to identify catalysts that could meet our fuel composition and cost targets. At that time the amount and identity of reaction byproducts was largely unknown and by the time these species were rigorously evaluated, concrete decisions had to be made about which catalyst systems would be scaled and demonstrated. We also explained the breakdown of financial resources for MoS and rhodium catalysts and noted that this provided a research platform in which late-stage evaluation and development could be carried out (MoS) and up and coming research could be maintained (Rh). Finally, we disagree that industry is uninterested in this technology, As we stated in the Q&A session, we are aware of at least three major companies (Dow, Haldor Topsoe, Albemarle) who are actively developing these catalysts. It is true that no one is producing mixed alcohols commercially, but we're certain that these companies have evaluated the market and are either a) waiting for market conditions to change to launch the technology or b) addressing issues with the technology that they feel are addressable and a good use of their R&D funds. Otherwise, these companies would not be spending millions to develop the materials.

**Comment – On project relevance:** “The performance improvements in both catalysts are impressive, and contributed significantly in meeting the cost target of \$2.05 gge for mixed alcohols. However, the project would have been more relevant if ethanol, rather than mixed alcohols, were the primary production goal.”

**Response –** As mentioned in our responses to the comments on our Project Approach, ethanol was the primary production goal. We stated in the presentation that we would have optimized our system differently if mixed alcohols had been the target, and we provided justification for why mixed alcohols may be more economically viable than fuel grade ethanol, but the focus of this project was always ethanol production.

# Publications and Patents (FY13 to Present)

- Hensley, JE; Lovestead, TM; Christensen, E; Dutta, A; Bruno, TJ; McCormick, R, **2013**, “Compositional Analysis and Advanced Distillation Curve for Mixed Alcohols Produced Via Syngas on a K-CoMoS<sub>x</sub> Catalyst” *Energy & Fuels*, 27, p. 3246.
- Hensley, J.E.; Pylypenko, S.; Ruddy, D.A., **2014** “Deactivation and stability of K-CoMoS<sub>x</sub> mixed alcohol synthesis catalysts” *J. Catal.*, 309, p. 199.
- Bain, R.L.; Magrini-Bair, K.A.; Hensley, J.E.; Jablonski, W.S.; Smith, K.M; Gaston, K.R., & Yung, M.M., **2014** “Pilot Scale Production of Mixed Alcohol from Wood” *IECR*, 53, p. 2204.
- Dutta, A.; Hensley, J.E.; Bain, R.L.; Magrini, K.; Tan, E.C.D.; Apanel, G.; Barton, D.; Groenendijk, P.; Ferrari, D.; Jablonski, W.S.; & Carpenter, D., **2014** “Technoeconomic Analysis for the Production of Mixed Alcohols via Indirect Gasification of Biomass Based on Demonstration Experiments” *IECR*, 53, p. 12149.
- Zhang, G.; Hu, B.; Das, U.; Kim, H.; Schaidle, J. A.; Ruddy, D. A.; Kraft, S.; Hensley, J. E.; Curtiss, L.; Stair, P.; Miller, J.; Hock, A., **2015** “The role of Ga ion reducibility on silica and H-BEA zeolite for propane dehydrogenation” *ACS Catal.*, in revision.
- Behl, M.; Schaidle, J.A.; Christensen, E.; Hensley, J.E. **2015** “Synthetic distillate-range hydrocarbons via catalytic dimerization of branched olefins derived from renewable bio-Dimethyl Ether” *Energy & Fuels*, submitted.
- Schaidle, J.; Ruddy, D.; Habas, S.; Pan, M.; Zhang, G.; Miller, J.; Hensley, J. **2015** “Conversion of Dimethyl Ether to 2,2,3-trimethylbutane over a Cu/BEA Catalyst: Productivity Improvements through Hydrogen Incorporation” *ACS Catal*, DOI: 10.1021/cs501876w.
  
- Provisional Patent NREL docket PROV/14-49: “HIGHLY ACTIVE AND SELECTIVE METAL-MODIFIED ZEOLITE CATALYSTS FOR THE PRODUCTION OF LIQUID FUELS”

# Presentations (FY13 to Present)

- Menart, M; Hensley JE; Costelow, K, “Thermal Decomposition of Bulk K-CoMoS<sub>x</sub> Mixed Alcohol Catalyst Precursors.” Presented by JE Hensley at *American Institute of Chemical Engineers annual meeting*, **October 28, 2012**, Pittsburgh, PA.
- Hensley, JE, “Synthesis, Use, Lifetime, and Deactivation of Sulfide Catalysts for Renewable Cellulosic Ethanol.” Presented by JE Hensley at *Colorado School of Mines, Chemistry Department Invited Speaker Series*, **January 18, 2013**, Golden, CO.
- Hensley, JE; Ruddy, DR; Schaidle, JA; Ferrell, JR; Thibodeaux, J, “Stability and Lifetime of K-CoMoS<sub>x</sub> Mixed Alcohol Catalysts.” Presented by JE Hensley at *American Chemical Society annual spring meeting*, **April 7, 2013**, New Orleans, LA.
- Ferrell, JR; Hensley, JE, “Mixed Alcohol Synthesis on K-CoMoS<sub>x</sub> Catalysts: Recycle Studies.” Presented by JR Ferrell at *Western States Catalysis Club annual meeting*, **April 19, 2013**, Provo UT.
- Hensley, J.E., “Fuels from biomass: catalyst considerations” *Phillips66 invited speaker series*, **July 2013**, Bartlesville, OK.
- Hensley, J.E.; Lovestead, T.; Christensen, E.; Dutta, A.; Bruno, T.; & McCormick, R, “Compositional Analysis and Advanced Distillation Curve for Mixed Alcohols Produced via Syngas.” Presented by JE Hensley at *AIChE Fall Meeting*, **November 2013**, San Francisco, CA.
- Schaidle, J.; Ruddy, D.R.; Habas, S.; Pan, M.; Hensley, J.E., “Metal-modified BEA Zeolite Catalysts for Triptane Synthesis: The Role of the Metal Sites” presented by J Schaidle at *ACS Spring Meeting*, **March 2014**, Dallas, TX.
- Hensley, J.E., “Deactivation and stability of K-CoMoS<sub>x</sub> mixed alcohol synthesis catalysts” *ACS Spring Meeting*, **March 2014**, Dallas, TX.
- J. Schaidle, D. Ruddy, S. Habas, M. Pan, G. Zhang, J. Miller, J. Hensley, “Metal-impregnated BEA Zeolite Catalysts for Triptane Synthesis: The Role of the Metal Sites” presented by J Schaidle at the *6th Federation of European Zeolite Associations Conference*, **September 9th, 2014**, Leipzig, Germany.
- Hensley, J.; Schaidle, J.; Ruddy, D.; Cheah, S.; Habas, S.; Pan, M.; Zhang, G.; Miller, J “Conversion of Dimethyl Ether to Branched Hydrocarbons over M-BEA: the Roles of the Lewis Acidic and Metallic Sites in H<sub>2</sub> Incorporation” accepted for presentation at the *24<sup>th</sup> Meeting of the North American Catalysis Society*, **June 15, 2015**, Pittsburgh, PA.
- Behl, M.; Schaidle, J.; Hensley, J. “Effect of Reaction Conditions on the Production of Synthetic Middle-Distillates via Catalytic Dimerization of Biomass-derived Olefins” accepted for presentation at the *24<sup>th</sup> Meeting of the North American Catalysis Society*, **June 15, 2015**, Pittsburgh, PA.