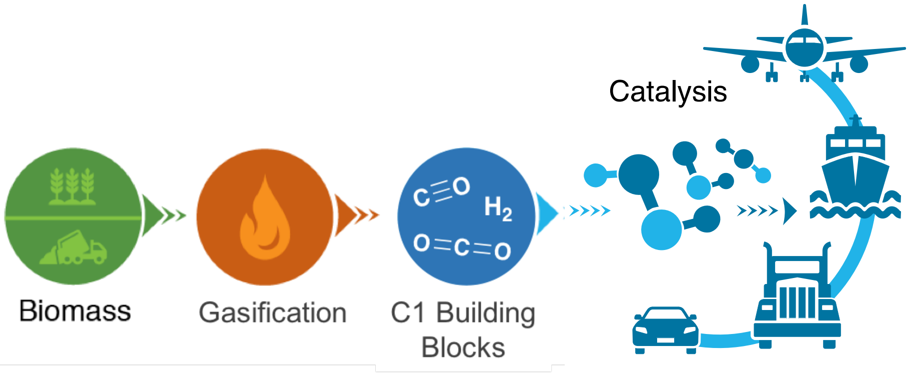
Process Intensification for Direct Conversion of Biomass-Based Syngas to High Octane Gasoline

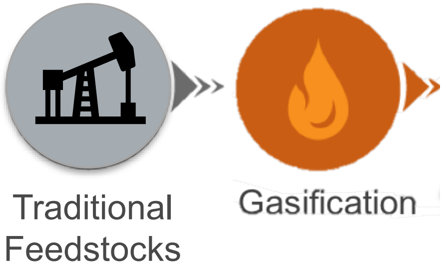
Claire Nimlos, Connor Nash, Anh To, Dan Dupuis, Daniel Ruddy*

Catalytic Carbon Transformation & Scale-up Center, National Renewable Energy Laboratory



2021 AIChE Annual Meeting
Breakthroughs in C1 to Chemicals and Processing Engineering
November 16, 2021

Traditional processes for syngas-to-fuels



E. Tan, et al., *Biofuel Bioprod. Bioref*. **2017**, *11*, 41.

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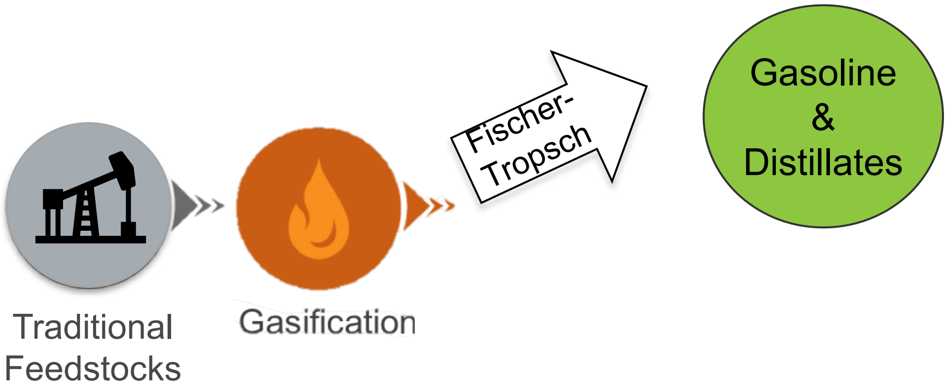

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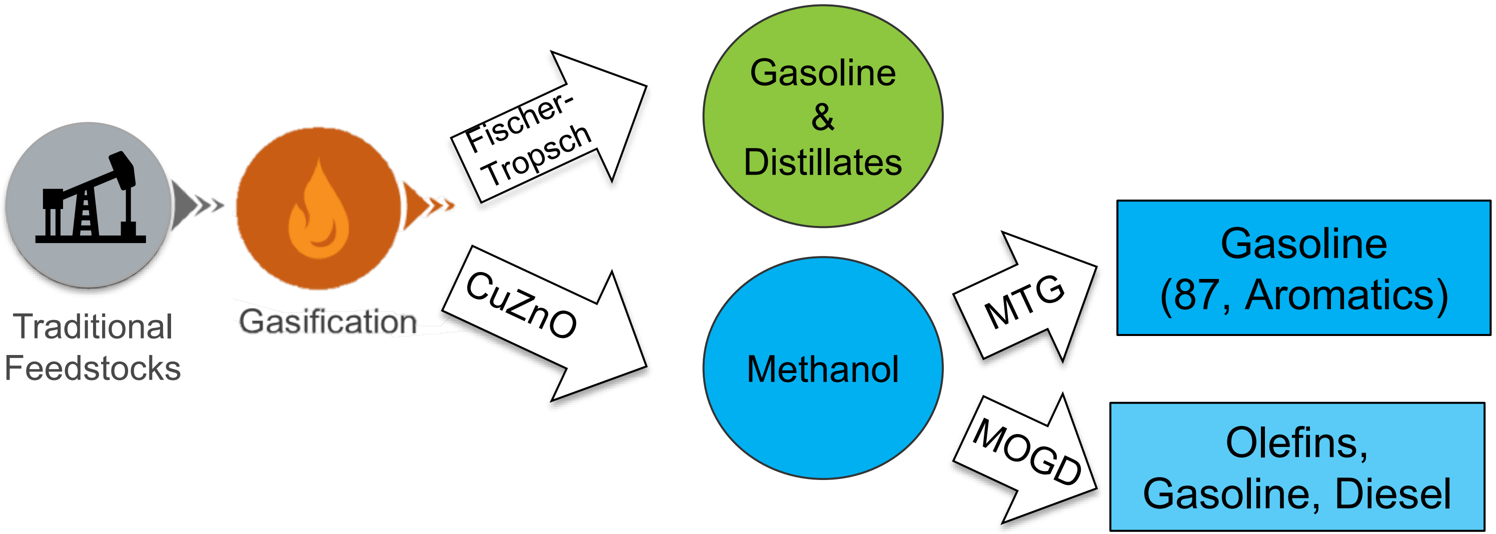

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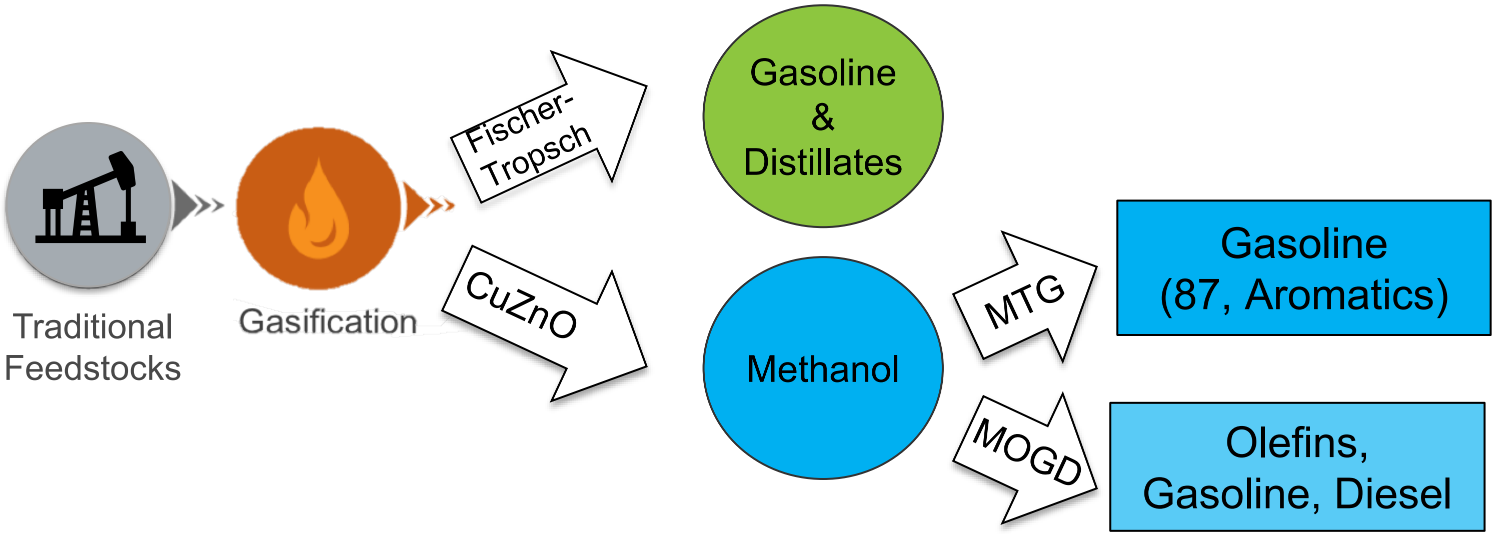
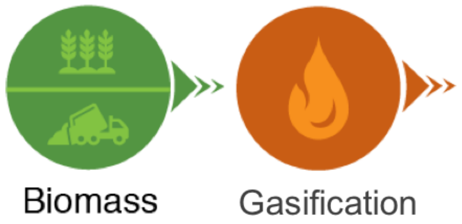


Traditional syngas to fuels have known drawbacks, with reduction in process complexity and separations while producing ***higher value*** *products necessary*

E. Tan, et al., *Biofuel Bioprod. Bioref*. **2017**, *11*, 41.

Conversion of biomass to sustainable hydrocarbon products



Fuel Product

Fuel gas

"High Octane Gasoline"

"Sustainable Aviation Fuel"

D. A. Ruddy et al. *Nat. Catal.*, **2019,** 2, 632

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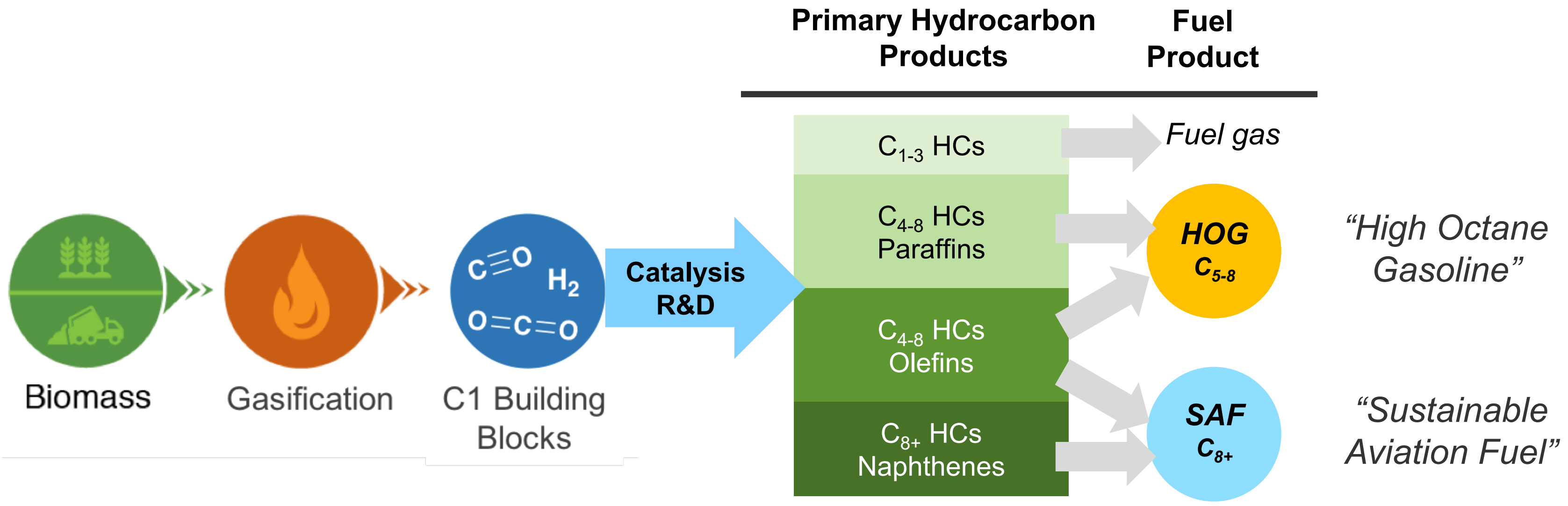

D. A. Ruddy et al. *Nat. Catal.*, **2019,** 2, 632

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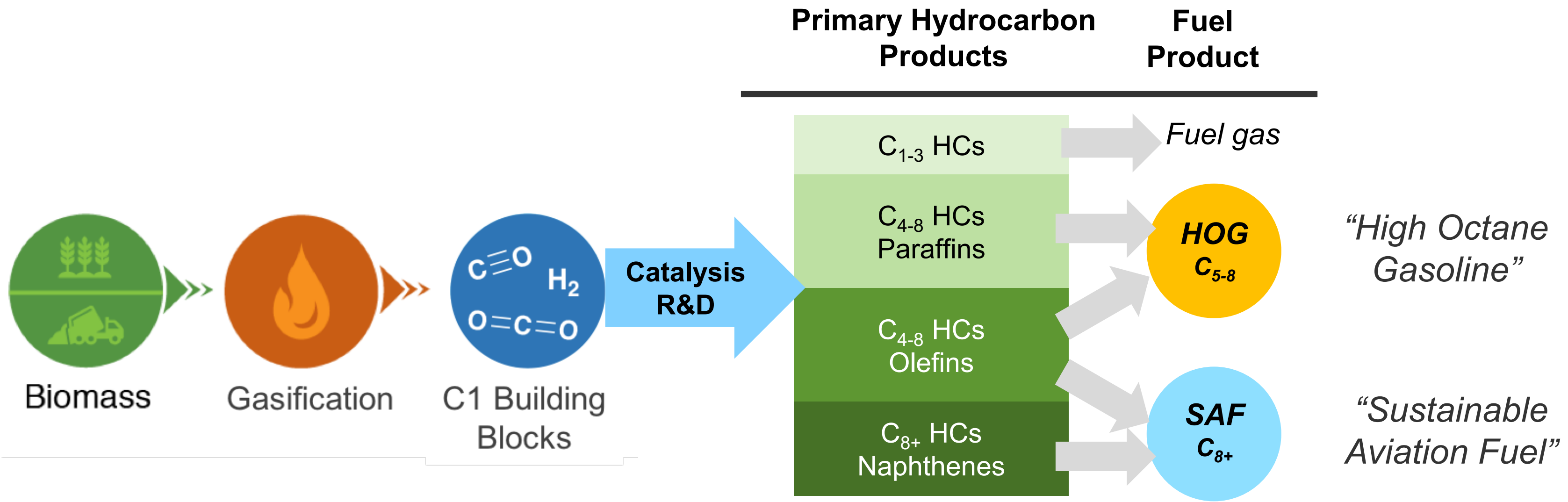

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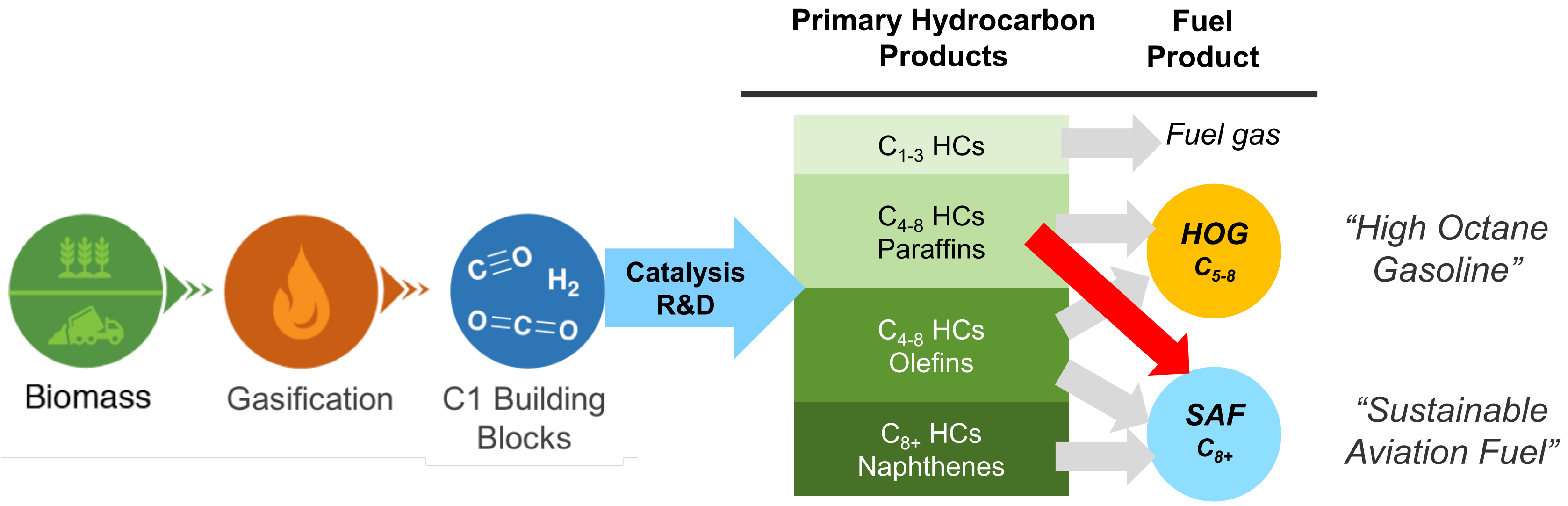
Development of a biorefinery process to convert renewable C1 intermediates into a suite of fuel products to meet market demand

Conversion of biomass to sustainable hydrocarbon products

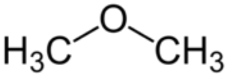


D. A. Ruddy et al. *Nat. Catal.*, **2019,** 2, 632

Development of a biorefinery process to convert renewable C1 intermediates into a suite of fuel products to meet market demand

DME homologation on acid zeolites

Dimethyl Ether (DME)



or Methanol

CH_3OH

Ahn et al., *Angew. Chem.*, **2009**, 48, 3814

Simonetti et al., *J. Catal.*, **2011**, 277, 173

Simonetti et al., *Chem. Cat. Chem*, **2011**, 3, 704

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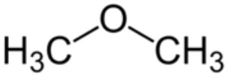
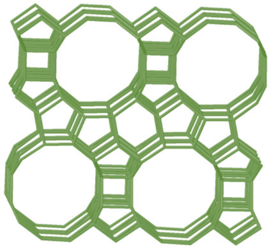


or Methanol

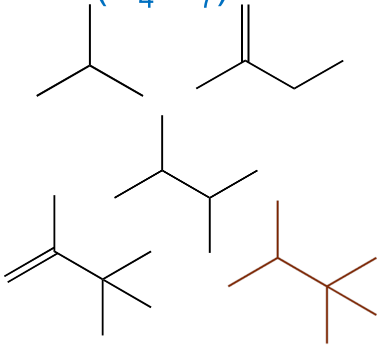
CH_3OH

175-225 °C,
100-1000 kPa

Large-pore acidic zeolites



Branched hydrocarbons (C_4-C_7)



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DME homologation on acid zeolites …

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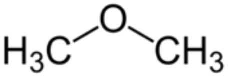

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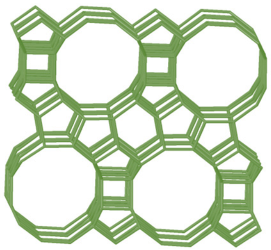

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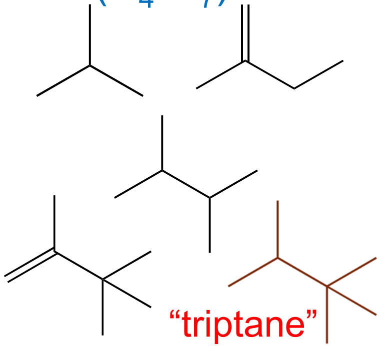
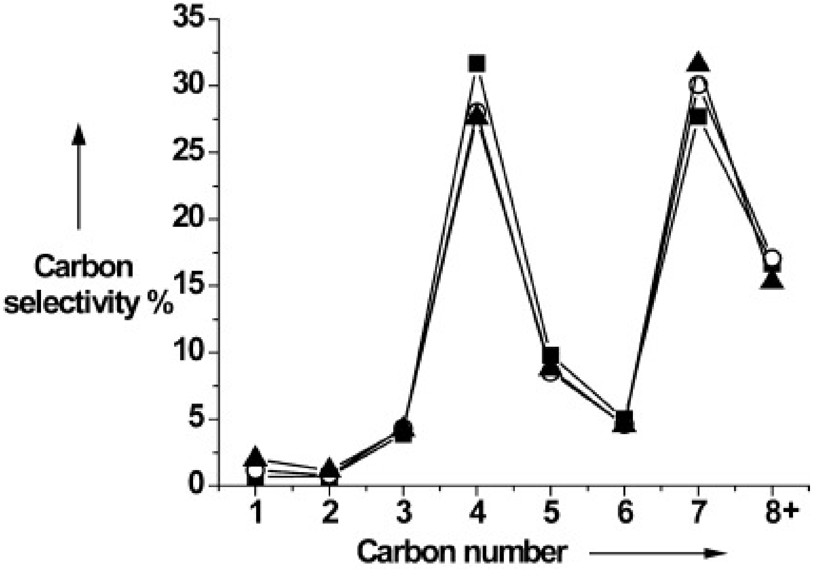


"triptane"
C_7H_{16}



Beta zeolite higher selectivity to C_7 due to stabilization of the bulky transition state in larger cage/intersections

Ahn et al., *Angew. Chem.*, **2009**, 48, 3814
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DME homologation on acid zeolites and the limitations

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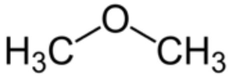

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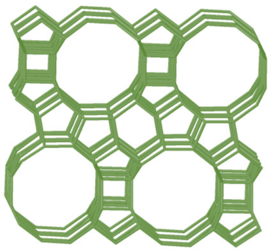
Large-pore acidic zeolites



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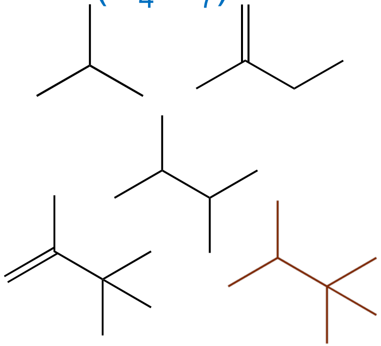

Hydrogen Deficiency

$CH_3OCH_3 \rightarrow 2\ \text{“}CH_2\text{”} + H_2O$

Need an additional 2H per alkane produced

DME homologation on acid zeolites and the limitations

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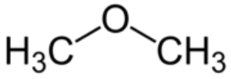

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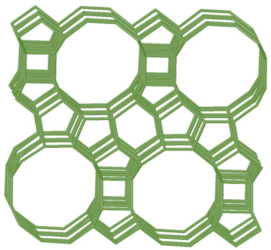

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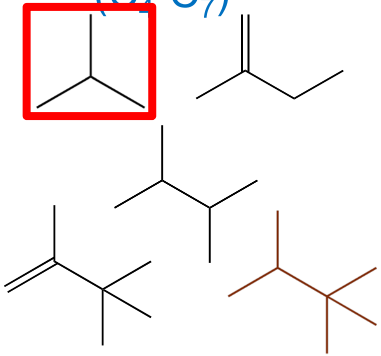
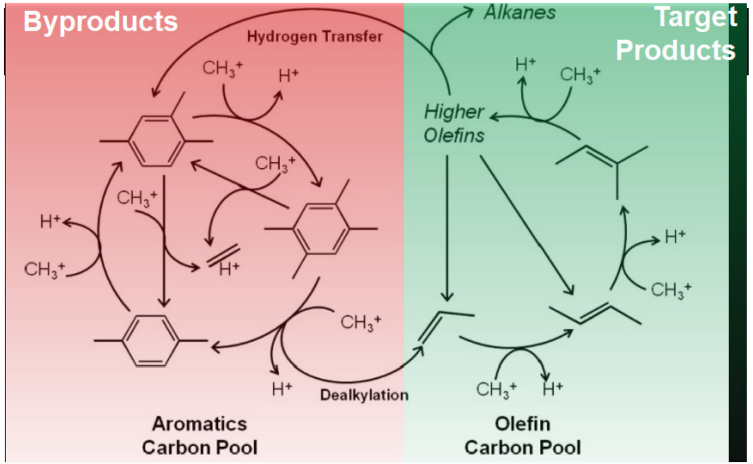
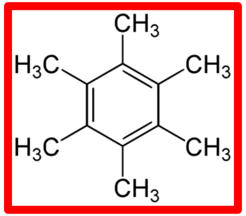


Mechanism



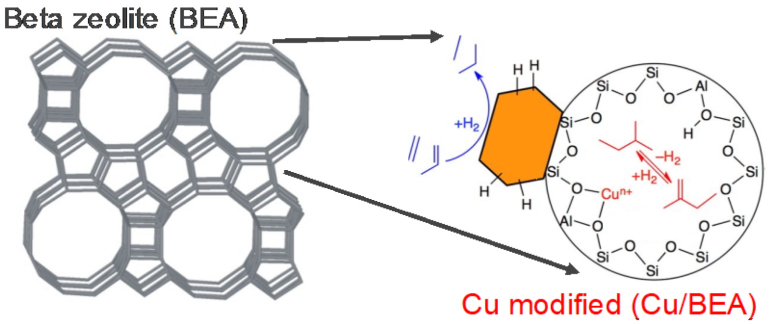
S. Ilias, A. Bhan, *ACS Catal.*, **2013** 3,18

Hydrogen Deficiency	*Yield Loss – aromatics and C_4*
$CH_3OCH_3 \rightarrow 2$ "CH_2" $+ H_2O$	$33\ CH_3OCH_3 \longrightarrow 6\ C_7H_{16} + 33\ H_2O$ **+ 2 $C_6(CH_3)_6$**
Need an additional 2H per alkane produced	H/BEA leads to formation of heavy unsaturated hydrocarbons or terminal products like isobutane



"HMB"

Cu-modified beta zeolites for DME conversion



J. A. Schaidle et al. *ACS Catal.*, **2015**, 5, 1794

US Pat # 9,803,142 B1
US Pat App 62/482,315
US Pat App 62/515,087

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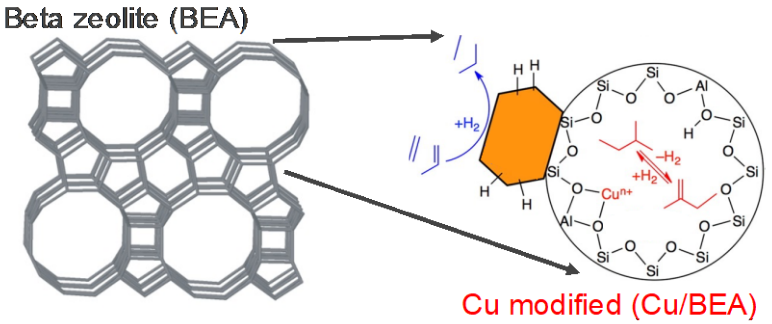

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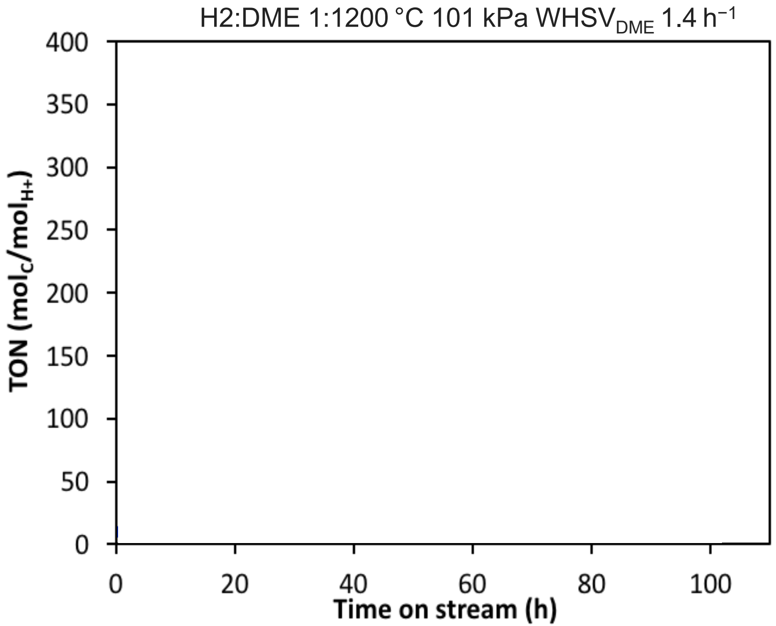
- Maintains high selectivity to branched C_4 and C_7 hydrocarbons
- High yield for HOG range products



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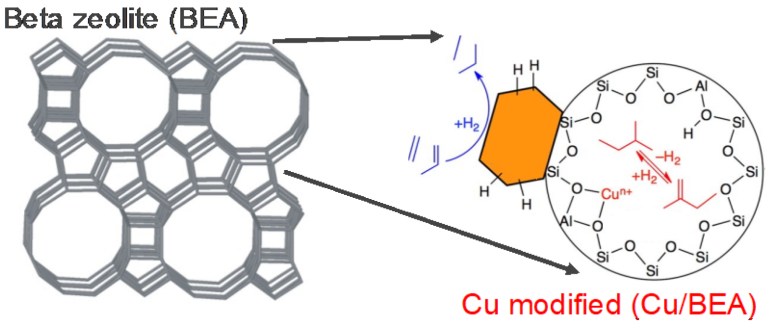

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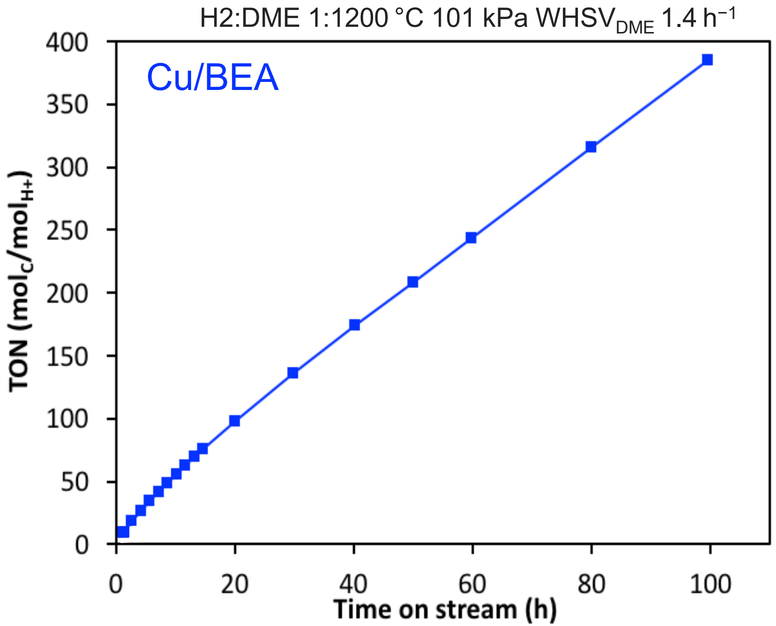

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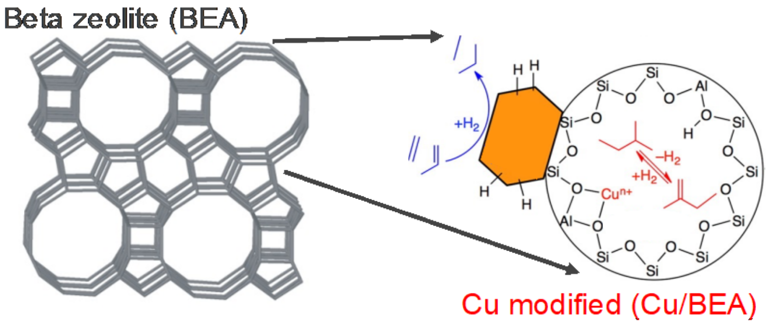

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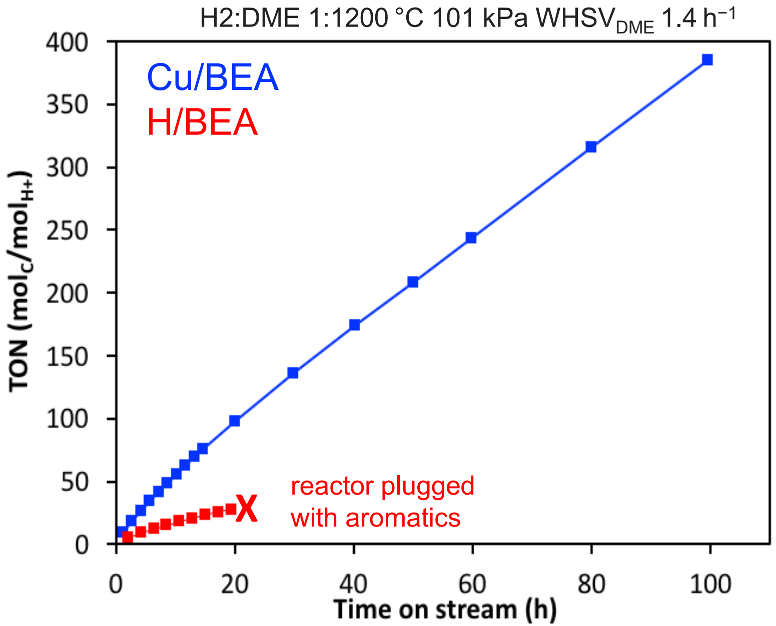

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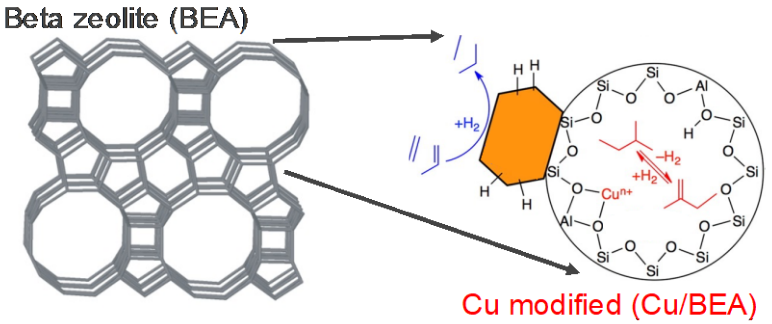

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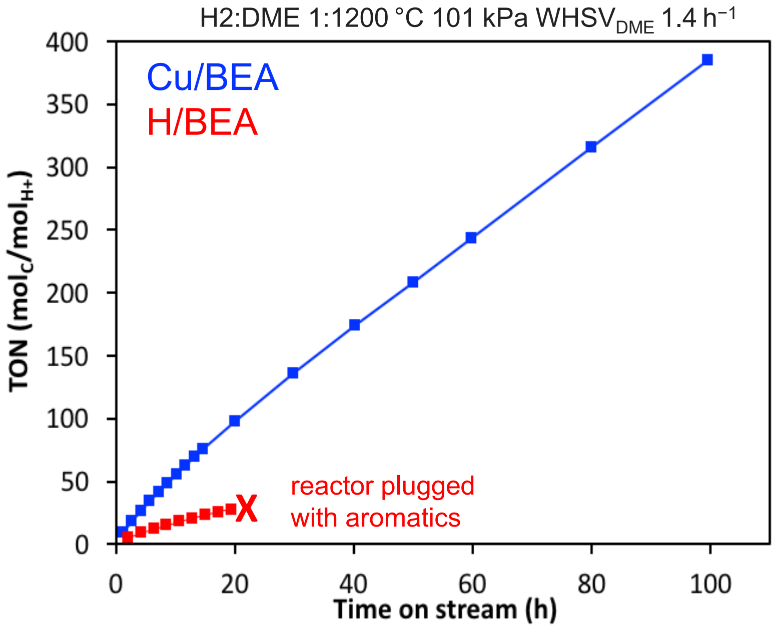

D. A. Ruddy et al. *Nat. Catal.*, **2019,** 2, 632

- Maintains high selectivity to branched C_4 and C_7 hydrocarbons
- High yield for HOG range products

Cu/BEA had improved hydrocarbon yields over H/BEA while minimizing aromatic formation and increased catalyst lifetime

US Pat # 9,803,142 B1
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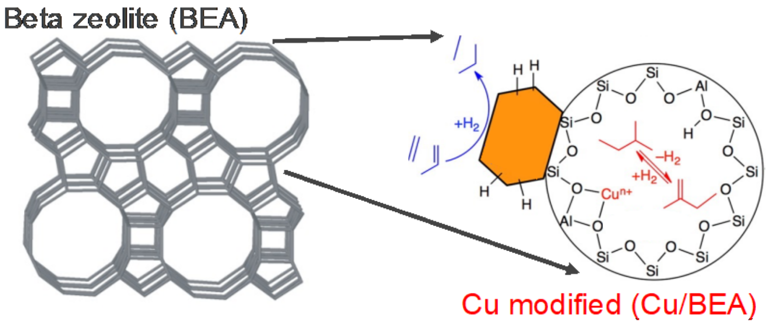
Utilizing zeolites in a single reactor for syngas conversion



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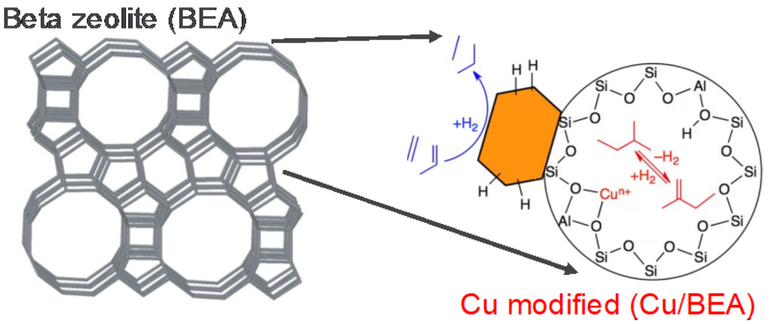

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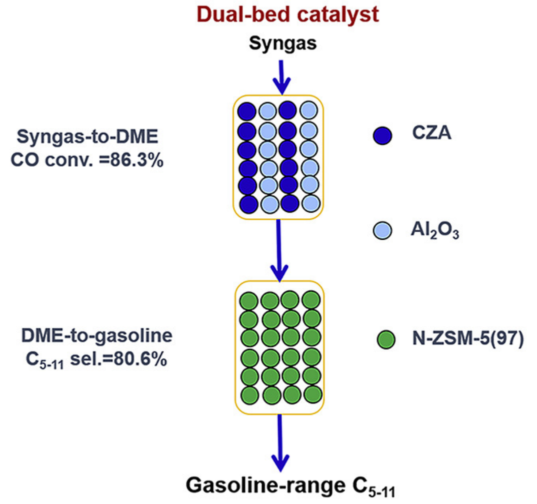
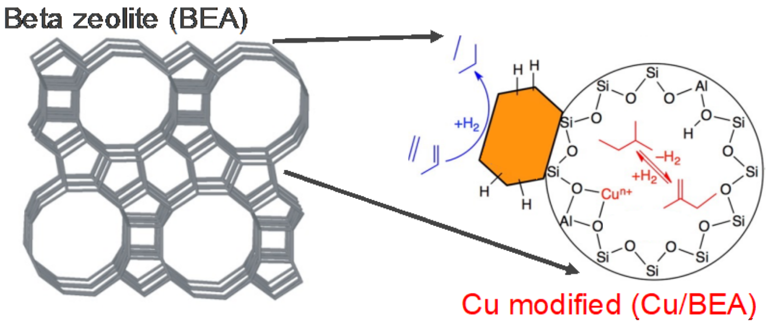


A dual-bed catalyst achieved an 80.6% gasoline selectivity at 86.3% CO conversion

Y. Ni et al. *Chem Catal.*, **2021**, 1, 383

- Nano-sized ZSM-5 downstream of commercial methanol and DME synthesis catalysts
- High selectivity to gasoline range hydrocarbon products

Conversion of syngas in a single reactor system



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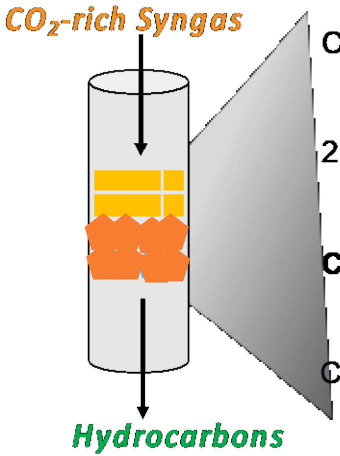

$CO + 2\,H_2 \leftrightarrow CH_3OH$
[Reaction 1; methanol synthesis]

$2\,CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$
[Reaction 2; methanol dehydration]

$CH_3OCH_3 + H_2 \rightarrow C_nH_{2n+2} + H_2O$
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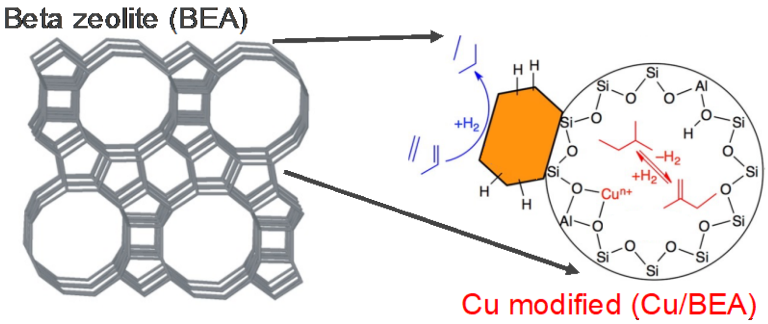

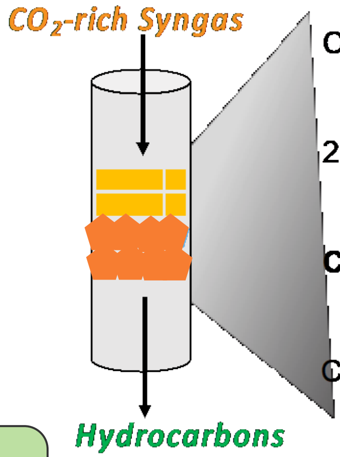

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Systematic configuration and composition changes to improve performance

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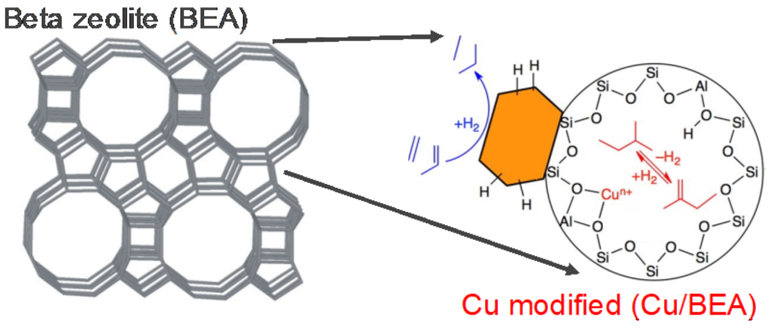

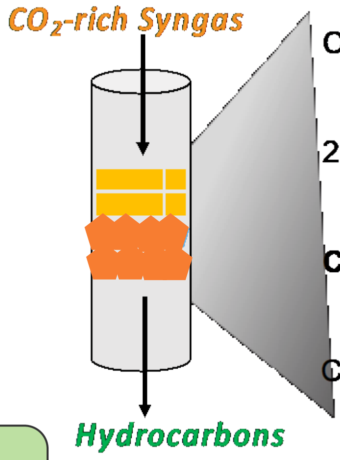

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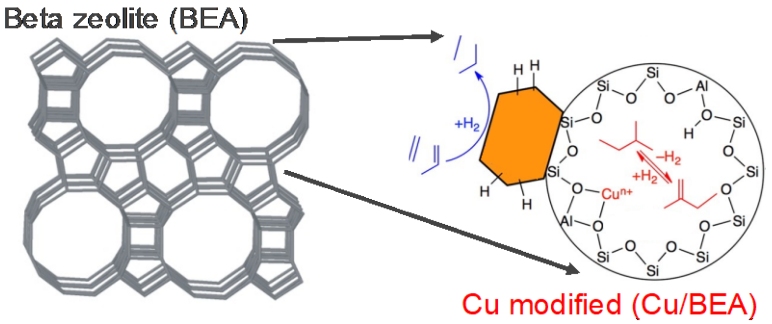

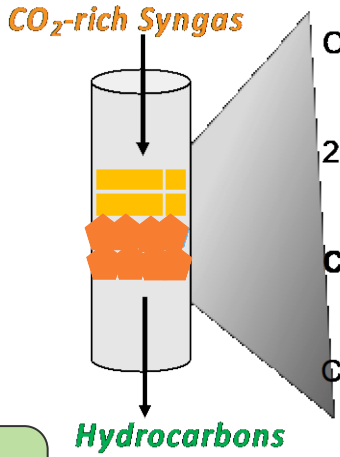

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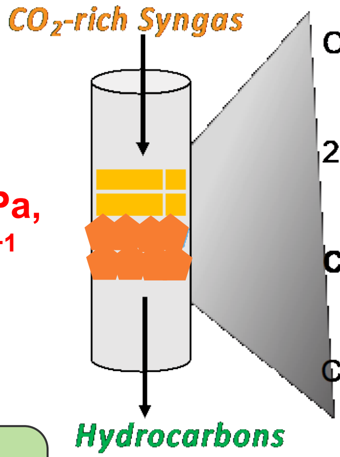
Study CO_2 rich syngas simulated feed to understand its impact on hydrocarbon yields and overall performance

Conversion of syngas in a single reactor system

220 °C, 750 kPa, $WHSV_{CO}$ 0.3 h^{-1}



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Utilize commercially available catalysts for the syngas to DME reactions

- "CZA" $Cu/ZnO/Al_2O_3$, Megamax 800, Clariant
- "A" γ-Al_2O_3, NorPro® SA6173, St. Gobain-Norpro

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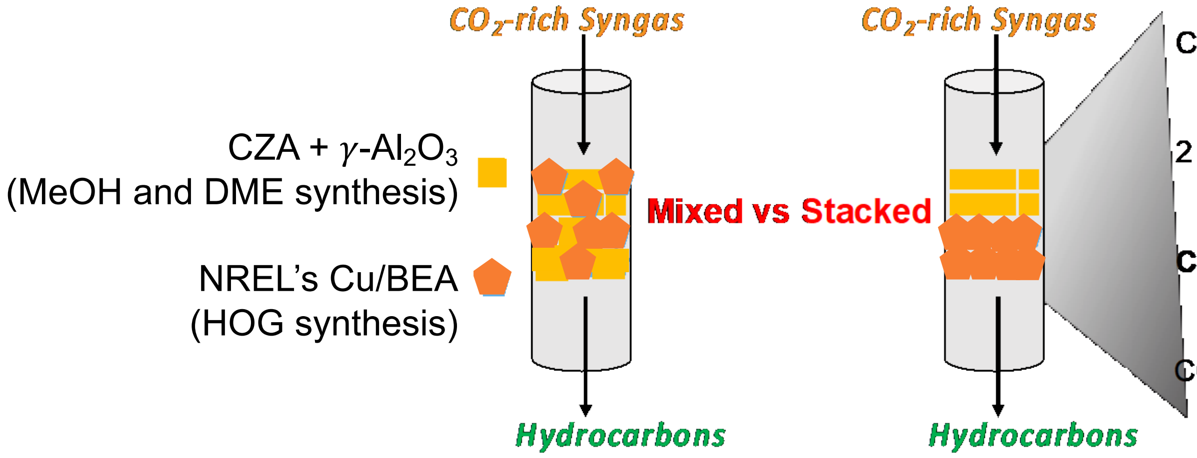

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"mixed-bed" catalyst#1+catalysts #2
"stacked-bed" top-catalyst|bottom-catalyst

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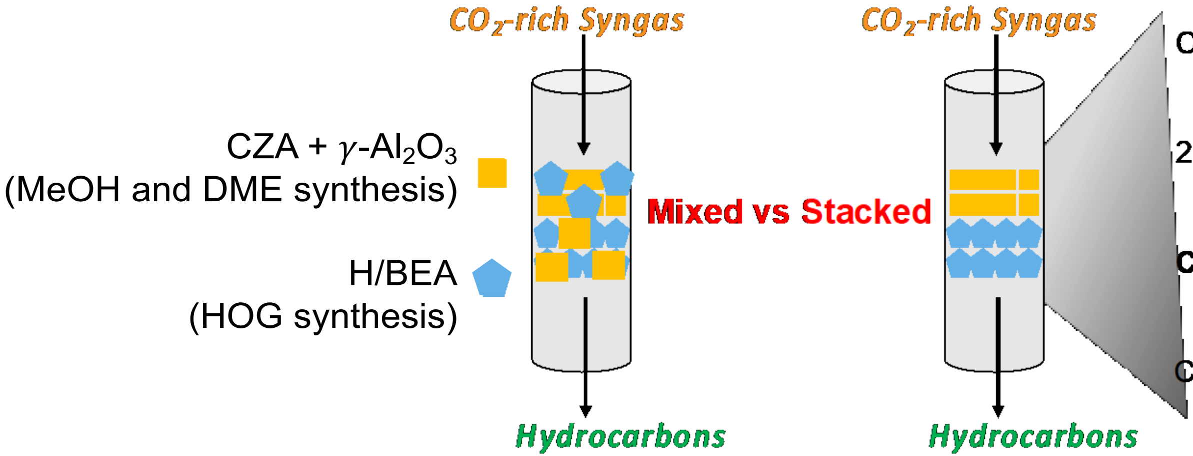
- "A" γ-Al_2O_3, NorPro® SA6173, St. Gobain-Norpro

Conversion of syngas in a single reactor system



$CO + 2\,H_2 \leftrightarrow CH_3OH$
[Reaction 1; methanol synthesis]

$2\,CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$
[Reaction 2; methanol dehydration]

$CH_3OCH_3 + H_2 \rightarrow C_nH_{2n+2} + H_2O$
[Reaction 3; HOG synthesis]

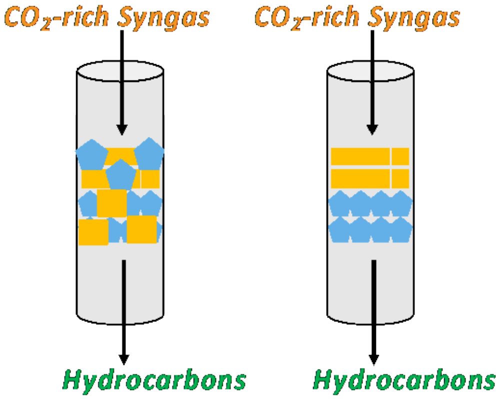
$CO + H_2O \leftrightarrow CO_2 + H_2$
[Reaction 4; water-gas shift reaction]

“mixed-bed” catalyst#1+catalysts #2
“stacked-bed” top-catalyst|bottom-catalyst

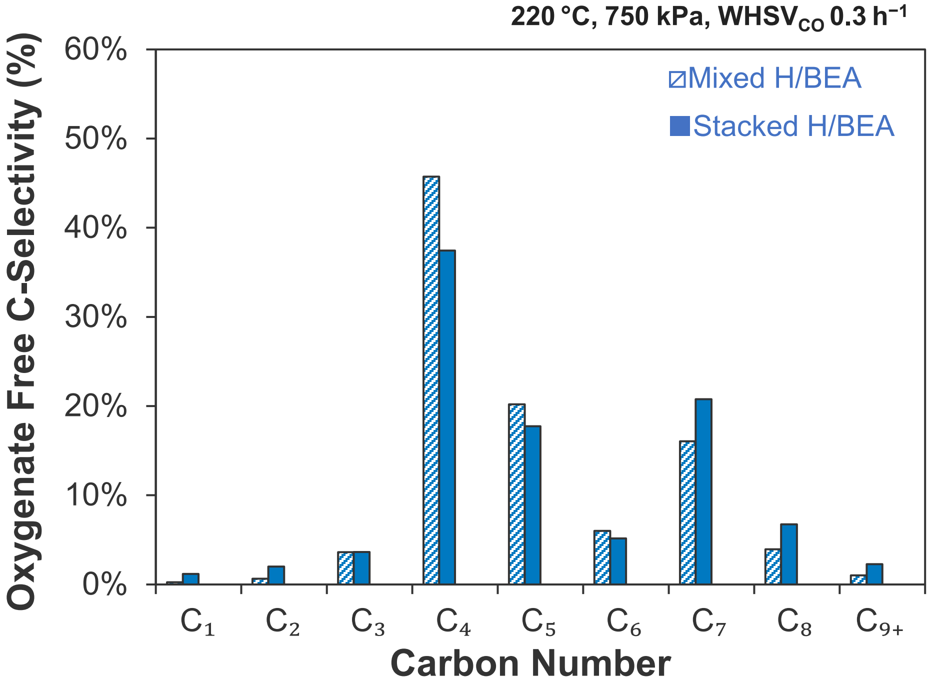
Utilize commercially available catalysts for the syngas to DME reactions

- “CZA” $Cu/ZnO/Al_2O_3$, Megamax 800, Clariant
- “A” γ-Al_2O_3, NorPro® SA6173, St. Gobain-Norpro

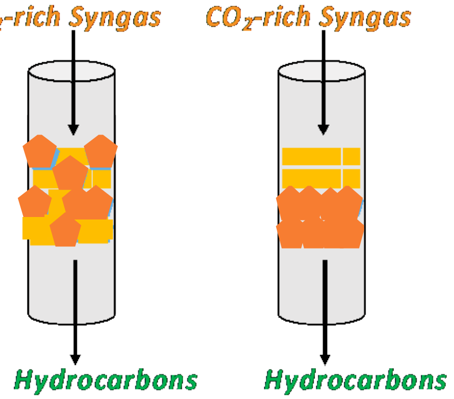
Reactor configuration influence on syngas conversion



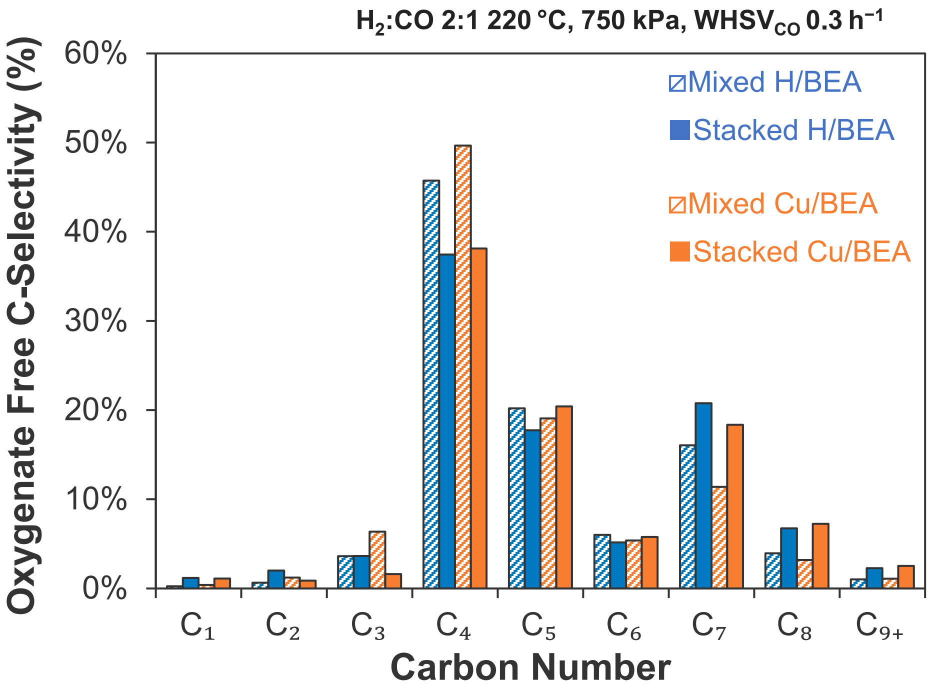
	H/Beta	
	Stacked	Mixed
CO Conversion %	64.1	40.9
C_{4+} Product Yield %	6.4	28.9
CO_2 Selectivity %	36.8	49.8



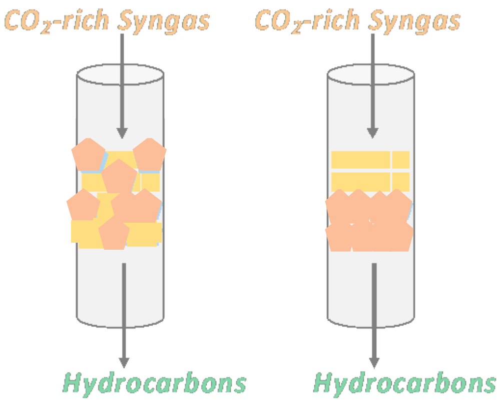
Reactor configuration influence on syngas conversion

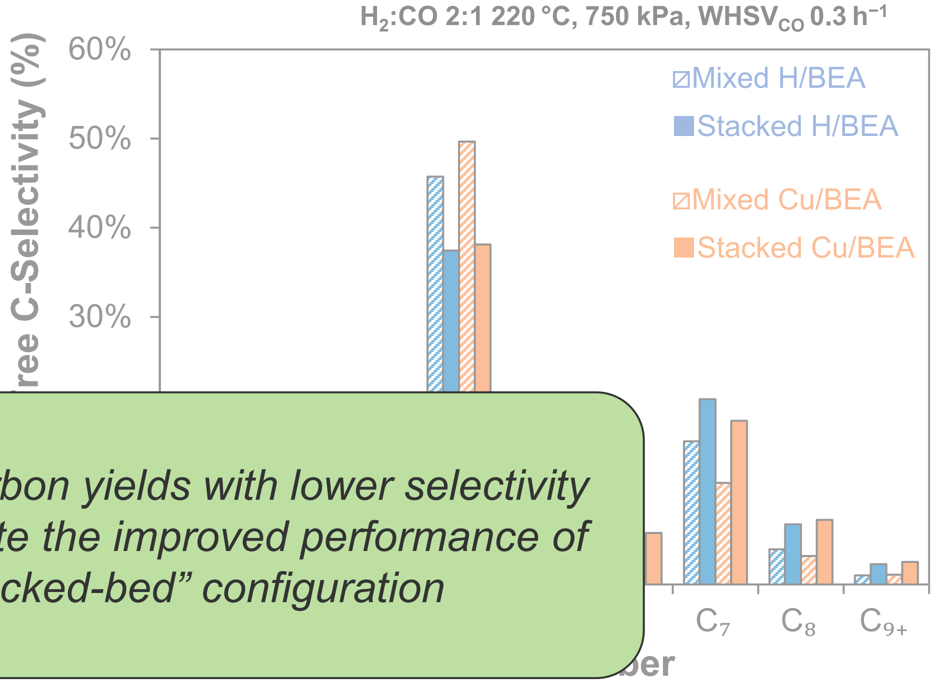


	H/Beta		Cu/Beta	
	Stacked	Mixed	Stacked	Mixed
CO Conversion %	64.1	40.9	46.5	21.2
C_{4+} Product Yield %	6.4	28.9	23.6	24.5
CO_2 Selectivity %	36.8	49.8	38.1	52.6



Reactor configuration influence on syngas conversion





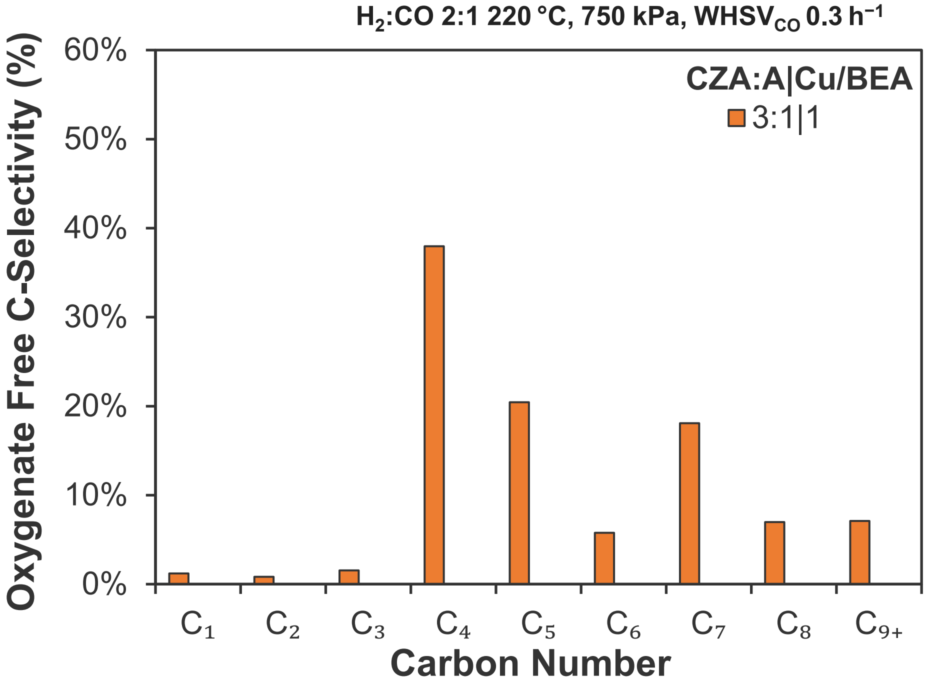
	Stac…			
CO Conversion %	64…			
C_{4+} Product Yield %	6.4…			
CO_2 Selectivity %	36.8	49.8	38.1	52.6

Balancing high hydrocarbon yields with lower selectivity towards CO_2 demonstrate the improved performance of Cu/BEA in a “stacked-bed” configuration

Consideration of Cu/BEA content on hydrocarbon formation

	CZA:γ-Al_2O_3|Cu/BEA
	3:1|1
CO Conversion %	46.5
C_{4+} Product Yield %	23.6
CO_2 Selectivity %	38.1

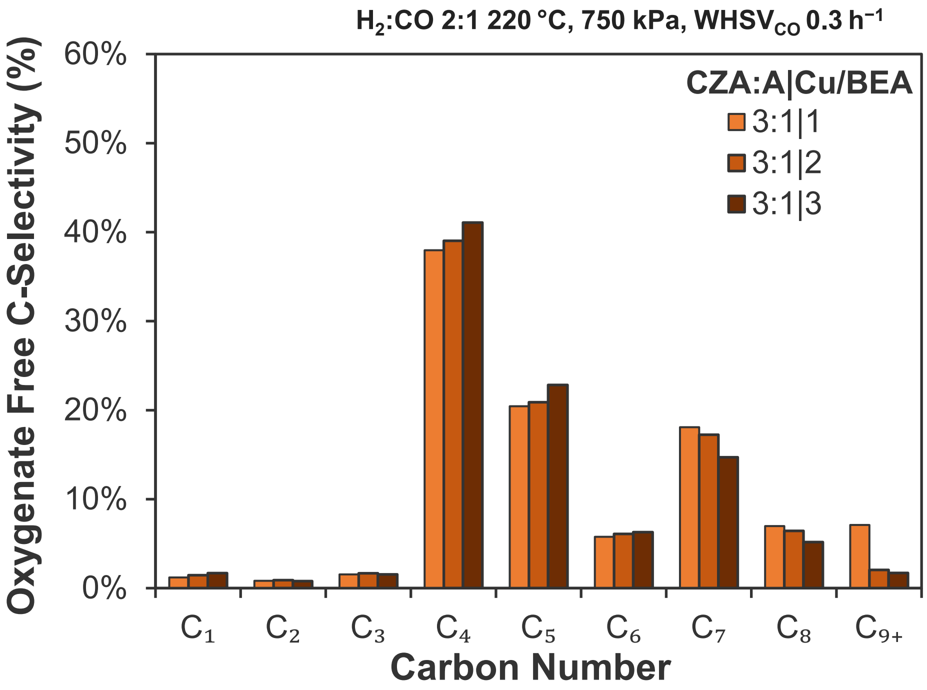
Measured at same time on stream (~12h)



Consideration of Cu/BEA content on hydrocarbon formation

	CZA:γ-Al_2O_3|Cu/BEA		
	3:1|1	3:1|2	3:1|3
CO Conversion %	46.5	56.4	55.8
C_{4+} Product Yield %	23.6	19.3	24.7
CO_2 Selectivity %	38.1	39.9	40.0

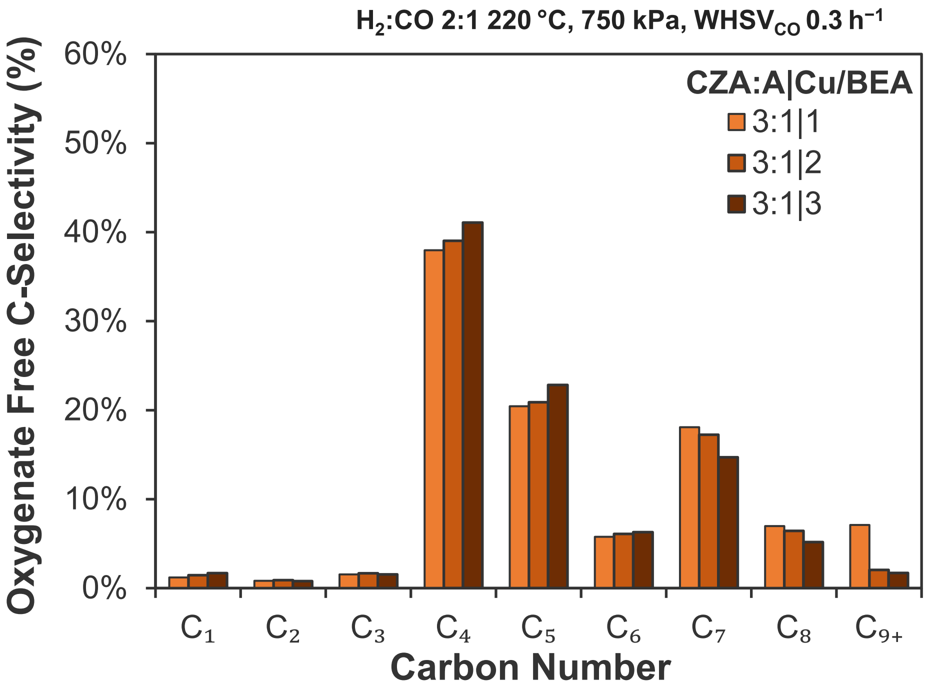
Measured at same time on stream (~12h)



Consideration of Cu/BEA content on hydrocarbon formation

	CZA:γ-Al_2O_3|Cu/BEA		
	3:1|1	3:1|2	3:1|3
CO Conversion %	46.5	56.4	55.8
C_{4+} Product Yield %	23.6	19.3	24.7
CO_2 Selectivity %	38.1	39.9	40.0
DME Product Yield %	20.7	10.9	3.5
Total HC Productivity ($g\ g_{Cu/BEA}^{-1}\ h^{-1}$)	0.105	0.063	0.053
Turnover Number ($mol_{HC}\ mol_{H+}^{-1}$)	86	64	44

Measured at same time on stream (~12h)



Consideration of Cu/BEA content on hydrocarbon formation

	CZA:γ-Al_2O_3|Cu/BEA		
	3:1|1	3:1|2	3:1|3
CO Conversion %	46.5	56.4	55.8
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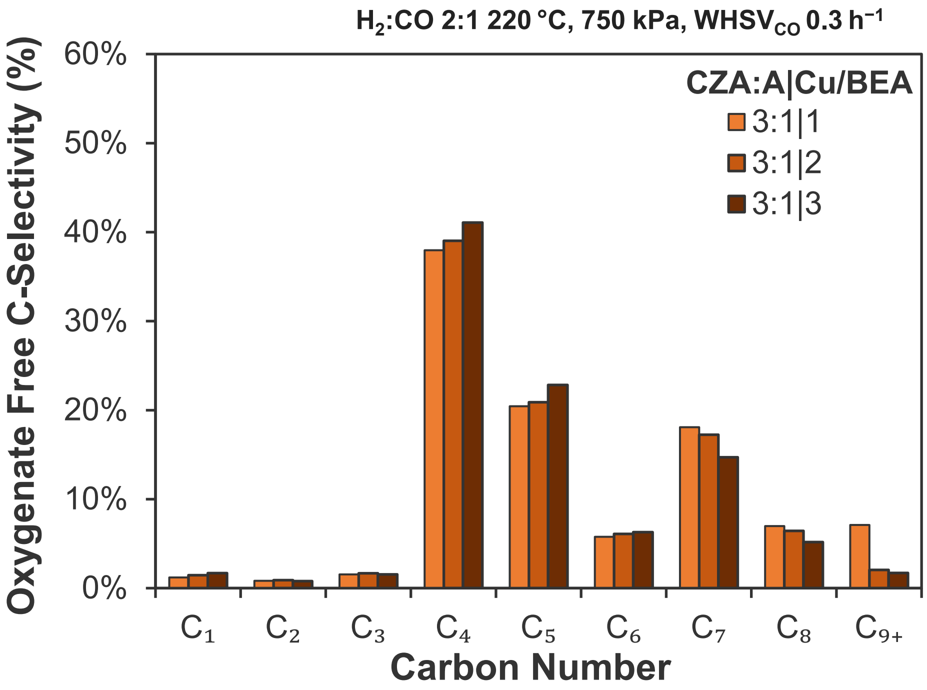
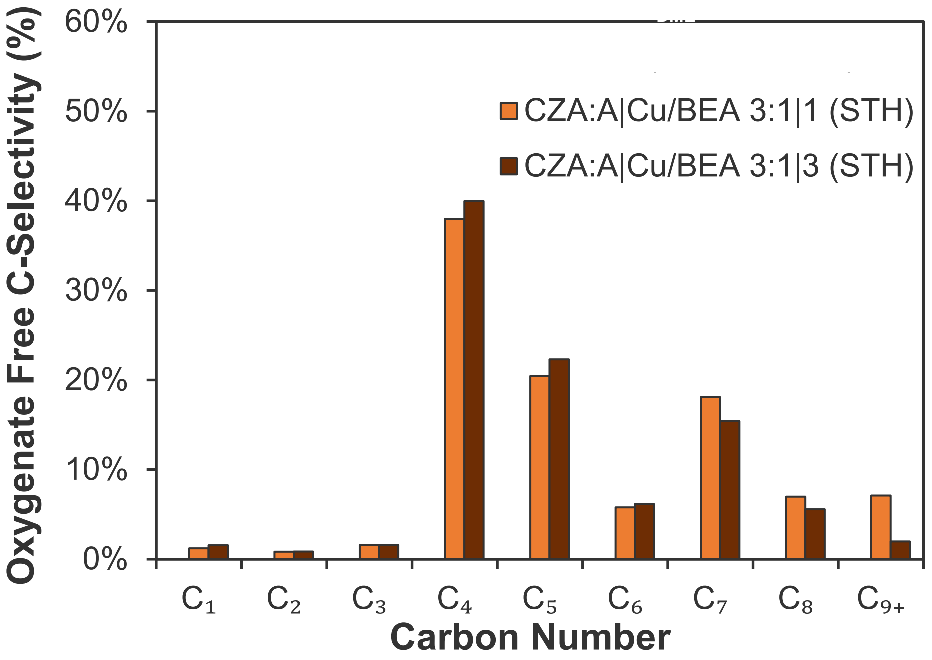


Improved hydrocarbon production achieved when considering the efficient utilization of in-situ formed of DME

Syngas conversion compared to DME conversion

Syngas: H_2:CO 2:1 220 °C, 750 kPa, $WHSV_{CO}$ 0.3 h^{-1}

	CZA+A|Cu/Beta (STH)	
	3:1|1	**3:1|3**
CO Conversion %	46.5	55.0
C_{4+} C-Yield %	23.6	23.8
HC Productivity (g $g_{Cu/Beta}^{-1}$ h^{-1})	0.105	0.051
Turnover Number (mol_{HC} mol_{H+}^{-1})	86	77

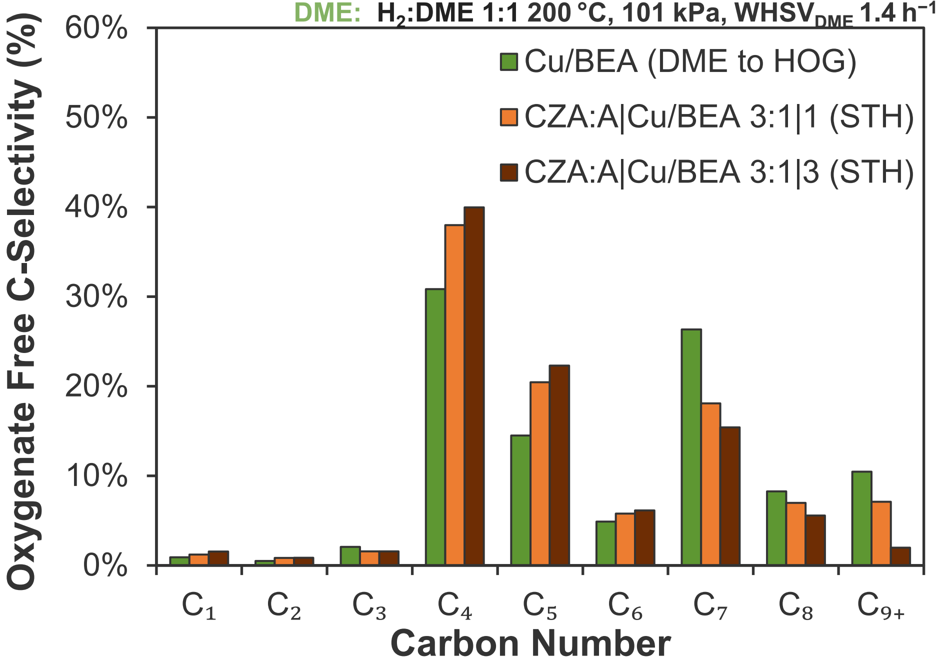


Syngas conversion compared to DME conversion

	Cu/Beta (DME)	CZA+A|Cu/Beta (STH)	
		3:1|1	3:1|3
DME or CO Conversion %	9.3	46.5	55.0
C_{4+} C-Yield %	6.7	23.6	23.8
HC Productivity ($g\ g_{Cu/Beta}^{-1}\ h^{-1}$)	0.050	0.105	0.051
Turnover Number ($mol_{HC}\ mol_{H+}^{-1}$)	83	86	77

Measured at comparable TON

Syngas: H_2:CO 2:1 220 °C, 750 kPa, $WHSV_{CO}$ 0.3 h^{-1}
DME: H_2:DME 1:1 200 °C, 101 kPa, $WHSV_{DME}$ 1.4 h^{-1}



Q. Wu et al. *Appl. Catal. B,* **2021, 287**, 119925

Syngas conversion compared to DME conversion

	Cu/Beta (DME)	CZA+A|Cu/Beta (STH) 3:1|1	CZA+A|Cu/Beta (STH) 3:1|3
DME or CO Conversion %	9.3	46.5	55.0
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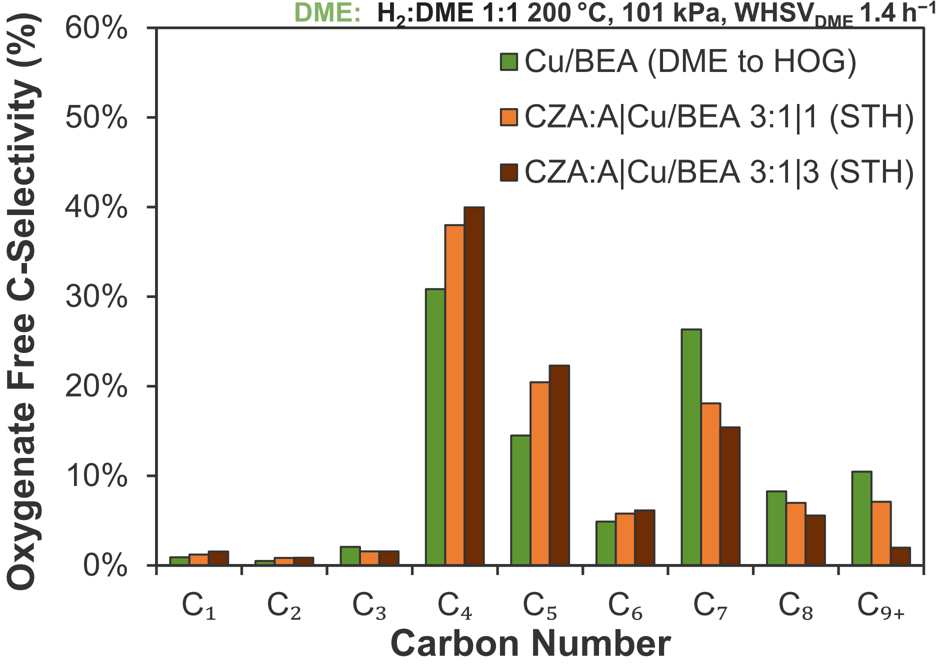
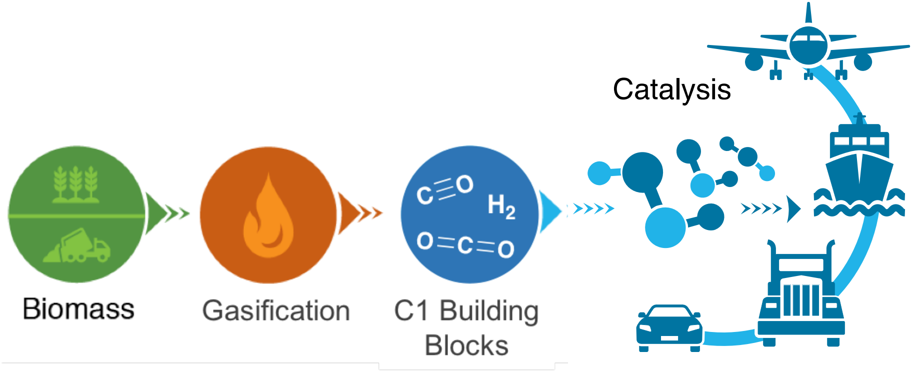
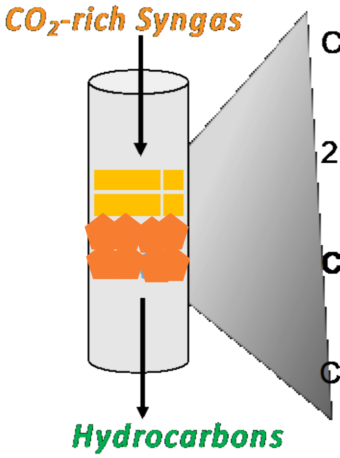


Direct syngas to hydrocarbon performance improved over DME homologation while maintaining high selectivities to HOG range products

Q. Wu et al. *Appl. Catal. B*, **2021, 287**, 119925

Introduction of CO_2 into syngas





$CO + 2 H_2 \leftrightarrow CH_3OH$
[Reaction 1; methanol synthesis]

$2 CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$
[Reaction 2; methanol dehydration]

$CH_3OCH_3 + H_2 \rightarrow C_nH_{2n+2} + H_2O$
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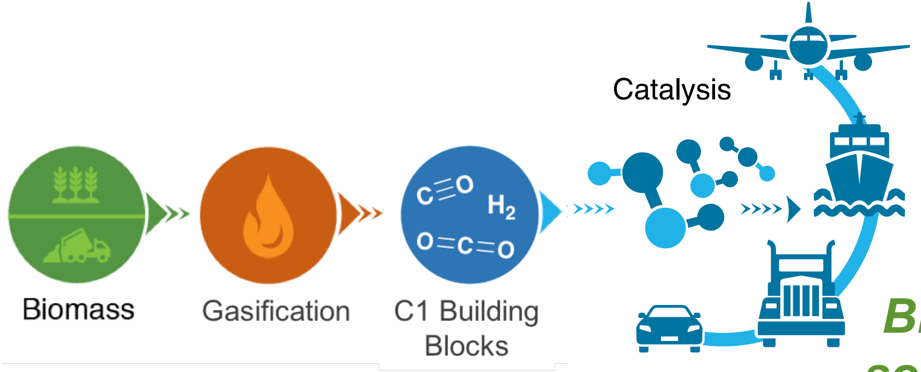
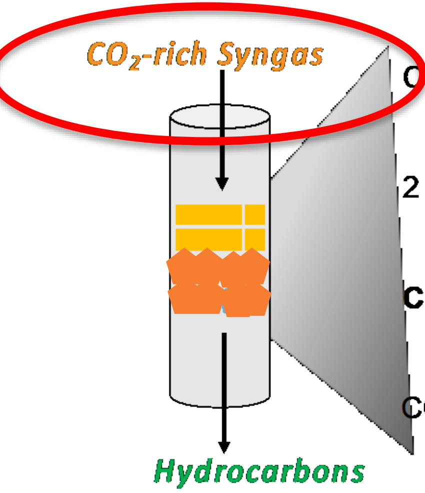
$CO + H_2O \leftrightarrow CO_2 + H_2$
[Reaction 4; water-gas shift reaction]

Introduction of CO_2 into syngas





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[Reaction 3; HOG synthesis]

$CO + H_2O \leftrightarrow CO_2 + H_2$
[Reaction 4; water-gas shift reaction]

Biomass derived sources of syngas

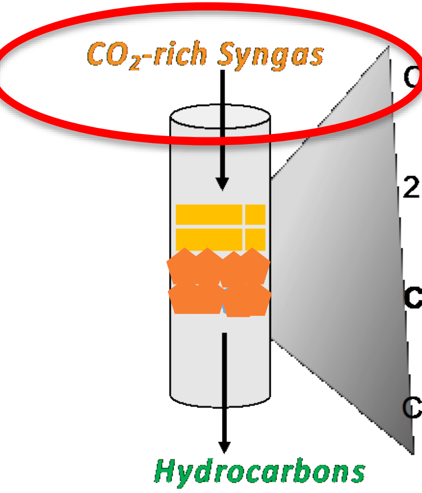
Feedstock	H_2 (vol %)	CO (vol %)	CO_2 (vol %)
Miscanthus	57.8	21.6	20.4
Switchgrass	57.9	22.2	19.7
Forest Residue	56.7	20.0	22.9

D.P. Dupuis et al. *Appl. Energy*, **2019**, 241, 25

Introduction of CO_2 into syngas

Assess syngas conversion in the single reactor with co-fed CO_2

- Molar ratios of H_2:CO:CO_2 2:1:0.8
- CZA+A|Cu/BEA bed composition 3:1|3



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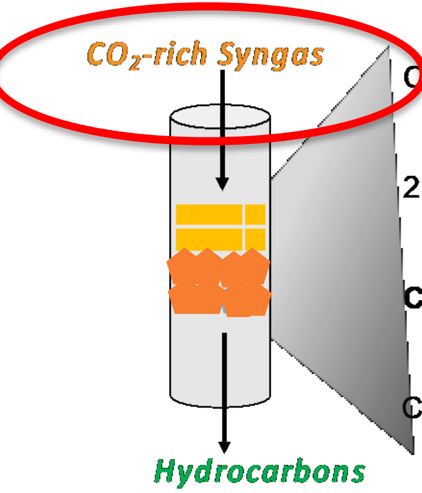

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$CO + H_2O \leftrightarrow CO_2 + H_2$
[Reaction 4; water-gas shift reaction]

	CZA+A|Cu/BEA 3:1|3	
	Without CO_2	With CO_2
CO+CO_2 Conversion %	77.3	27.0
C_{4+} Product Yield %	40.8	23.8
CO_2 Selectivity %	38.3	28.4
Hydrocarbon Productivity ($g\ g_{Cu/BEA}^{-1}\ h^{-1}$)	0.098	0.054

CO_2 incorporation into hydrocarbon products

Assess syngas conversion in the single reactor with co-fed CO_2

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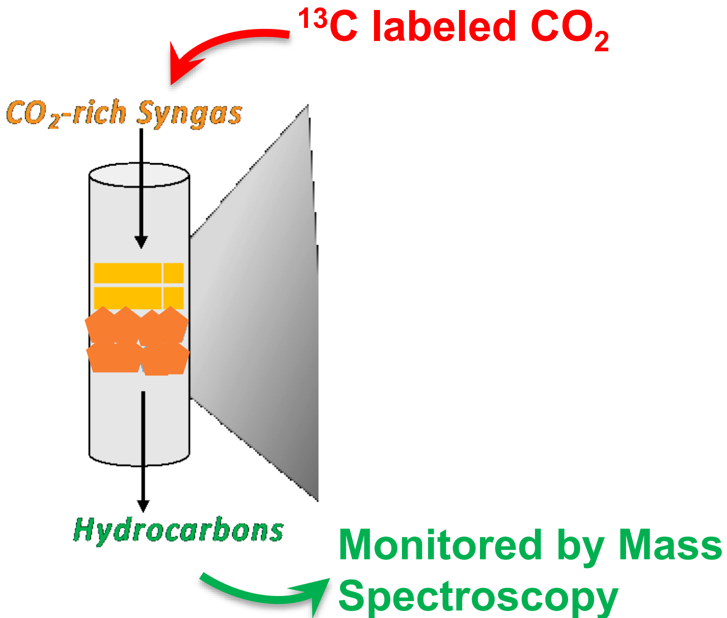

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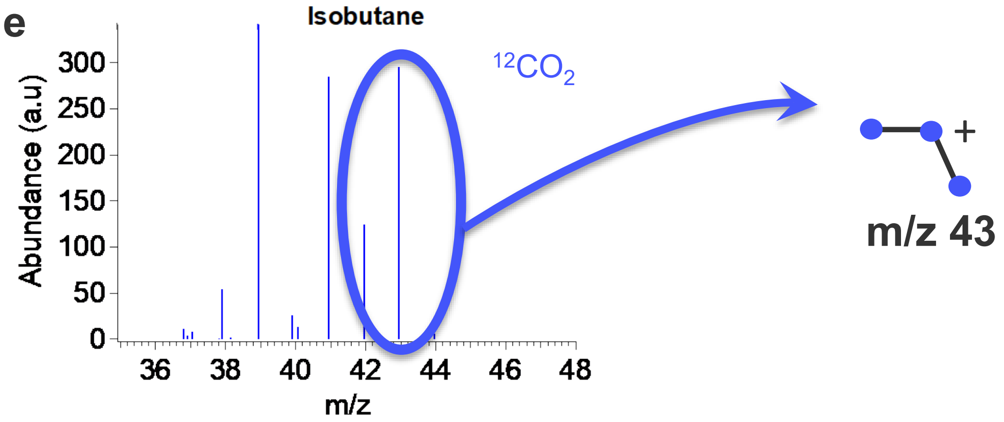

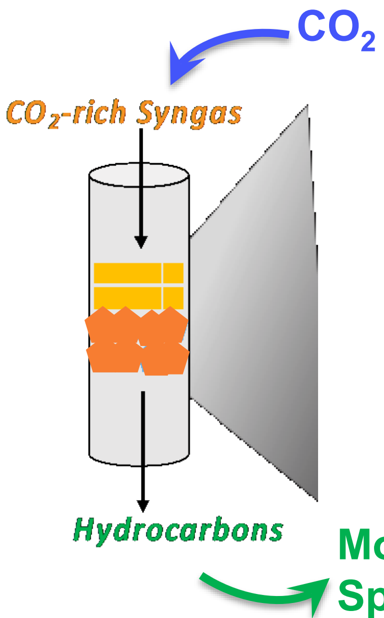

Monitored by Mass Spectroscopy

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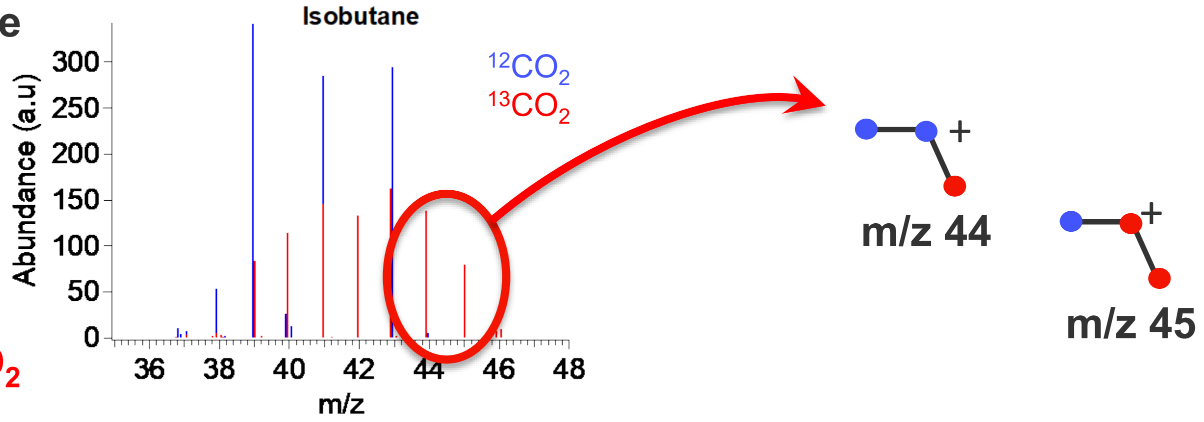
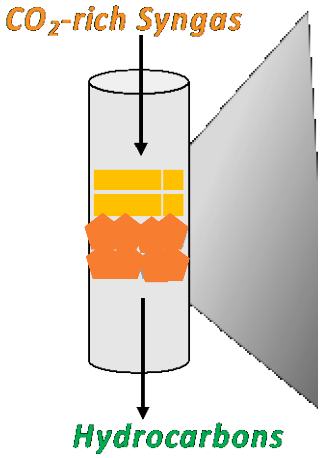


^{13}C labeled CO_2



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CO_2 incorporation into hydrocarbon products

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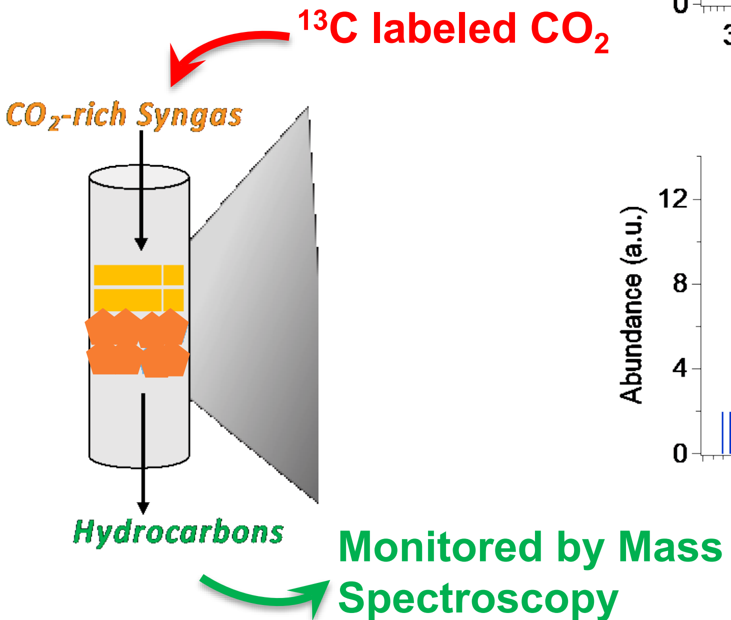

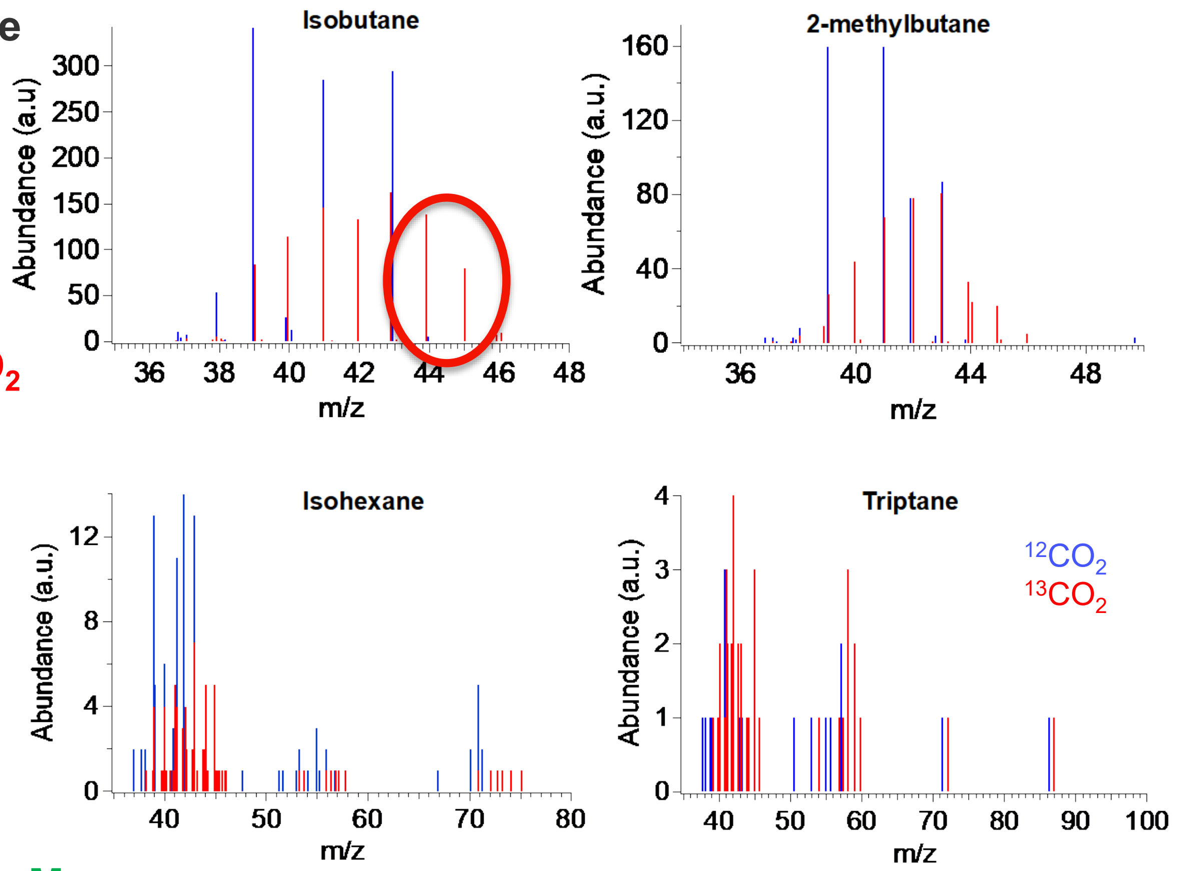

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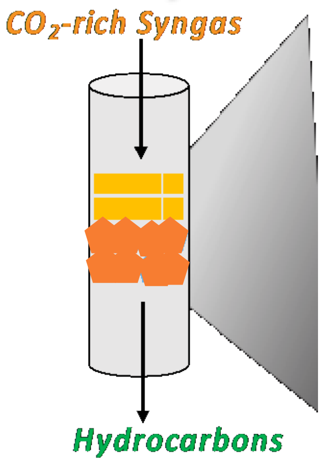
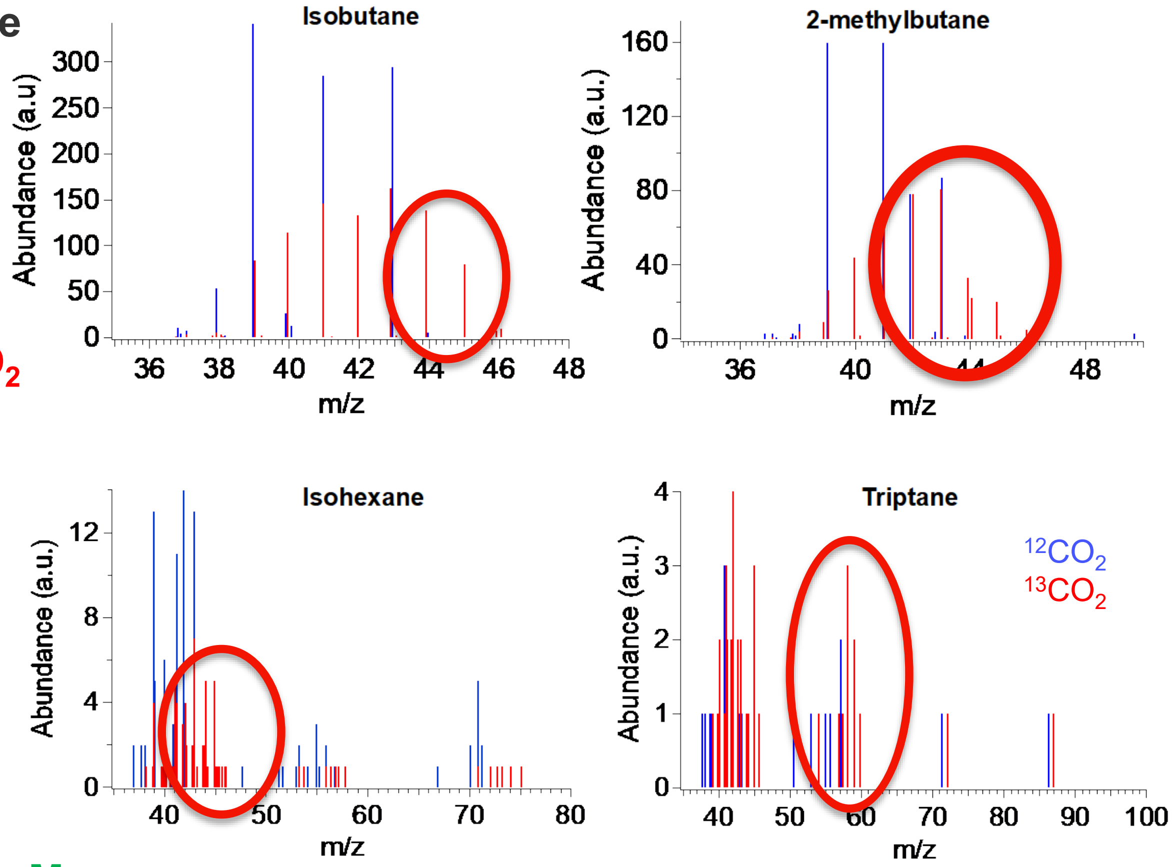


Monitored by Mass Spectroscopy



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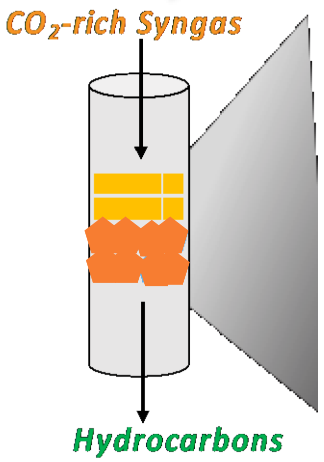
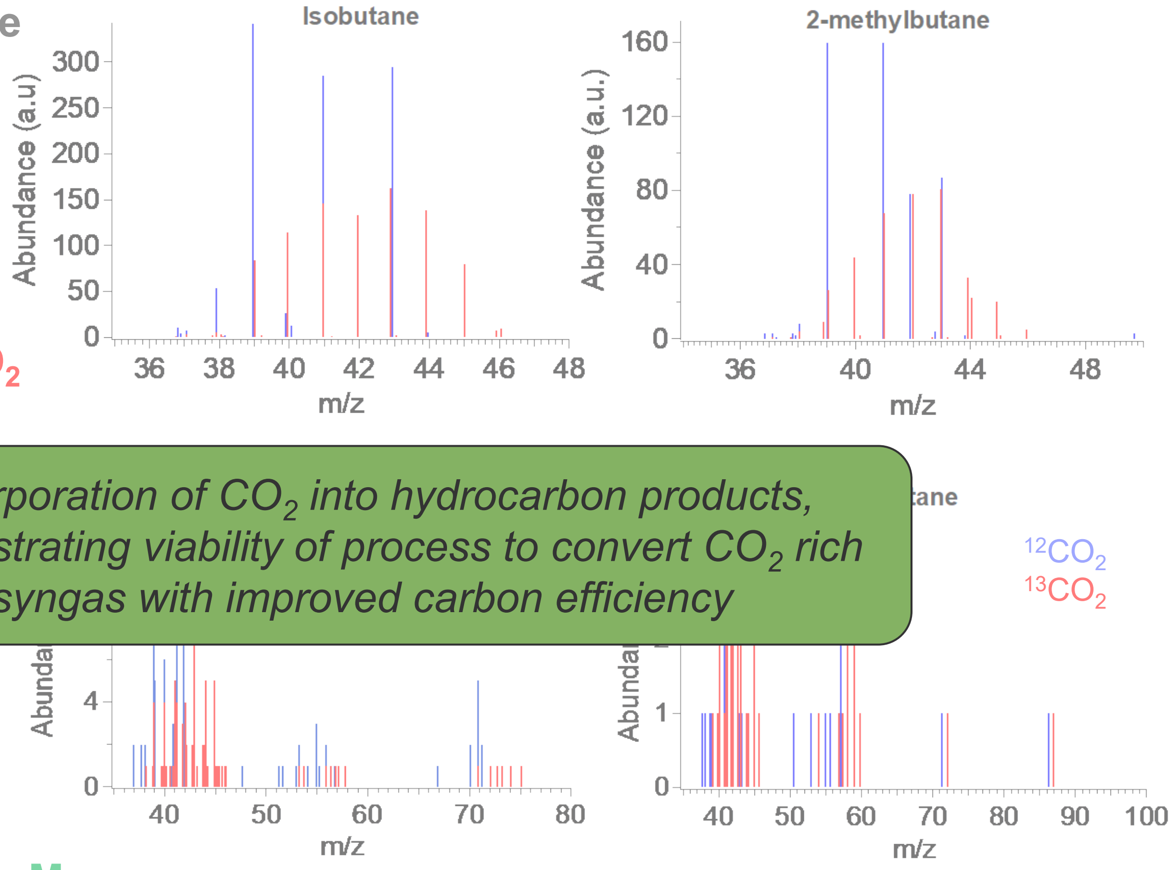
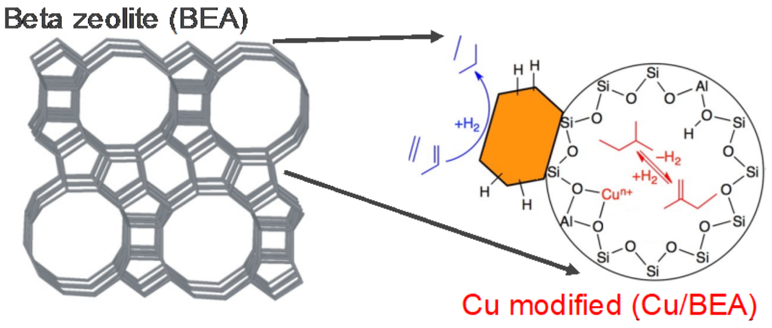


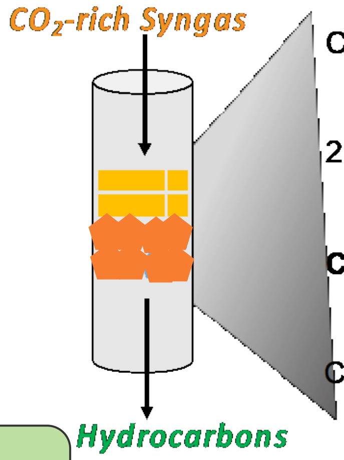
Monitored by Mass Spectroscopy



Incorporation of CO_2 into hydrocarbon products, demonstrating viability of process to convert CO_2 rich syngas with improved carbon efficiency

Conversion of CO_2- rich syngas in a single reactor system





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[Reaction 4; water-gas shift reaction]

Systematic configuration & composition changes demonstrate ability to improve performance

Direct syngas to hydrocarbon performance improved over DME homologation while maintaining high selectivities to HOG range products

Incorporation of CO_2 into hydrocarbon products, demonstrating viability of process to convert CO_2 rich syngas with improved carbon efficiency

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

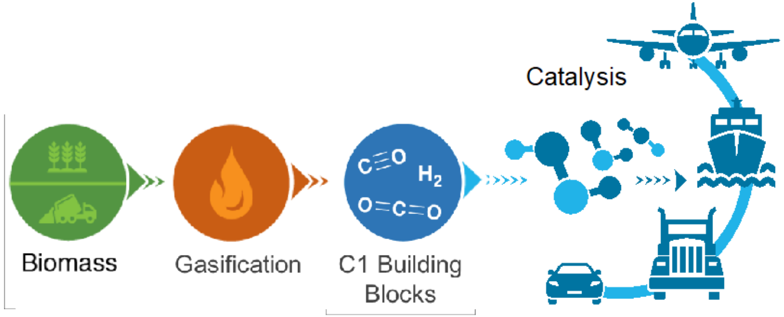
Bioenergy Technologies Office

ChemCatBio
Chemical Catalysis for Bioenergy

Energy Materials Network
U.S. Department of Energy

Thank you, questions?

www.nrel.gov



NREL/PR-5100-81468

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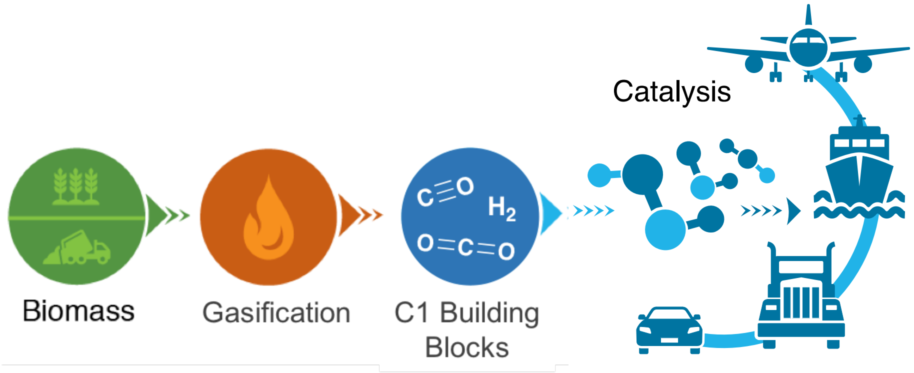
NREL
Transforming ENERGY

Supplementary Information

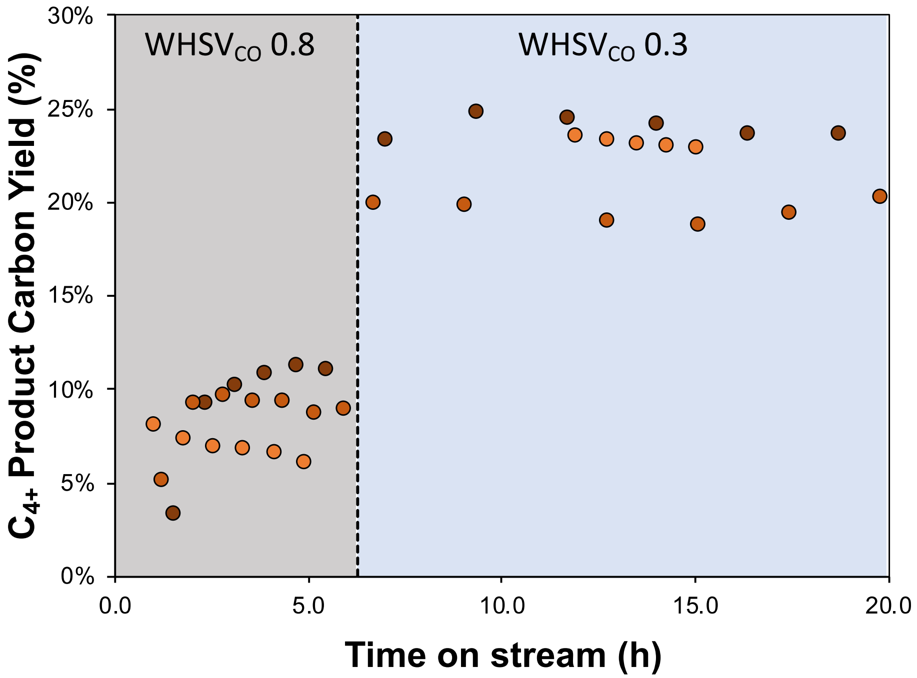
Process Intensification for Direct Conversion of Biomass-Based Syngas to High Octane Gasoline

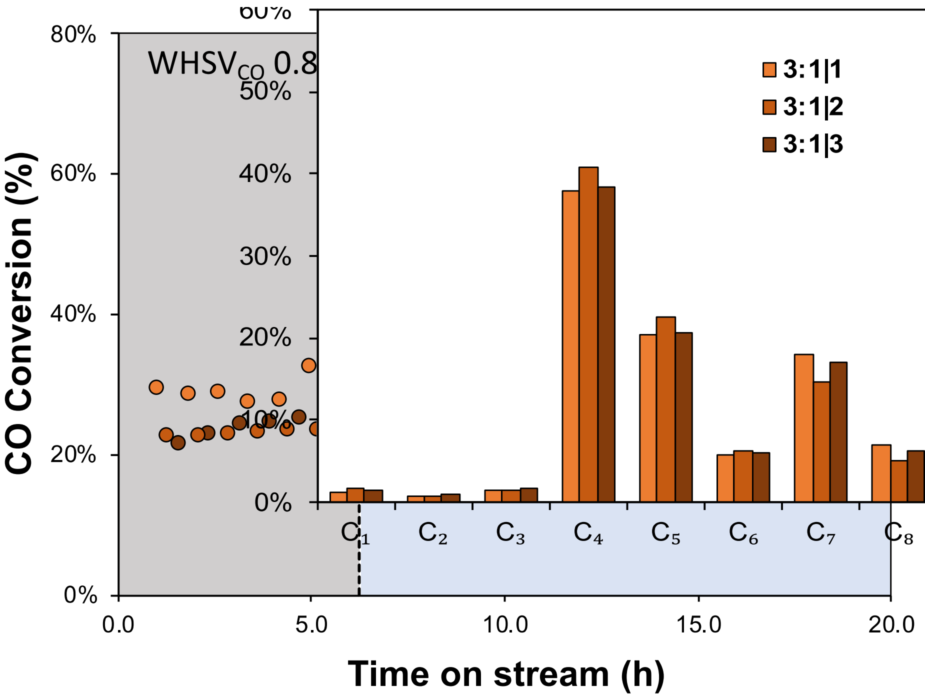
Claire Nimlos, Connor Nash, Anh To, Dan Dupuis, Daniel Ruddy*

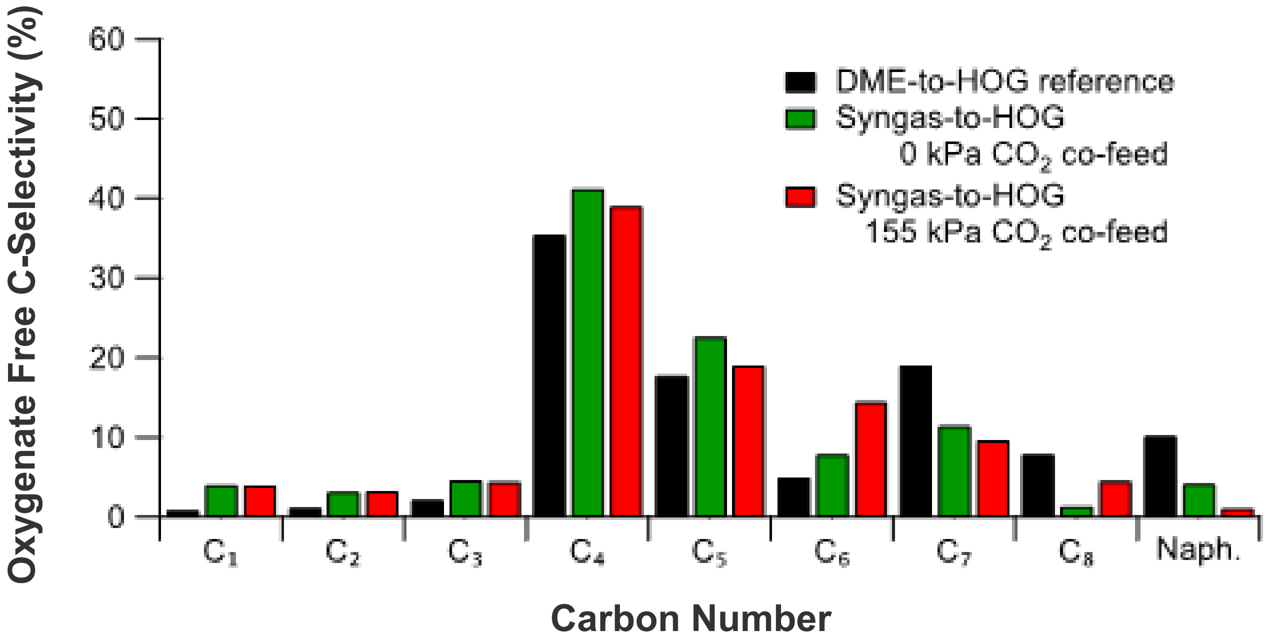
Catalytic Carbon Transformation & Scale-up Center, National Renewable Energy Laboratory



2021 AIChE Annual Meeting
Breakthroughs in C1 to Chemicals and Processing Engineering
November 16, 2021


WHSV$_{CO}$ 0.8
WHSV$_{CO}$ 0.3
C$_{4+}$ Product Carbon Yield (%)
Time on stream (h)
30%
25%
20%
15%
10%
5%
0%
0.0
5.0
10.0
15.0
20.0


WHSV$_{CO}$ 0.8
CO Conversion (%)
Time on stream (h)
80%
60%
40%
20%
0%
0.0
5.0
10.0
15.0
20.0
3:1|1
3:1|2
3:1|3
50%
40%
30%
20%
0%
C$_1$
C$_2$
C$_3$
C$_4$
C$_5$
C$_6$
C$_7$
C$_8$



Oxygenate Free C-Selectivity (%)
60
50
40
30
20
10
0
DME-to-HOG reference
Syngas-to-HOG
0 kPa CO_2 co-feed
Syngas-to-HOG
155 kPa CO_2 co-feed
C_1
C_2
C_3
C_4
C_5
C_6
C_7
C_8
Naph.
Carbon Number

Additional hydrocarbon species monitored