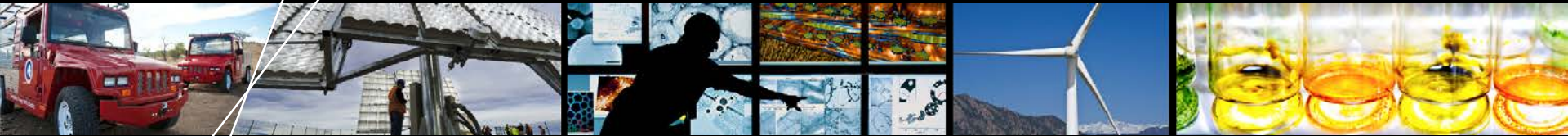


Heuristics for Producing Ethanol from Biomass Syngas over Metal Sulfide Type Catalysts



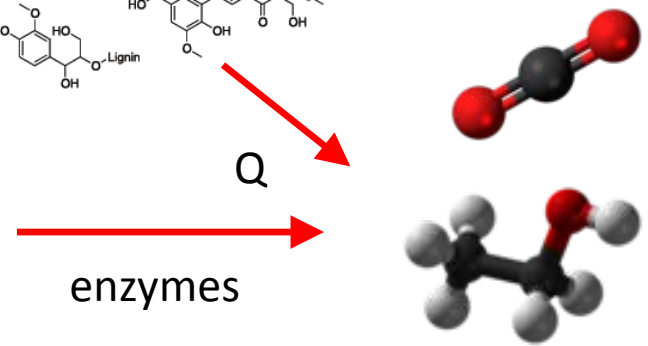
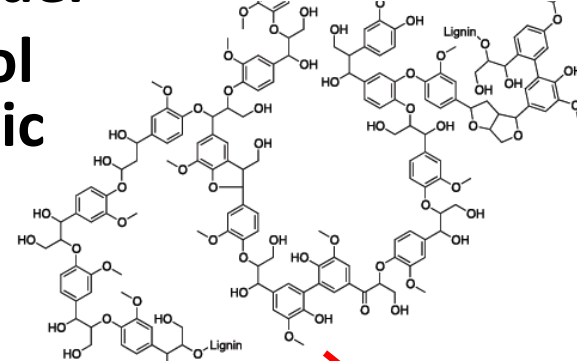
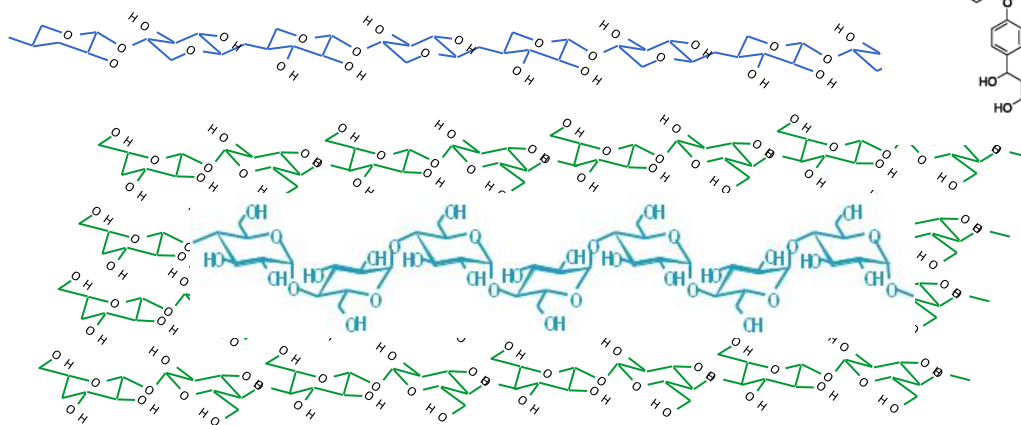
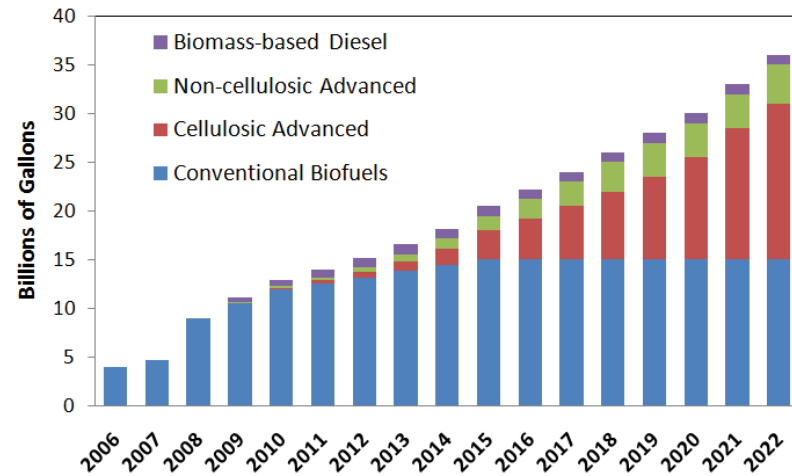
Frontiers in Biorefining

Jesse Hensley, Jack Ferrell, Josh Schaidle, & Jason Thibodeaux

24-October-2014

Recent Motivations for Thermochemical Ethanol

- EISA of 2007: 36 billion gallons renewable fuel by 2022 per RFS, displace gasoline by 30% by 2030 (for historical context only)
- “Food vs. Fuel”
- Adoption of E-85 and flex-fuel light vehicles: ethanol an *approved* fuel
- We’re experts at making ethanol from sugar, what about cellulosic material?

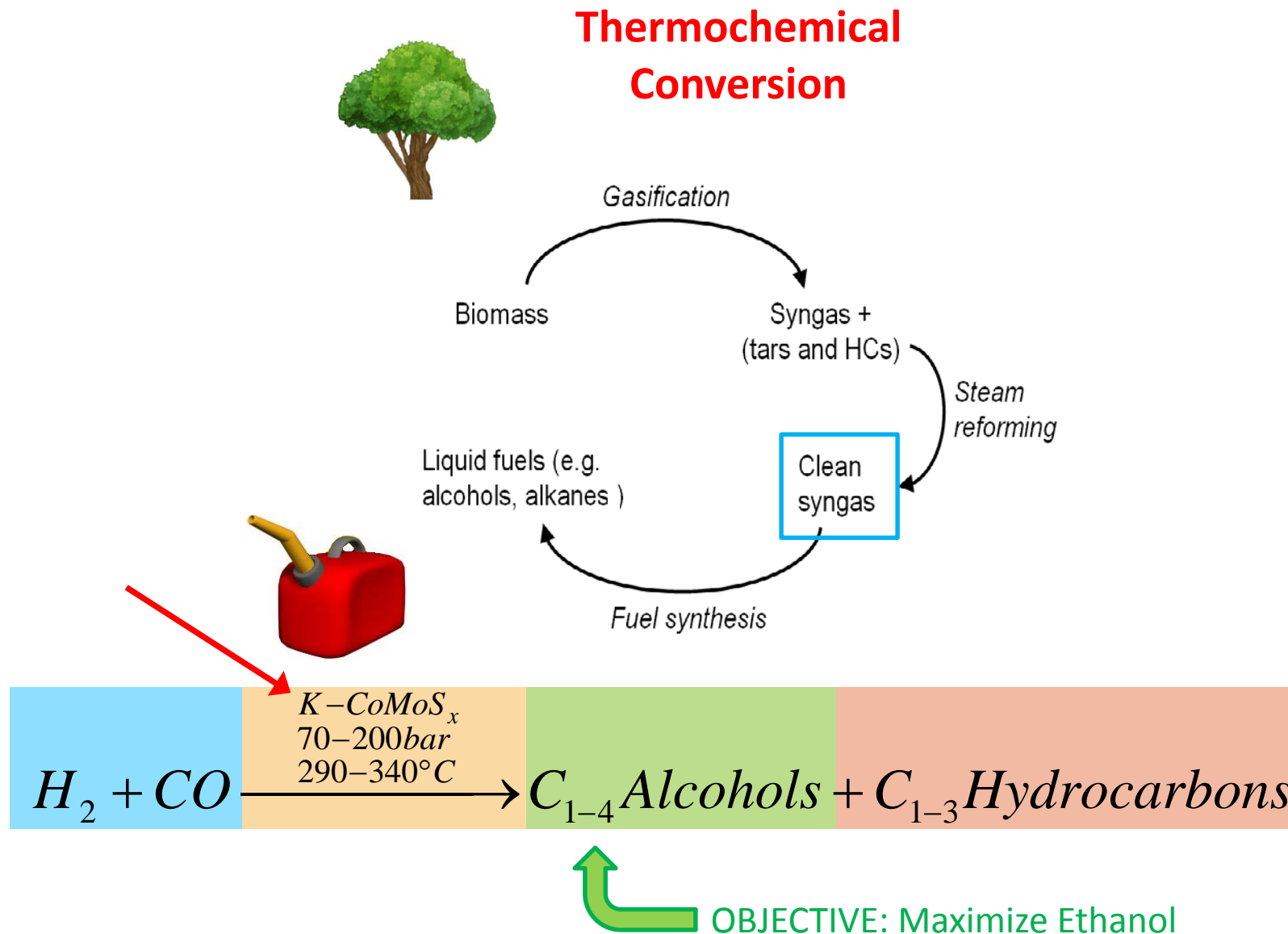


Can it Be Done?

- **Mixed alcohols were coproducts of first-generation FT catalysts in early 1900s**
 - Discovery of Co, Fe-based FT catalysts reduced selectivity to oxygenates, interest in mixed alcohols subsided
- **1927-1945—Mixed alcohols were produced for motor fuel in US and Germany (usually mixture of methanol and butanol)**
- **1970s—intense work from Dow and others to find an active LPG from syngas catalyst led to discovery of K-MoS₂ as an FT-type catalyst efficient at making low C # hydrocarbons**
 - 1981—G. Quarderer of Dow discovered liquid byproduct in reactor effluent—mixed alcohols
- **1980s—Dow and Union Carbide undertook a large study to find a stable, commercializable CoMoS_x catalyst**
 - Same time—IFP developed a modified FT catalyst for mixed alcohols
 - Same time—Tasumi et al. developed alkali-modified Mo catalysts for mixed alcohols
- **1990s—Activity in mixed alcohol catalysis subsided due to low oil prices**
- **2000s—Renewed interest in mixed alcohols from *biomass* syngas, more than a few startups**
- **Today—Not popular again**



Inserting Biomass Into the Equation



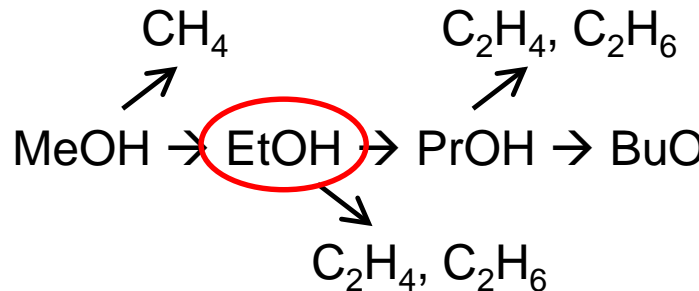
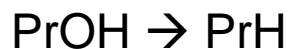
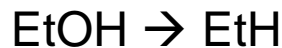
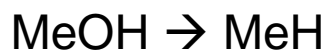
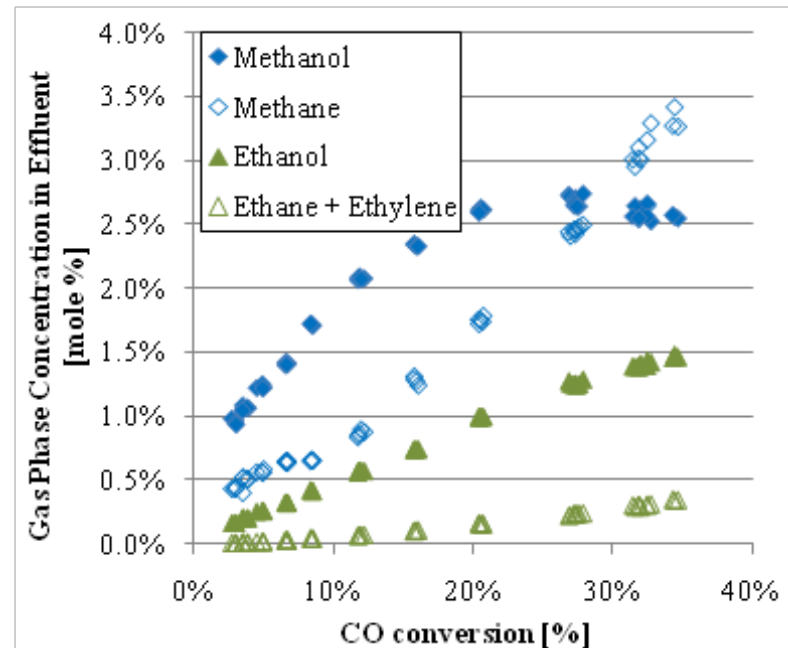
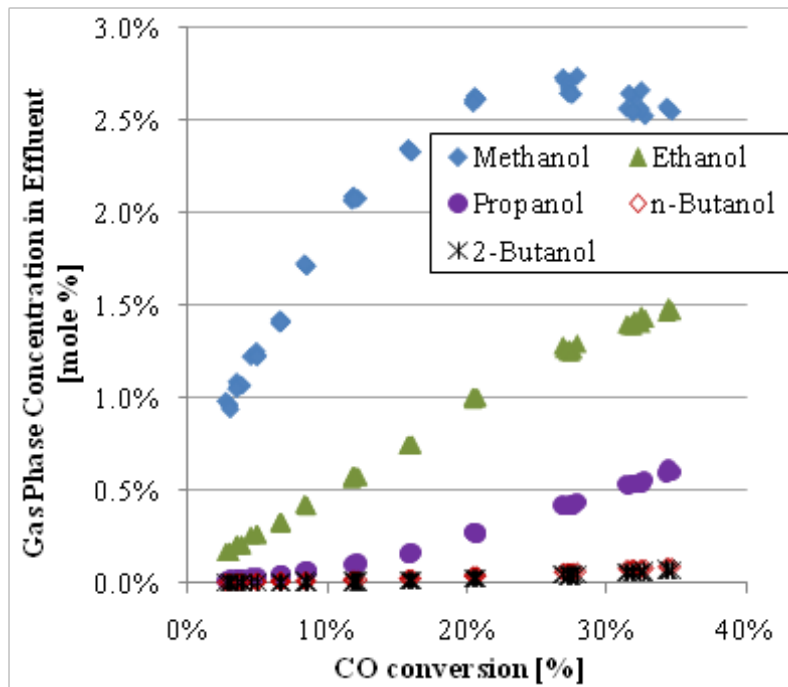
What We've Learned in 5 Years...

...about making ethanol from syngas over K-CoMoS_x

- 1. The economics of thermochemical alcohol fuel production look ok—if you have inexpensive feedstock and if your product doesn't have to be pure***
- 2. Selectivity to ethanol is limited and is more a function of process conditions than anything else**
- 3. Deactivation is slow and reversible if you maintain the catalyst correctly but fast and irreversible if you don't**
- 4. You can operate with relatively 'dirty' syngas**
- 5. Oxidation of the catalyst is the enemy**
- 6. The alcohol product is more complex than one might expect**

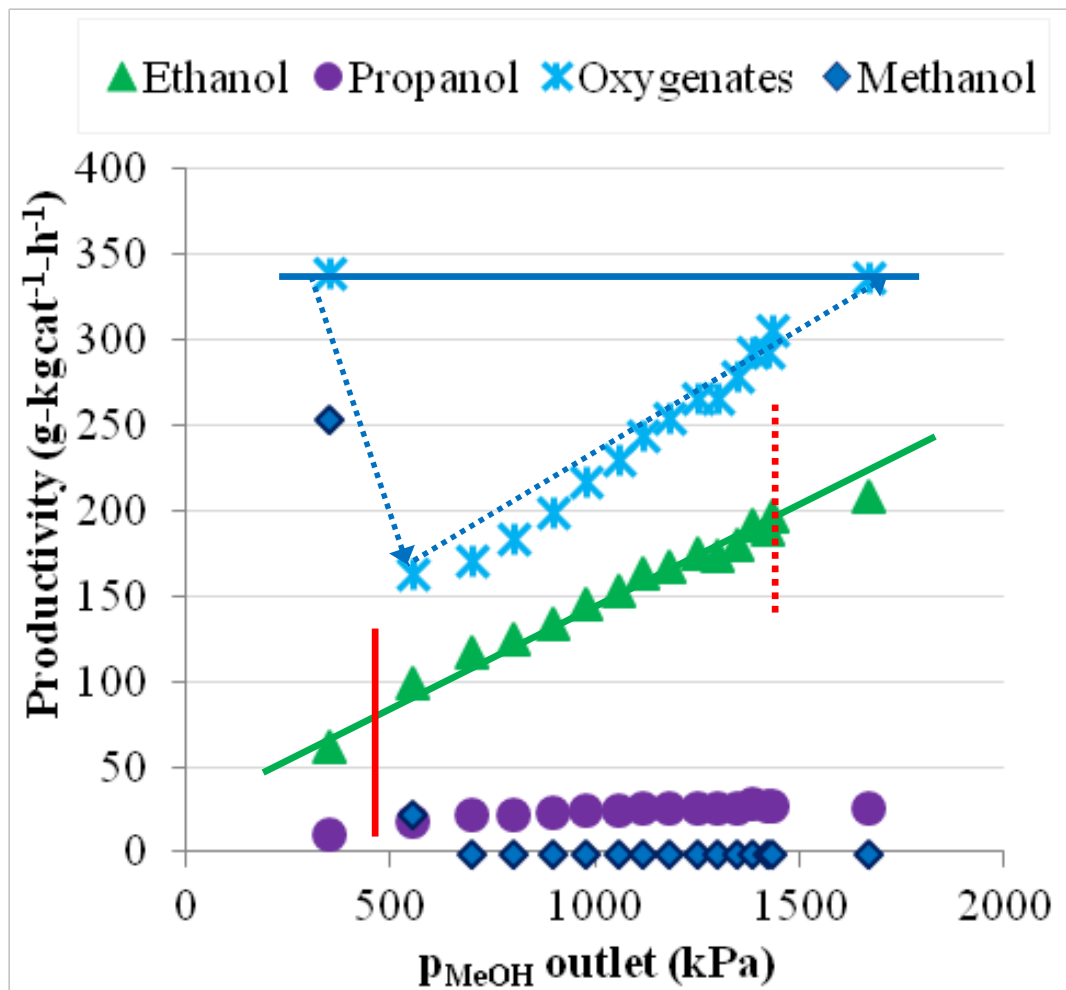
* Dutta et al., 2011 <http://www.nrel.gov/docs/fy11osti/51400.pdf>

Tuning for Ethanol Selectivity



Product selectivity a strong function of single-pass conversion

Process Solution: Pump MeOH to the Front



By recycling methanol to extinction, ethanol production is increased 3-fold

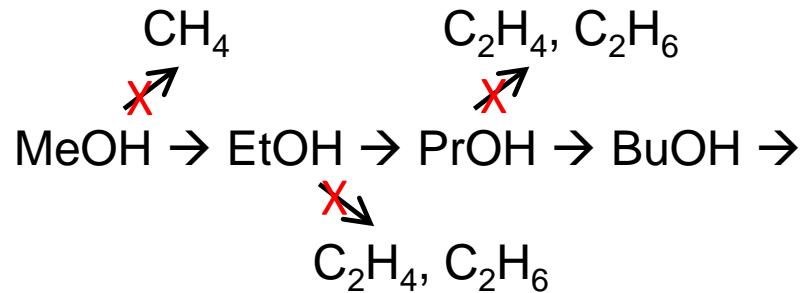
As recycle converges, total oxygenate production returns to max value, but this time without any net production of methanol

Recycling more methanol leads to more ethanol

Note: the rightmost point on the plot is the ONLY condition for which methanol would need to be produced upstream; Moving left to right, the methanol produced is recycled to the reactor inlet

Conclusion—Selectivity

On K-CoMoS_x, relative selectivity of alcohols is dictated by process conditions

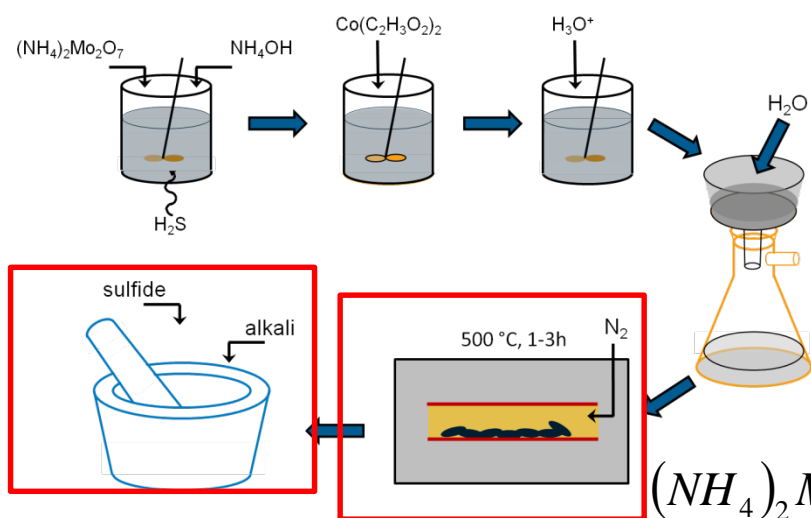


To improve selectivity to alcohols over hydrocarbons, improve the catalyst

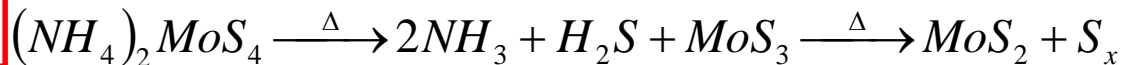
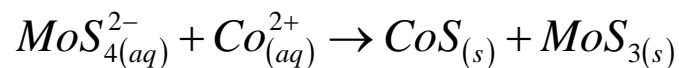
Catalyst *Selectivity*: Oxidation is Key

- The literature suggests that improved alcohol selectivity is possible, but most of the time what you're really seeing is:
 - Data from low conversion (low p_{ROH} , low rate of HC production)
 - Data from low temperature (kinetics suggest that alcohol dehydration is a stronger function of T than CO homologation)
 - Data from less active catalysts (again, lower conversion)

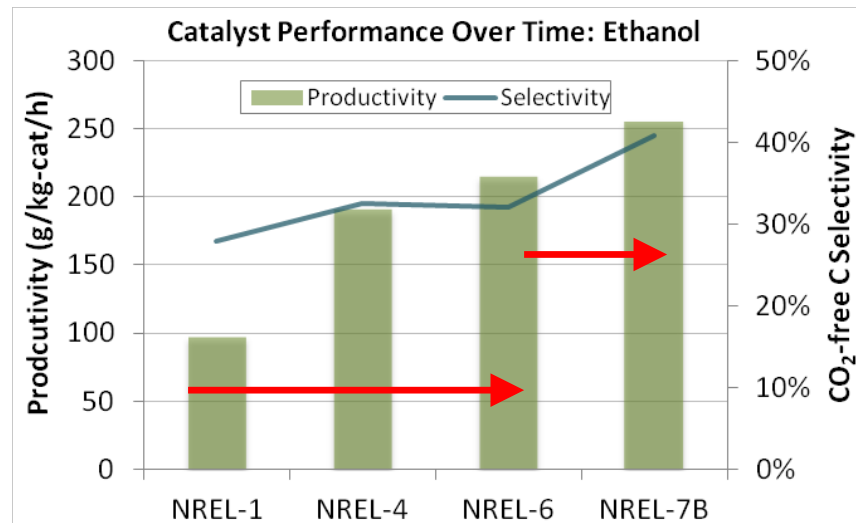
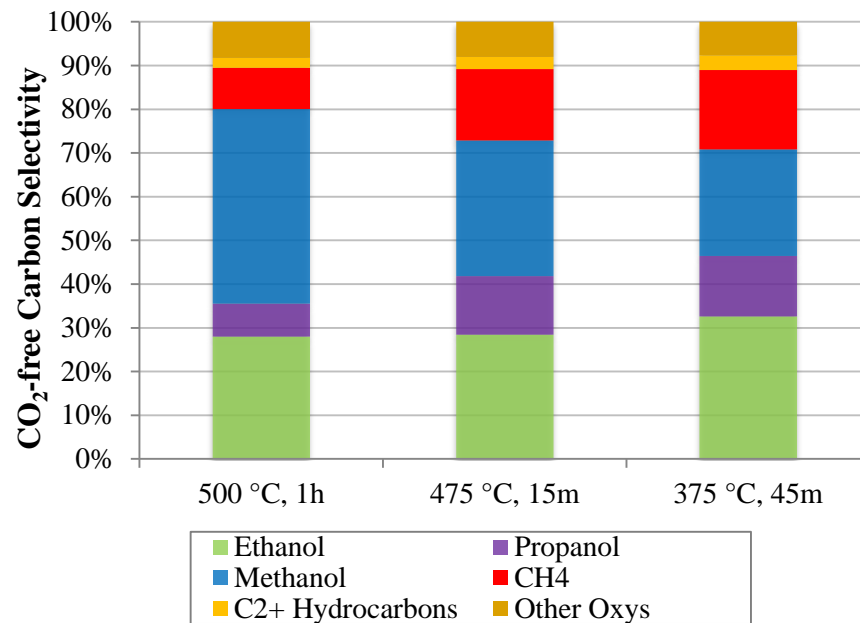
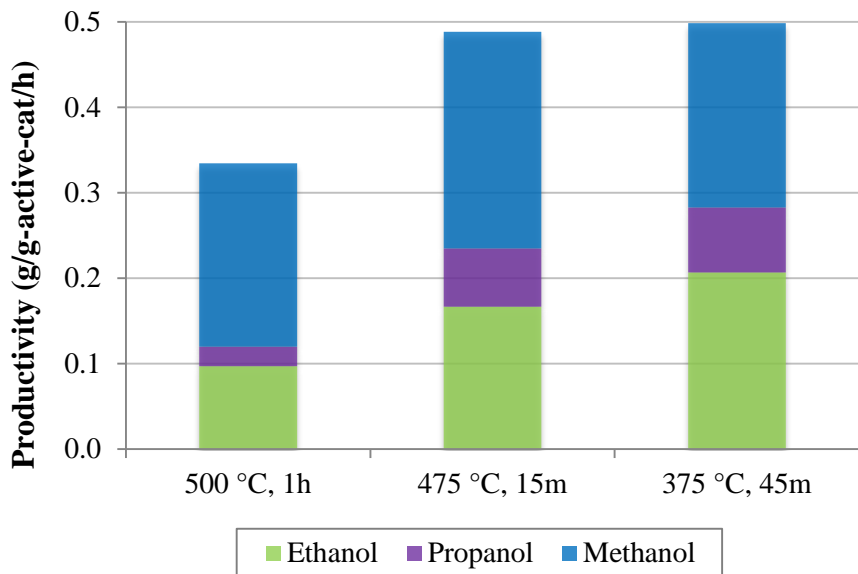
Where would oxidation occur?



Severe synthesis conditions lead to higher M:S
(M in higher oxidation state)



Some Examples

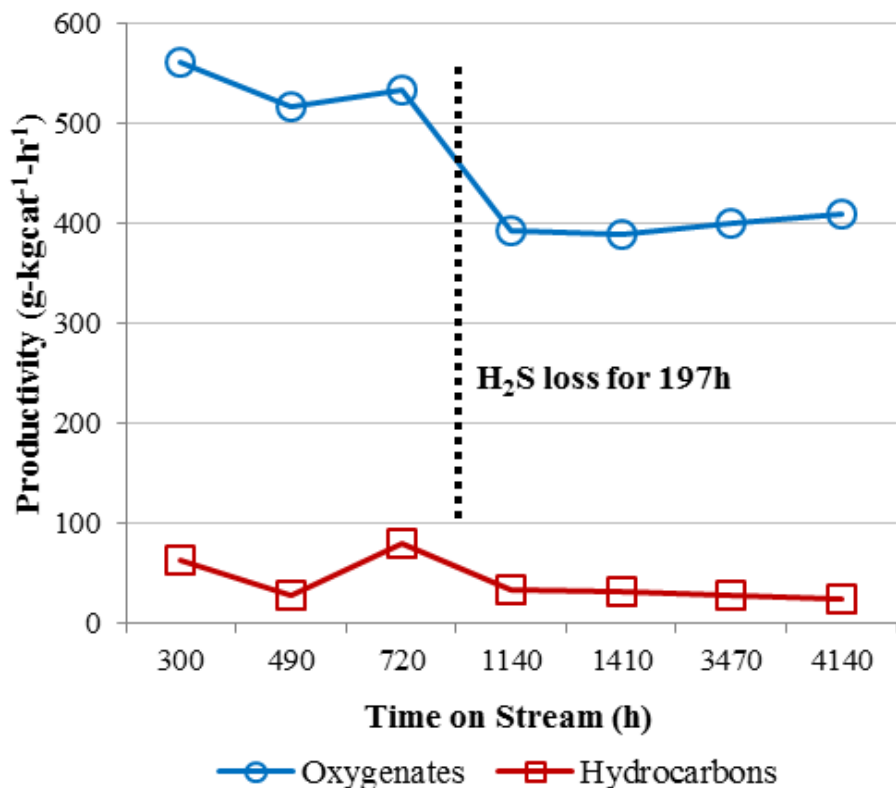


milder sulfide decomposition

move alkali addition step *before* catalyst becomes air sensitive

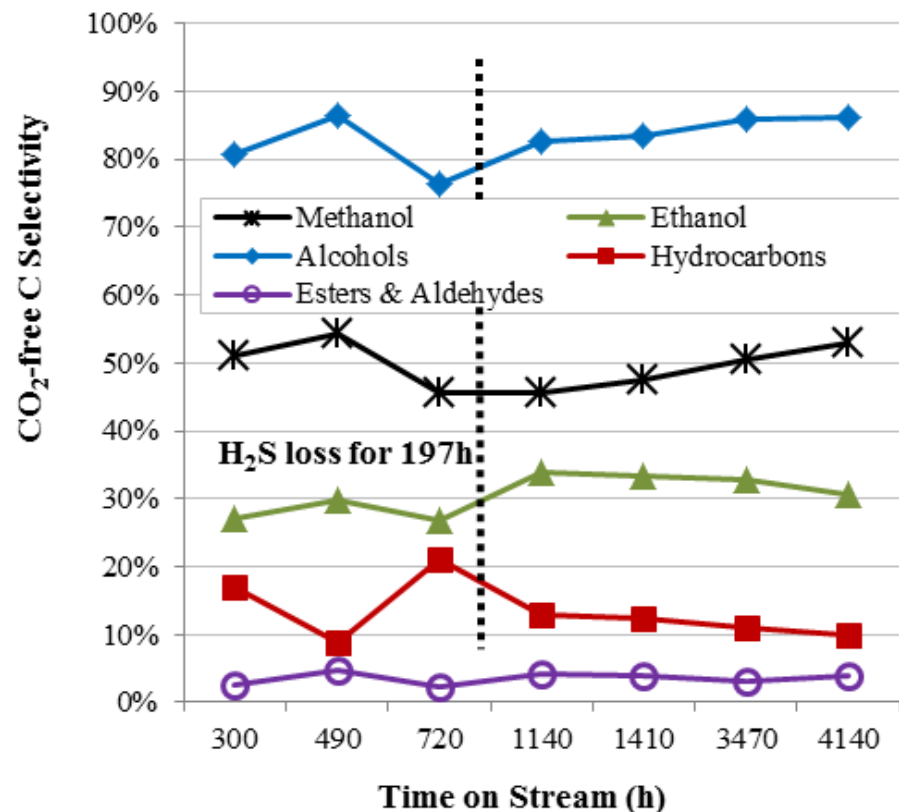
all data collected at 325 °C, 700 psi H₂ + 700 psi CO, 6000 NTPL-kgcat⁻¹h⁻¹

Deactivation is Minimal if Catalyst Remains Sulfided



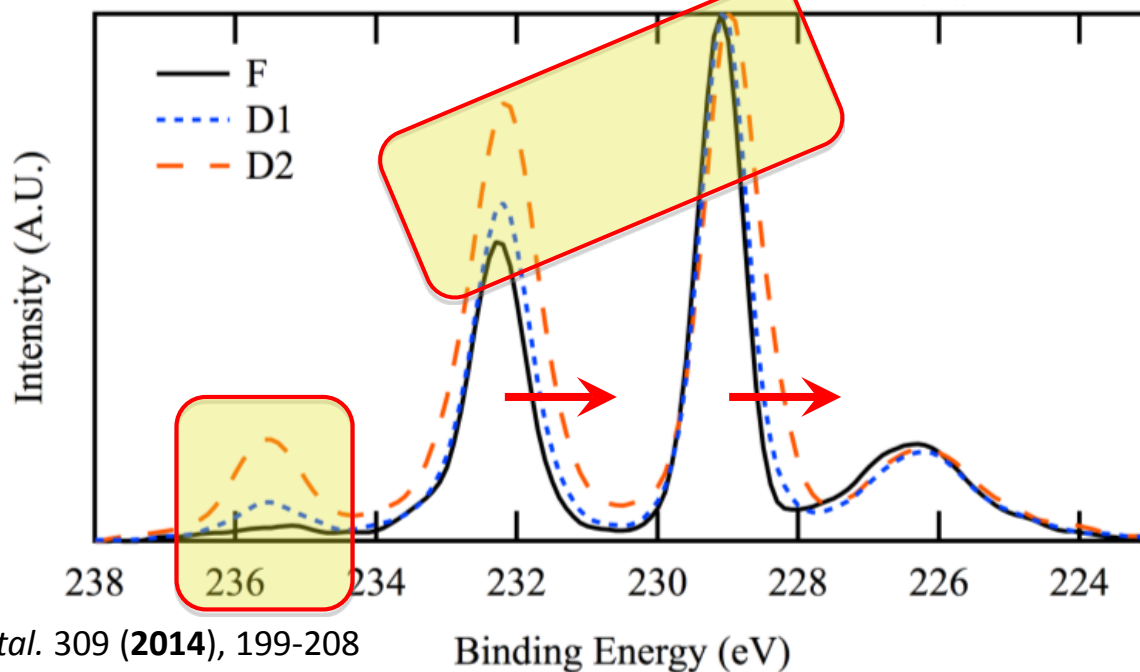
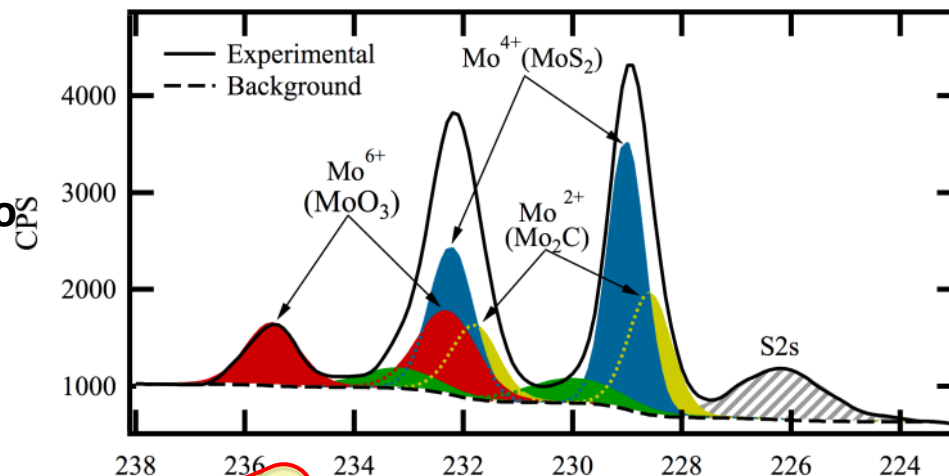
- Selectivity is maintained
- Turnovers decrease
- Catalyst may be losing active sites

- Repeat condition measured in between other operating conditions
- H₂S maintained on catalyst at 100ppm with noted exception



Fresh vs. No S Cofeed

- Increase in contribution from oxide-like Mo
- Change in ratio of Mo⁴⁺ doublet suggests increase in 'oxide' relative to 'sulfide'
- Shift in Mo⁴⁺ suggests contribution from Mo²⁺ 'carbide'

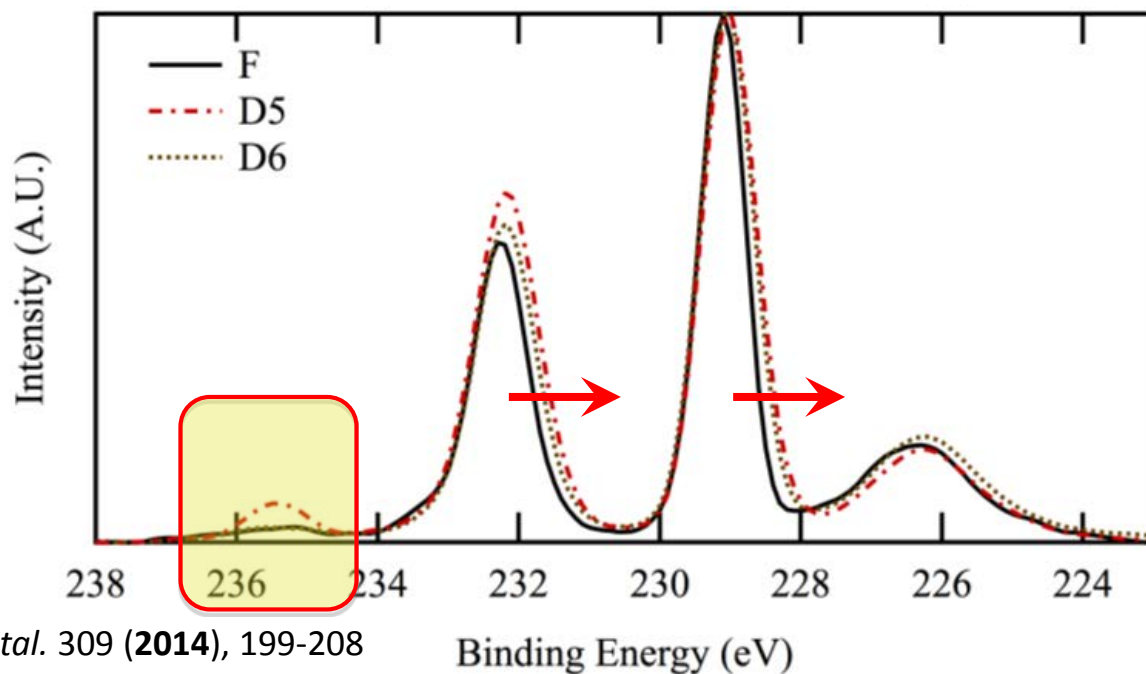
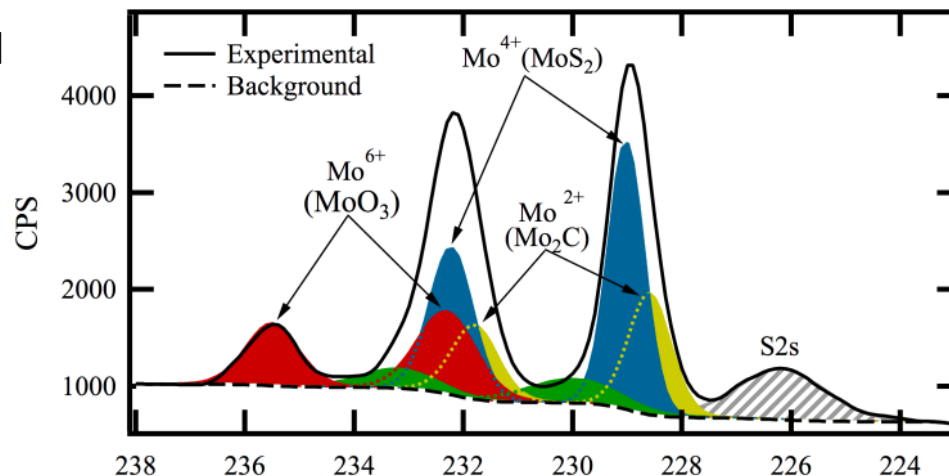


Hensley, JE et al., *J. Catal.* 309 (2014), 199-208

D1 – 120h no sulfur	D2 – 380h no sulfur	D3 – 300h (150h w/ DMDS)	D4 – 500h (300h w/ DMS)	D5 – 1000h w/ H ₂ S	D6 – 4000h w/ H ₂ S
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Fresh vs. Extended TOS

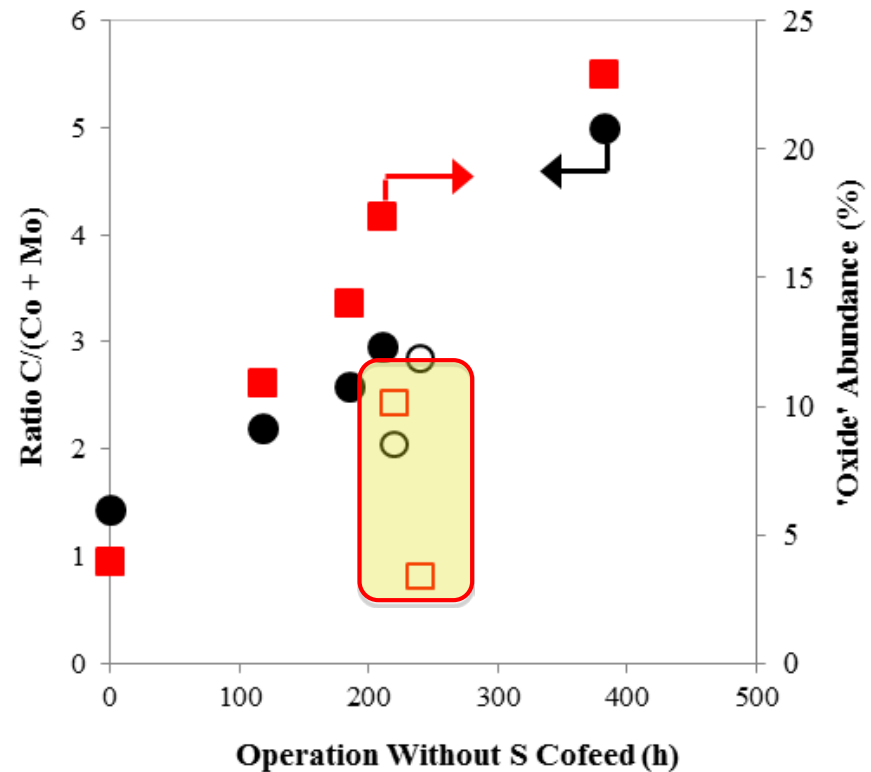
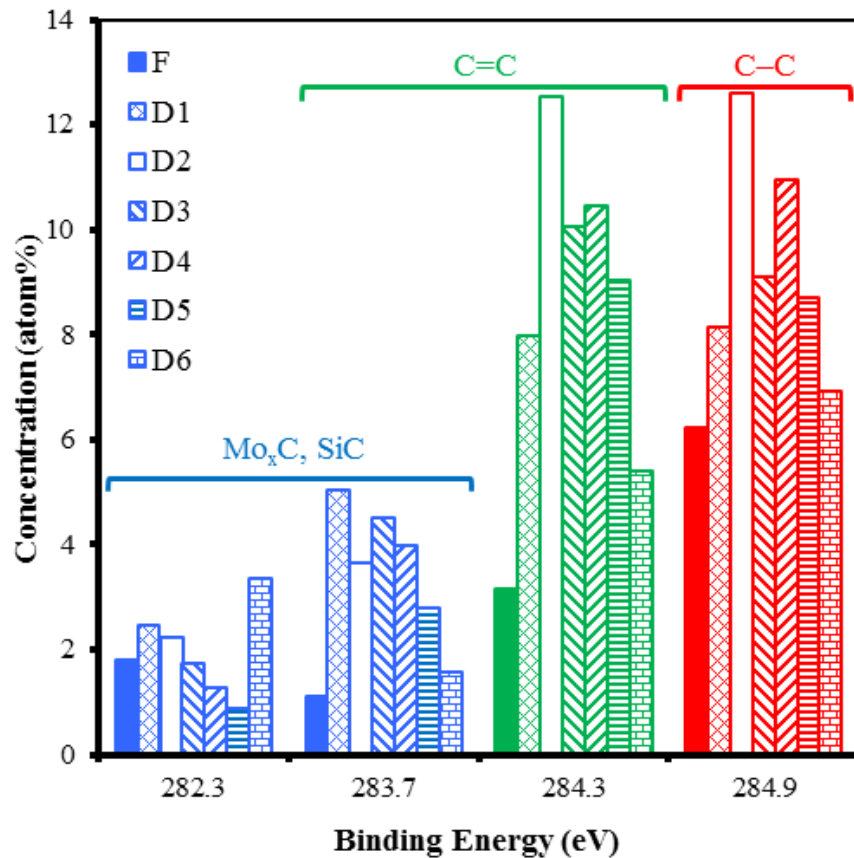
- Smallest changed fresh to discharged
- Longest-run catalyst least oxidized
- Suggests *activity* loss not due to oxidation
- *Selectivity* change could be due to oxidation
- Evidence of carbide formation



Hensley, JE et al., *J. Catal.* 309 (2014), 199-208

D1 – 120h no sulfur	D2 – 380h no sulfur	D3 – 300h (150h w/ DMDS)	D4 – 500h (300h w/ DMS)	D5 – 1000h w/ H ₂ S	D6 – 4000h w/ H ₂ S
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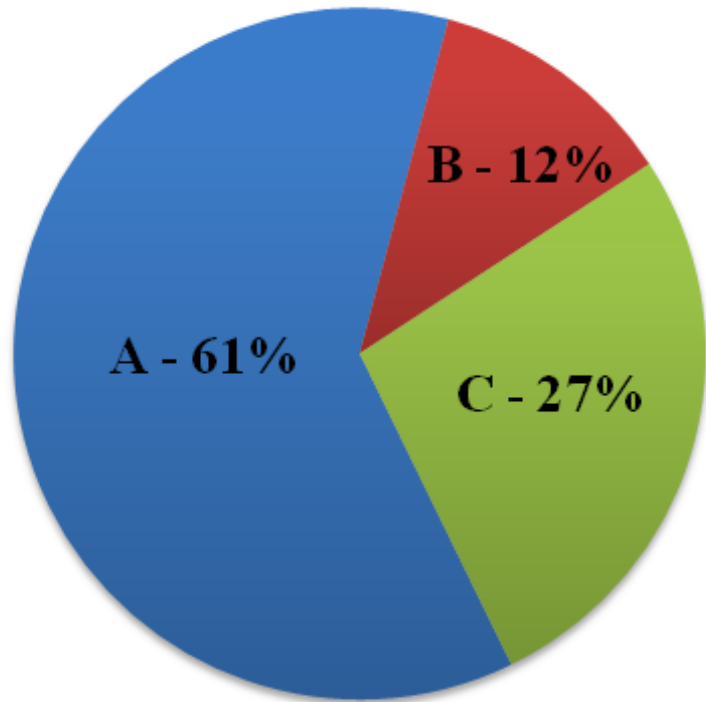
Deactivation Correlates with Oxidation, Coke



- Contributions from both carbide and coke-like C
- Total C increases with time on stream without S cofeed
- Abundance of oxide increases with time on stream without cofeed
- Suggests oxidized surface promotes coke formation (perhaps due to increased acidity)
- Catalysts with long periods in H₂S after interruption in feed less oxidized but still coked (suggests oxide formation reversed with H₂S but coke formation 'permanent')

D1 – 120h no sulfur | D2 – 380h no sulfur | D3 – 300h (150h w/ DMDS) | D4 – 500h (300h w/ DMS) | D5 – 1000h w/ H₂S | D6 – 4000h w/ H₂S

Mixed Alcohol Product is Complex



■ A-Oxygenates ■ B-Hydrocarbons ■ C-CO2

Median composition of crude product – samples collected over broad range of operating conditions

Alcohols (93-97.5% of oxygenates)

methanol	48-64%
ethanol	30-40%
1-propanol	2-9%
2-propanol	< 0.5%
1-butanol	0.3-2%
isobutanol	0.1-1.1%
1-pentanol	< 0.5%
isopentanol	< 0.25%
1-hexanol	< 0.15%
isohexanol	< 0.07%
1-heptanol	< 0.07%
1-octanol	< 0.03%

Aldehydes (0.5-2.5% of oxygenates)

acetaldehyde	26-55%
propanaldehyde	5-15%
ethane, 1,1-dimethoxy-*	22-49%
ethane, 1-ethoxy-1-methoxy*	13-34%
propane, 1,1-dimethoxy*	3-11%

Water (0.5-3% of oxygenates)**

Esters (0.5-4% of oxygenates)

methanol	52-
methyl acetate	72%
	23-
ethyl acetate	35%
propyl acetate	2-8%
propanoic acid, ethyl ester	1-8%
methyl butanoate	2-5%
butanoic acid, ethyl ester	3-9%

Methane (76-93% of hydrocarbons)

Paraffins (2.5-6% of hydrocarbons)

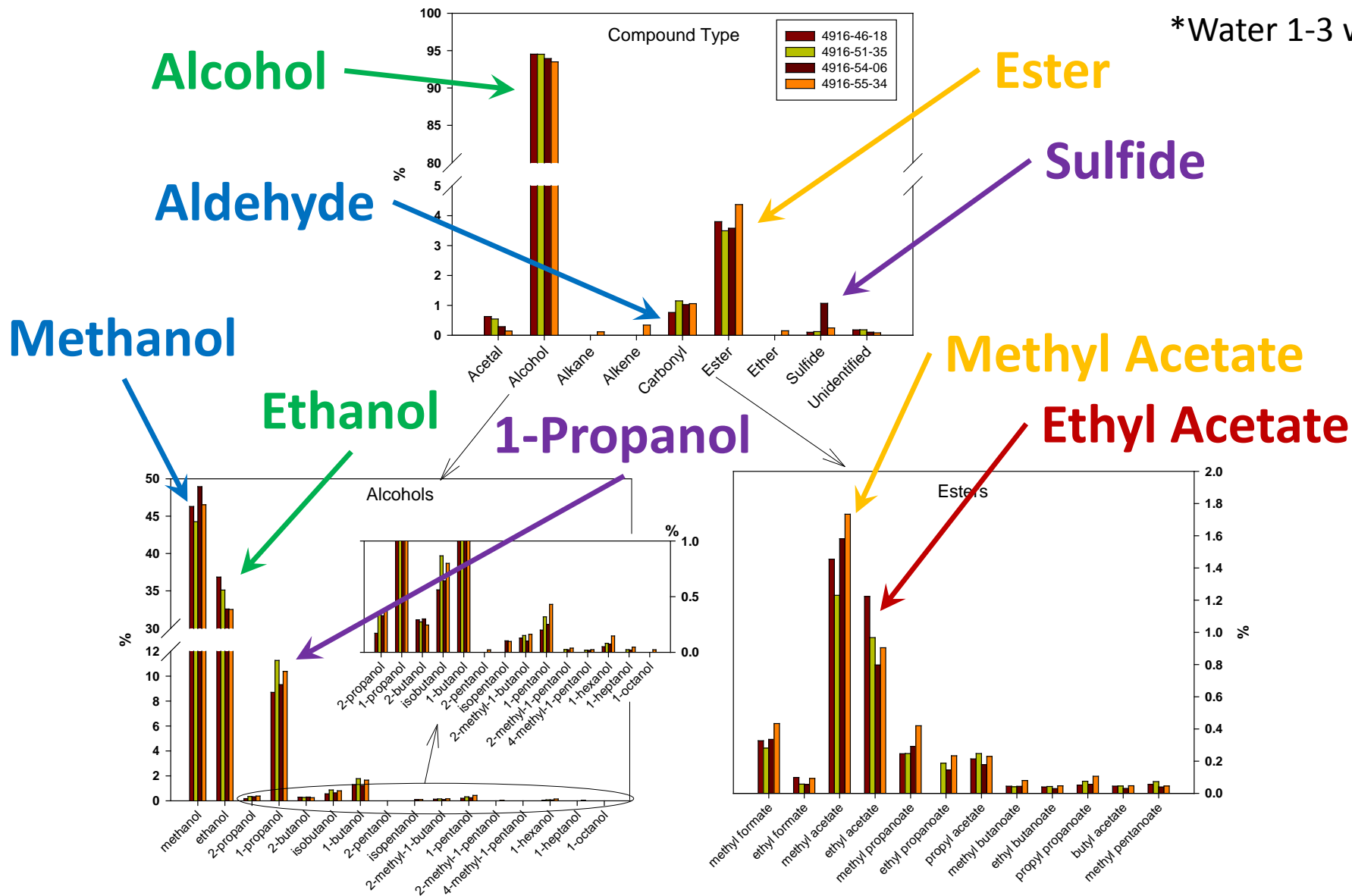
	75-
ethane	95%
propane	5-20%
butanes†	< 10%
pentanes^	< 1%

Olefins (4.5-18% of hydrocarbons)

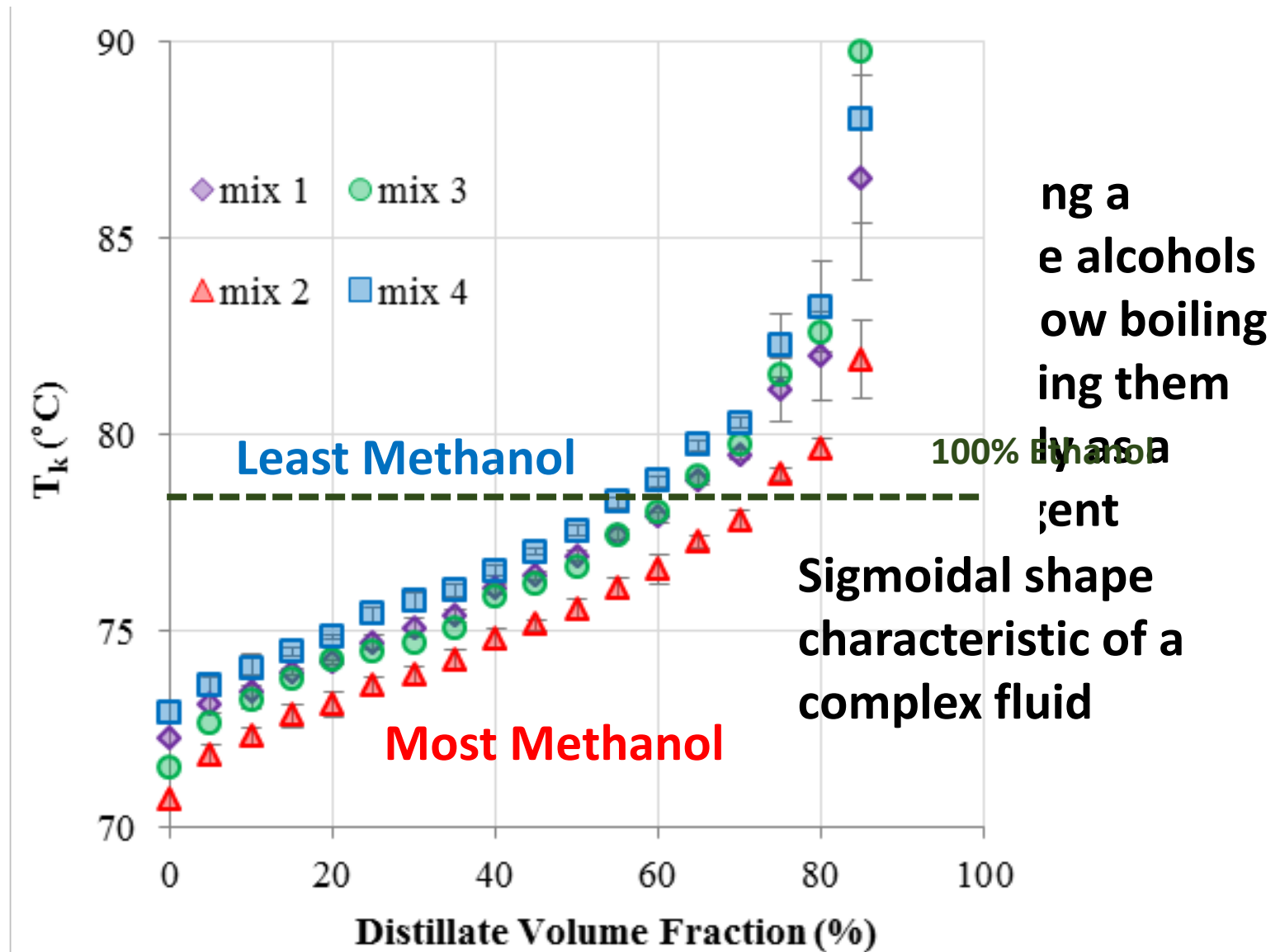
	60-
ethene	70%
	25-
propene	35%
butenes‡	5-10%
pentenes^	< 1%

...And Largely Indifferent to Process Conditions

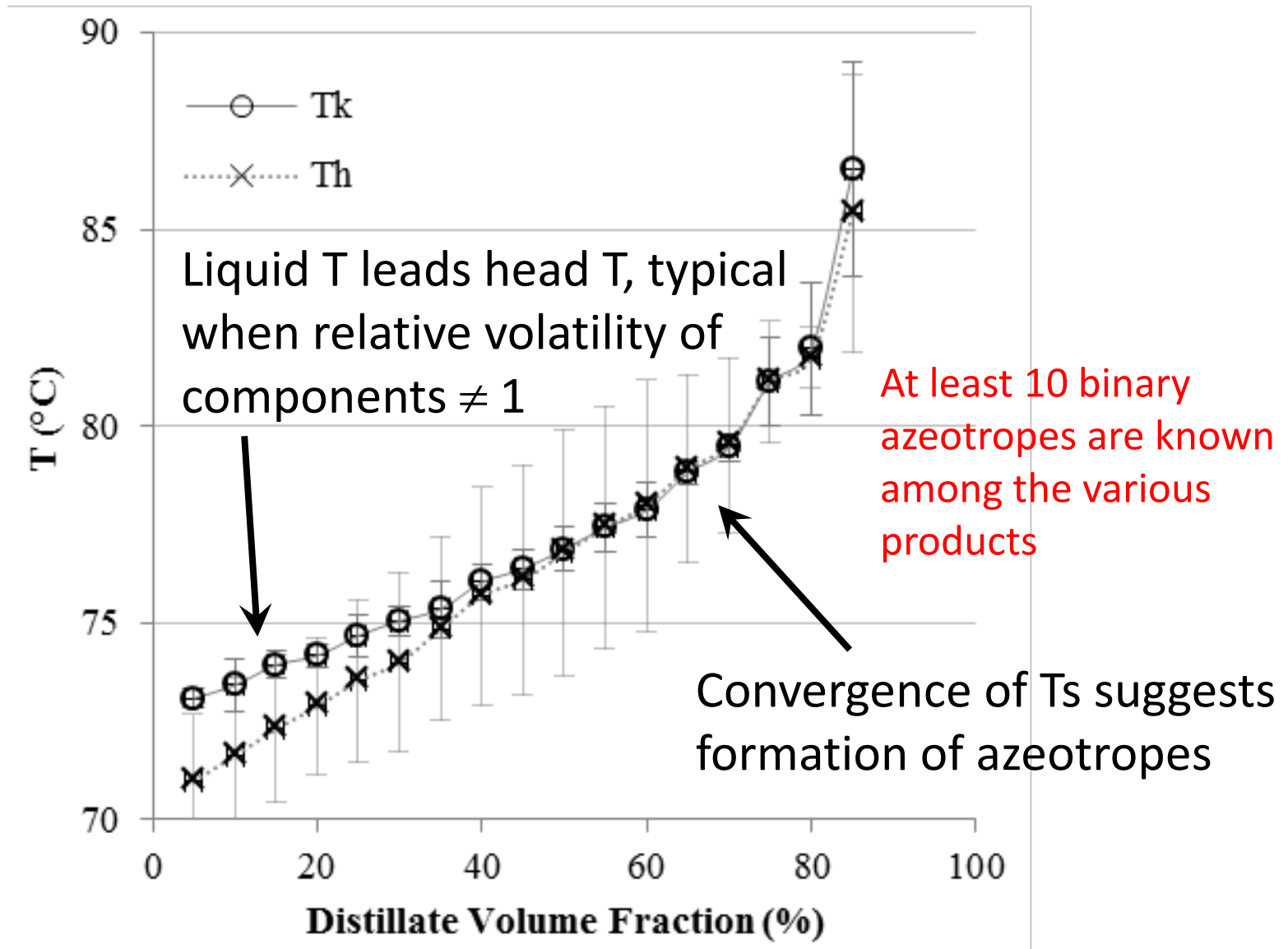
*Water 1-3 wt%



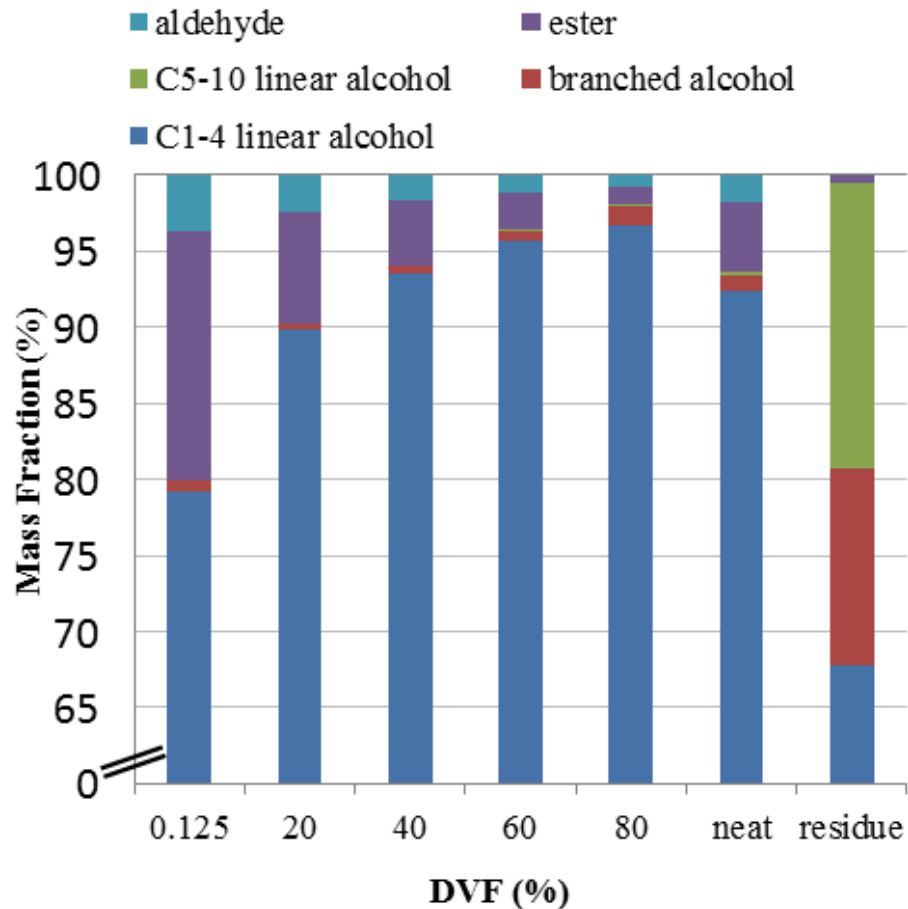
Crude Alcohols Much Different from Gasoline



Worse Yet, Separations not Straightforward



Composition of Distilled Fractions



Sulfides, non-alcohol oxygenates preferentially removed in first 20% of distilled volume
= **overhead product in fractional distillation**

Example Blends with Gasoline

- **Crude mixed alcohols**

- > 50% methanol
- No distillation
- Most S removal required
- Most non-ROH oxygenates

8.5 vol% in gasoline

- **Remove 50% MeOH**

- Larger ratio C2+ alcohol
- Moderate distillation duty
- S removed to level practical with distillation
- Non-ROH oxygenates substantially removed

9.2 vol% in gasoline

- **Remove 55-65% MeOH**

- Maximize blend limit for Octamix
- Greater distillation duty
- Negligible gains in non-ROH oxygenate and S removal

10 vol% in gasoline

Conclusions from Analyses of Crude Product

- **The crude product is complex**
- **Ethanol will be difficult/expensive to isolate**
- **Sulfur in the product (a big concern) is predominantly removed in simple distillation**
- **Given further study and certification, the mixed alcohol product is probably the more reasonable target product**

Acknowledgements



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(with contributions to these slides from)

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PURMET Development