

# Northwest Efforts Toward Producing Aviation Fuels Using Hybrid Approaches

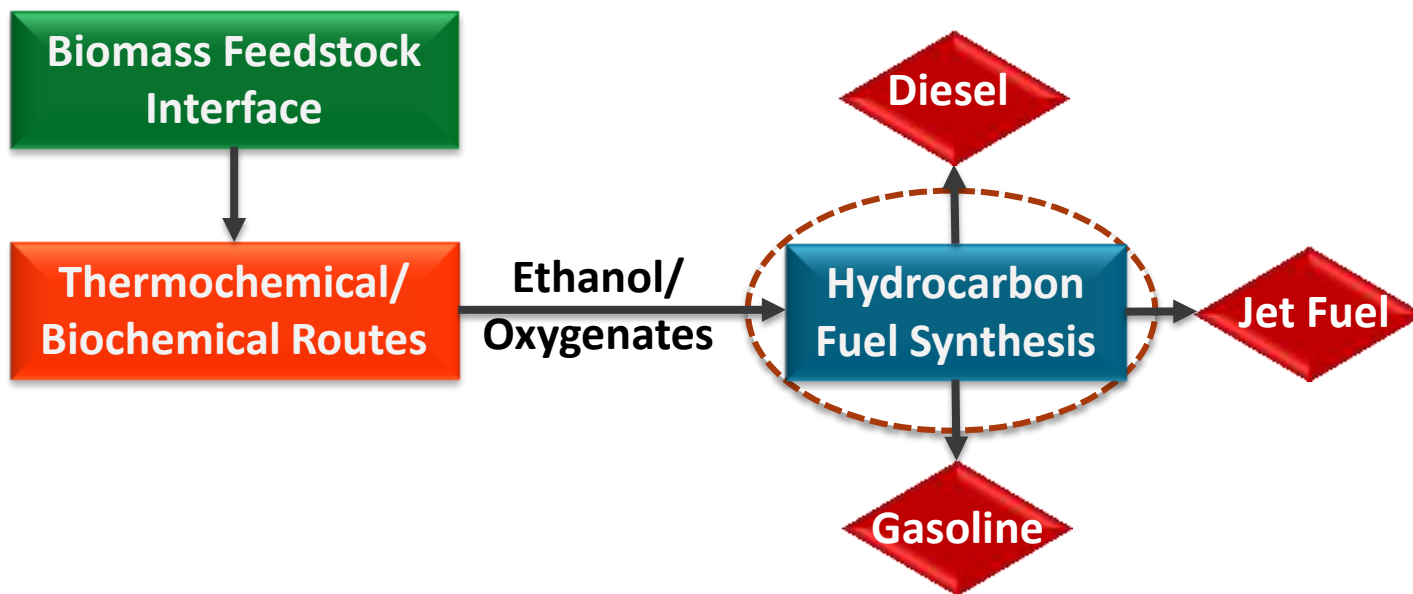
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# Ethanol and Other Oxygenates

- ▶ Upgrading of minimally treated, non-fuel grade ethanol, and/or
- ▶ Mixed alcohols and other oxygenates to hydrocarbon fuels



# Ethanol Case Study

- ▶ Partnership with Imperium Aviation Fuels
- ▶ Technical feasibility assessment supported by experimental data
- ▶ Demonstrated upgrading to hydrocarbon meeting jet specifications

Systems	MTG	MOGD-Base	MOGD-Jet
Energy yield (MJ/MJ energy input)			
Jet fuel	0	0.360	0.635
LPG	0.270	0	0
Gasoline	0.574	0.399	0.087
Diesel	0.037	0.048	0.085
Fuel gas	0.046	0	0
Total	0.927	0.807	0.807

- ▶ Models assembled to assessment routes for ethanol based upon literature data for MTG and MOGD like processes
- ▶ Energy efficiency of routes estimated using model
- ▶ Experimental data from MTG like process supports the production of a fraction of hydrocarbons that have jet fuel properties

# Ethanol Case Study

- ▶ Ethanol feed to a “MTG” like process (H-ZSM-5)
- ▶ Lab and bench scale experiments conducted
- ▶ Liter quantity of samples produced for further testing and evaluation



# Ethanol Case Study

- ▶ PNNL prepared samples for fuel property evaluation
- ▶ Off-site specification testing conducted by AFRL



- ▶ Possible jet fuel blend stock
- ▶ Large volume samples required for fit-for-purpose testing

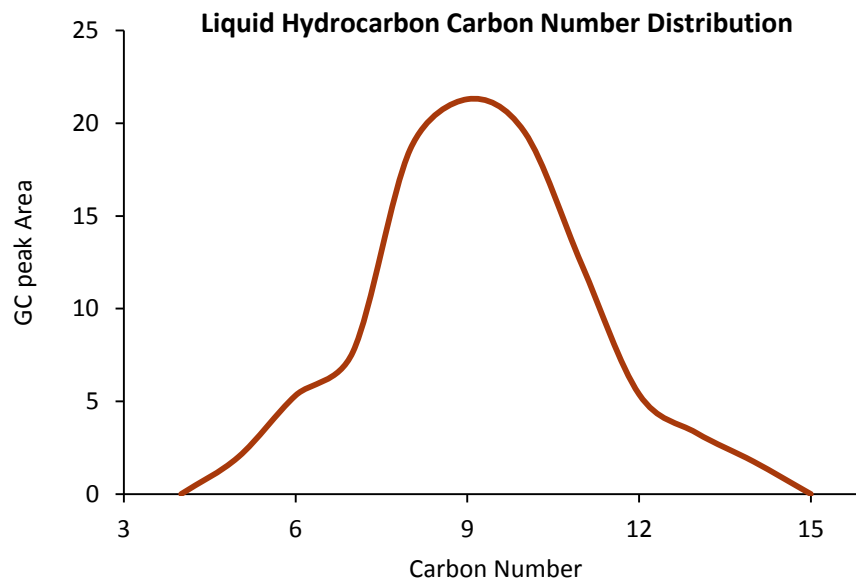


Specification Test	MIL-DTL-83133H Spec Requirement	PNNL-1	PNNL-2	FT-SPK	JP-8
Aromatics, vol %	≤25	1.9	2.2	0.0	18.8
Olefins, vol %		1.2	1.1	0.0	0.8
Heat of Combustion (measured), MJ/Kg	≥42.8	43.1	43.1	44.3	43.3
<b>Distillation:</b>					
IBP, °C		161	165	144	159
10% recovered, °C	≤205	165	171	167	182
20% recovered, °C		166	173	177	189
50% recovered, °C		171	183	206	208
90% recovered, °C		190	220	256	244
EP, °C	≤300	214	243	275	265
T90-T10, °C	22	25	49	89	62
Residue, % vol	≤1.5	1.1	1.1	1.5	1.3
Loss, % vol	≤1.5	1	0.8	0.9	0.8
Flash point, °C	≥38	44	48	45	51
Freeze Point, °C	≤-47	<-60	<-60	-51	-50
Density @ 15°C, kg/L	0.775 - 0.840 (0.751 - 0.770)	0.803	0.814	0.756	0.804

# Upgrading Mixed Alcohol Product

- ▶ Mixed alcohol product from PNNL Syngas to Alcohols Project
- ▶ Demonstrated feasibility of upgrading to hydrocarbon
- ▶ The product contains primarily aromatic components in the gasoline range carbon number with ~50% overlap with jet

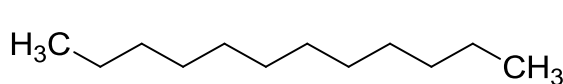
Compounds	Feed Concentration (wt%)
Methanol	0 to 2.5
Ethanol	8 to 28
C3+ Alcohols	1 to 3
Acetic Acid	4 to 14
C2+ Aldehydes	6 to 17
Ethyl Acetate	1 to 18
Water	41 to 60



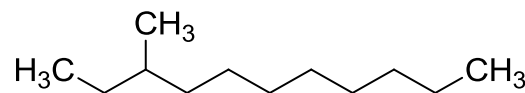
# The compound classes in jet fuels

## Ideal Carbon Length C8-C16

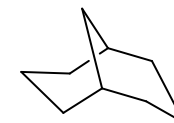
### Paraffins 70 - 85%



Normal Paraffins

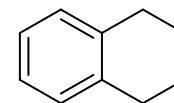
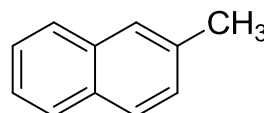
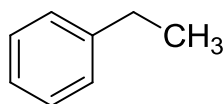


Iso-paraffins

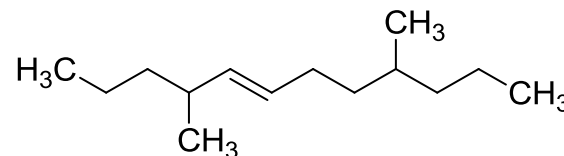
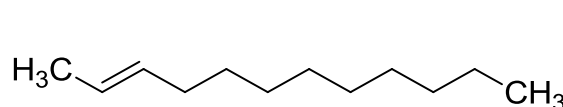


Cyclic Paraffins

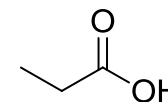
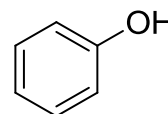
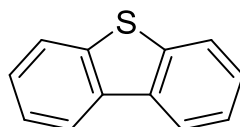
### Aromatic < 25%



### Olefins < 5%



### S, N, O containing Compounds < 5%



We desire fuels with composition similar to above  
(i.e. a replacement or “drop-in” fuel)



# Contribution of Different Hydrocarbon Classes to Jet Fuel

## Potential Contribution\* of Each Hydrocarbon Class to Selected Jet Fuel Properties (For hydrocarbons in the jet fuel carbon number range)

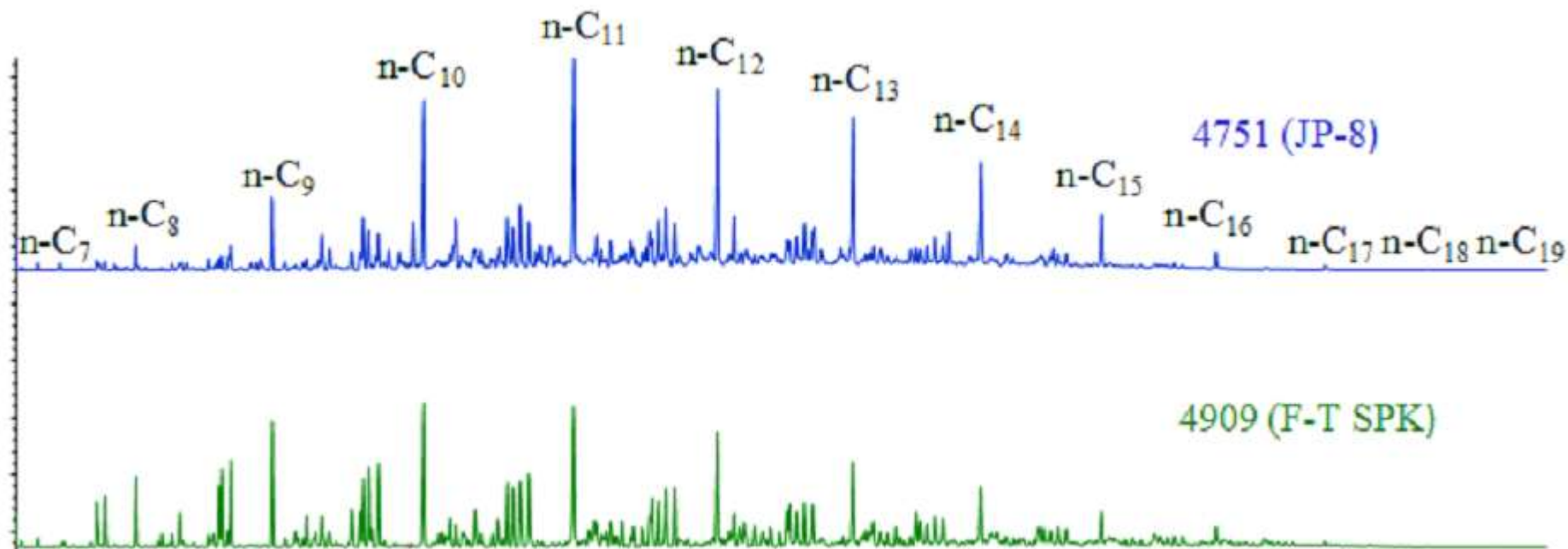
Jet Fuel Property	Hydrocarbon Class			
	n-Paraffin	Isoparaffin	Naphthene	Aromatic
Energy content:				
Gravimetric	+	+	0	-
Volumetric	-	-	0	+
Combustion quality	+	+	+	-
Low-temperature fluidity	--	0/+	+	0/-

\* "+" indicates a beneficial effect, "0" a neutral or minor effect, and "-" a detrimental effect.

- ❖ Aromatics in jet fuel also helps elastomers in the fuel system to swell and seal properly at low temperature

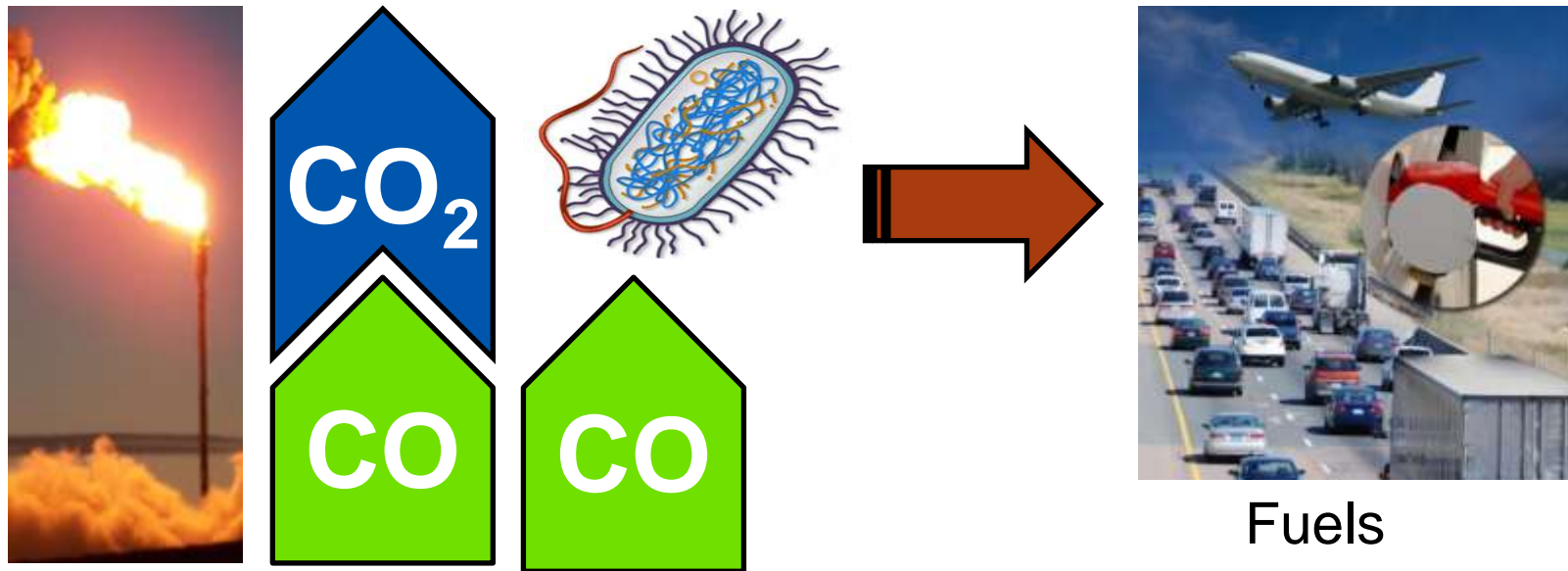


# Type of molecules



# Ethanol-to-Jet Requires Low Cost Ethanol

CO-rich gasses can be captured from syn gas or from industrial processes. Industrial-rich CO is **always** converted to CO<sub>2</sub> either before or after release into the atmosphere



*Intercept CO<sub>2</sub> formation by using  
CO for alcohol production*

# Gas flexibility opens up new options for waste resources

LanzaTech 



**Industrial flue gas**  
e.g. from Steel Mill



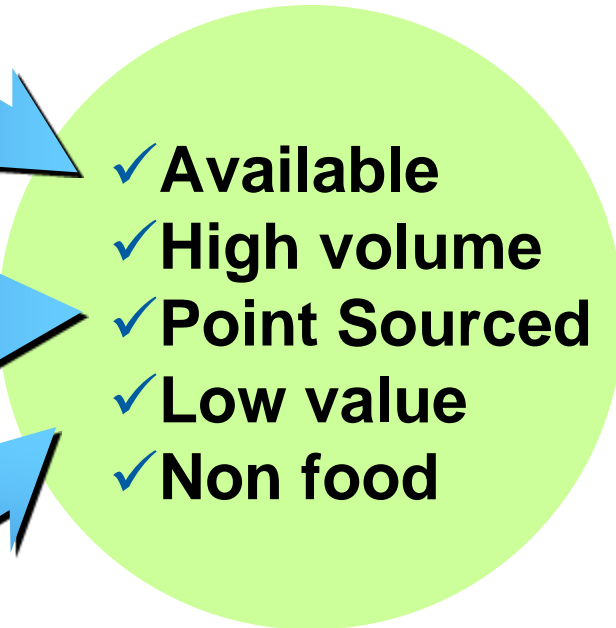
**Syngas**  
Municipal Solid  
Waste (MSW)



**Steam Reformed  
Methane**  
e.g. Biogas

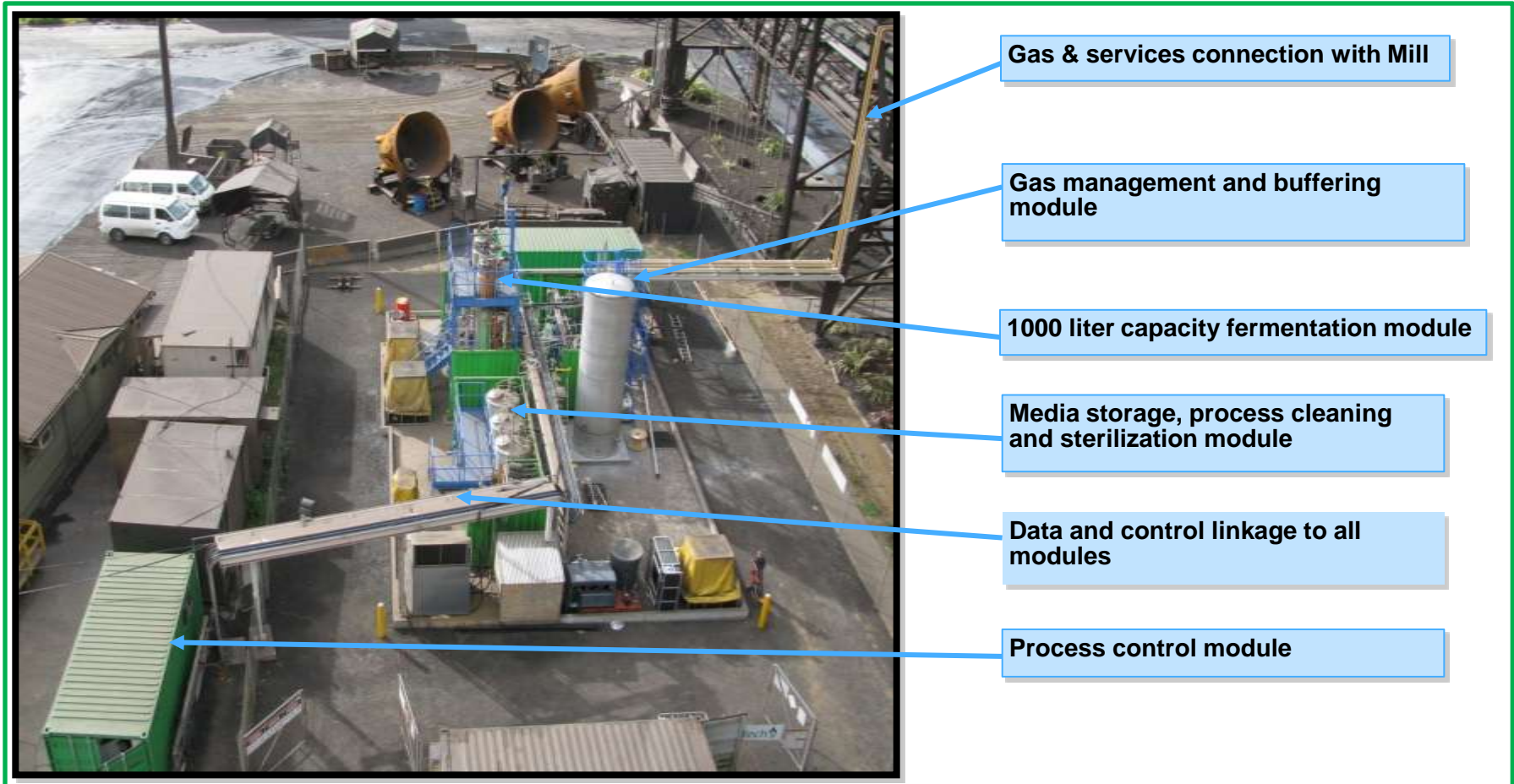


**Coke Ovens Gas**

- 
- ✓ Available
  - ✓ High volume
  - ✓ Point Sourced
  - ✓ Low value
  - ✓ Non food

***Focus of PNNL-Imperium-LanzaTech CRADA is on use of Biomass-Derived Synthesis Gas***

# Building from Pilot Plant Operations from Steel Mill waste gasses





# Initial demonstration using biomass shows promise...



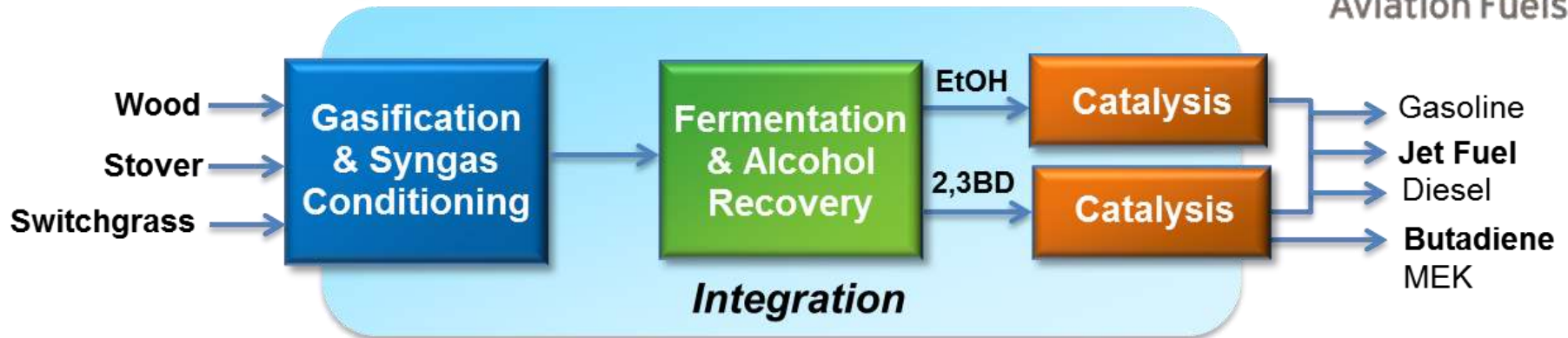
- ▶ Process used with biomass syngas
- ▶ Syngas from two biomass gasification technologies successfully tested
- ▶ Real biomass syngas used in all process demonstrations
- ▶ Initial results show ability to reach commercial production rates

- ✓ **Set up pilot unit at NREL**
- ✓ **Focus in CRADA effort will be to determine minimum processing needs of the syn gas and to demonstrate that commercial production rates can be achieved**

# Alcohol to Jet Technologies



Hybrid Thermal-Biotech-Catalytic Process



- ▶ Minimally processed alcohols produced by LanzaTech, at NREL, are being sent to PNNL
- ▶ PNNL, partnering with Imperium, is integrating the catalytic steps to produce the final fuels for the purpose of
  - Demonstrating the integration of catalytic unit operations
  - Demonstrating fuel quality (producing material for fuel qualification testing and for fit for purpose testing)
  - Develop catalyst process to produce higher value chemical compounds in the process in addition to the jet fuel

# Parting Thoughts

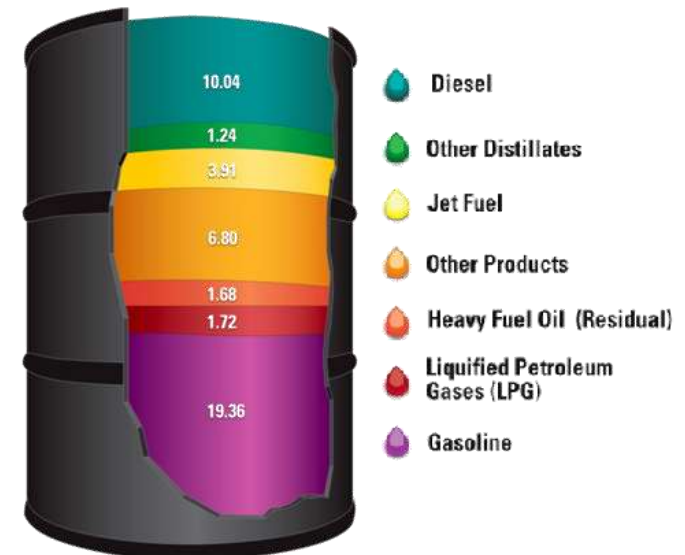
Drop-In and Renewable Fuels can provide:

- ▶ Increased US Security (Economic/Energy)
- ▶ Reduced environmental impact relative to fossil energy sources

Looking forward:

- ▶ Examine routes that maximize existing infrastructure and capital investments, and
- ▶ Seek to replace any of the carbon in the barrel of oil with equality and commitment to long term environmental considerations.

**Products Made from a  
Barrel of Crude Oil (Gallons)**  
(2009)



Source: Energy Information Administration, "Oil: Crude Oil and Petroleum Products Explained" and AEO2009, Updated February 2010, Reference Case.

# Acknowledgment

- ▶ Upgrading of oxygenates was supported by funding from Imperium Aviation Fuels and Battelle Memorial Institute through an Internal Research and Development Project.
- ▶ The LanzaTech-Imperium-PNNL project is funded by the US Department of Energy, Office of the Biomass Program



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Energy Efficiency &  
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