Process Development of Biomass to Aviation Biofuel via Gasification and Catalytic Conversion

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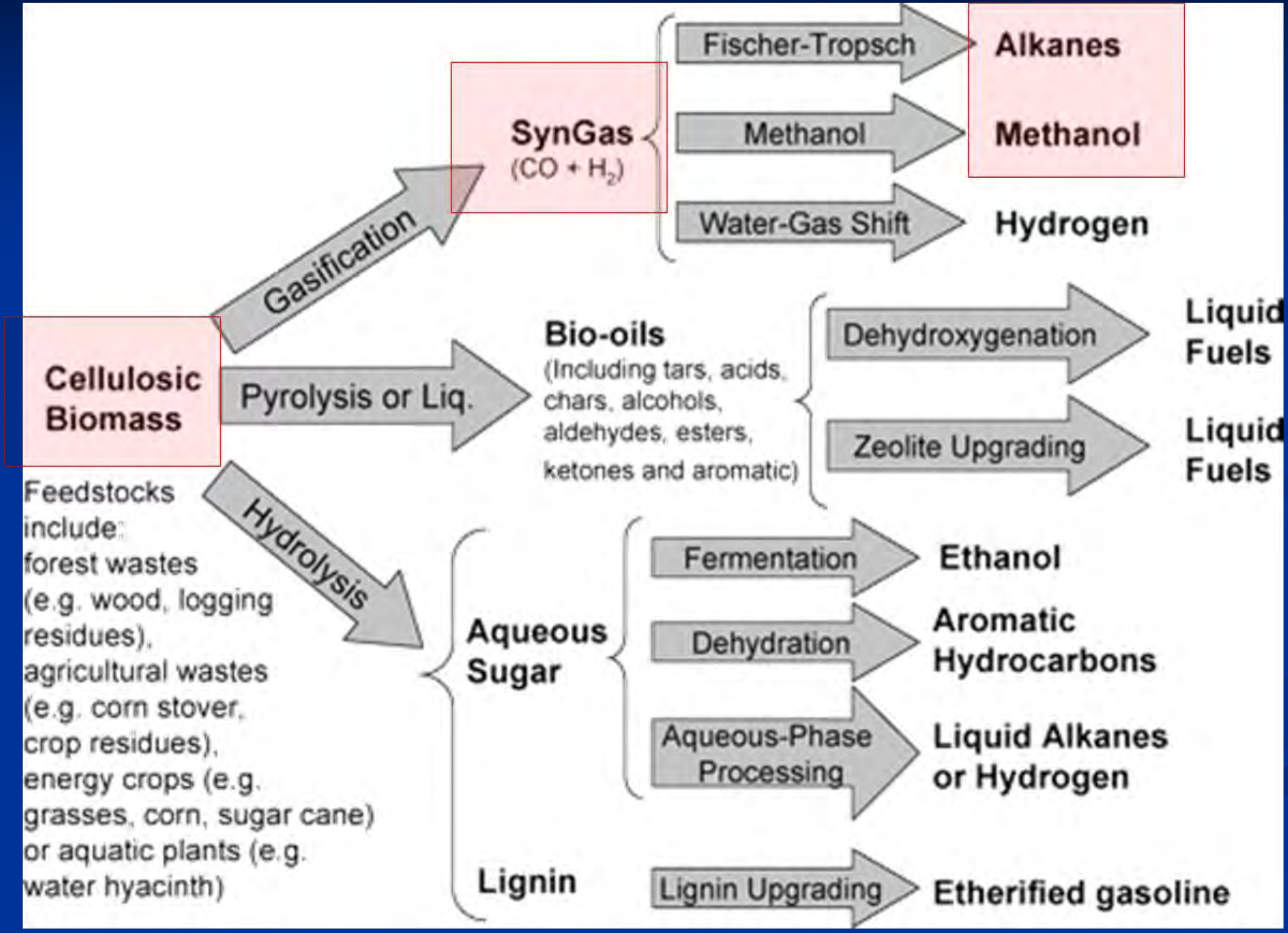
Auburn University, June 14

Outline of Presentation

- Strategies for Production of Fuels from Biomass
- Gasification of Biomass
- Cleaning of Bio-syngas
- Catalytic Upgrading Bio-syngas to Liquid Hydrocarbons

Biofuels Production from Biomass



Cellulosic Biomass

Feedstocks include: forest wastes (e.g. wood, logging residues), agricultural wastes (e.g. corn stover, crop residues), energy crops (e.g. grasses, corn, sugar cane) or aquatic plants (e.g. water hyacinth)

Gasification → **SynGas** ($CO + H_2$)
- Fischer-Tropsch → **Alkanes**
- Methanol → **Methanol**
- Water-Gas Shift → **Hydrogen**

Pyrolysis or Liq. → **Bio-oils** (Including tars, acids, chars, alcohols, aldehydes, esters, ketones and aromatic)
- Dehydroxygenation → **Liquid Fuels**
- Zeolite Upgrading → **Liquid Fuels**

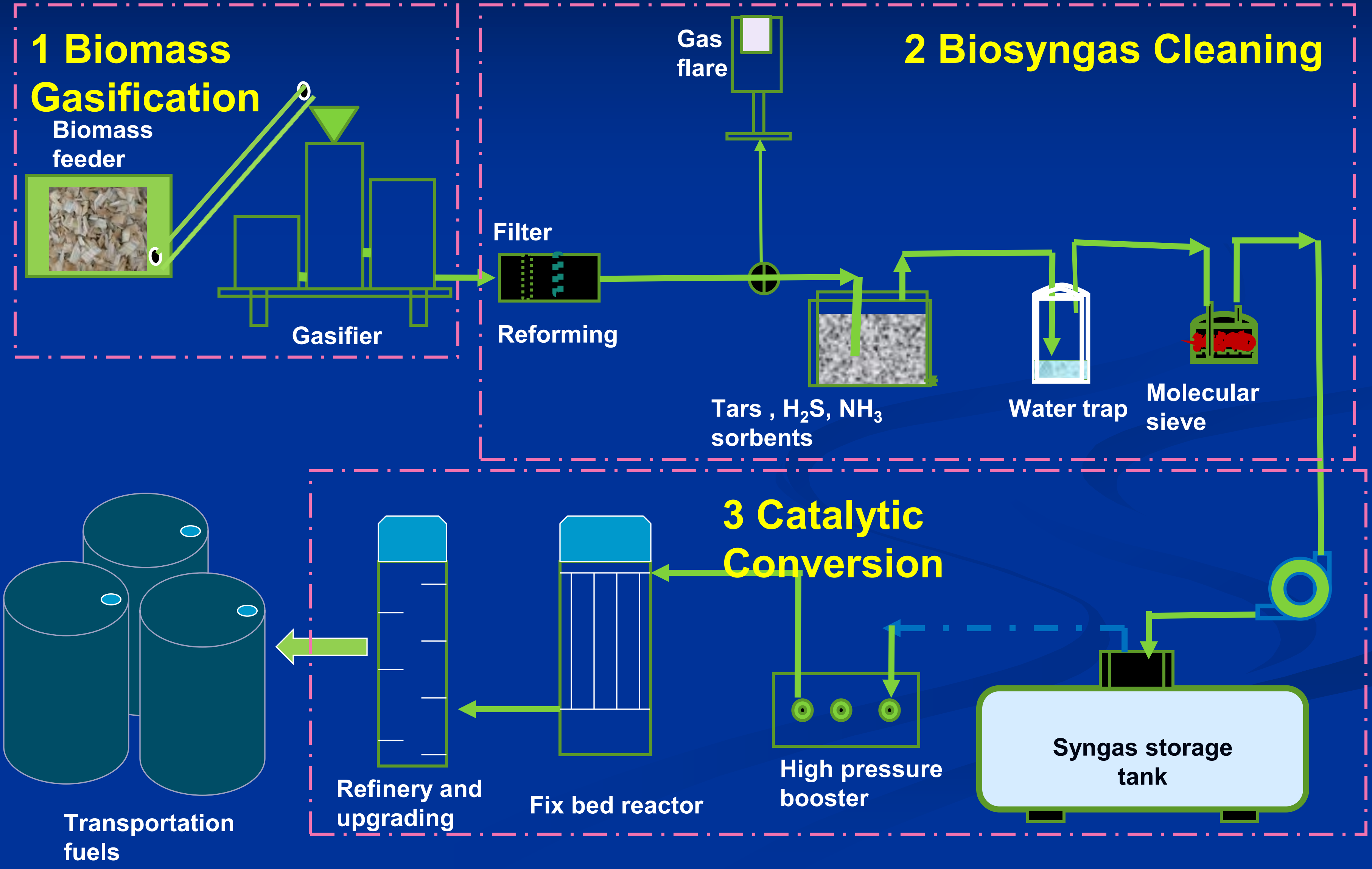
Hydrolysis →

Aqueous Sugar
- Fermentation → **Ethanol**
- Dehydration → **Aromatic Hydrocarbons**
- Aqueous-Phase Processing → **Liquid Alkanes or Hydrogen**

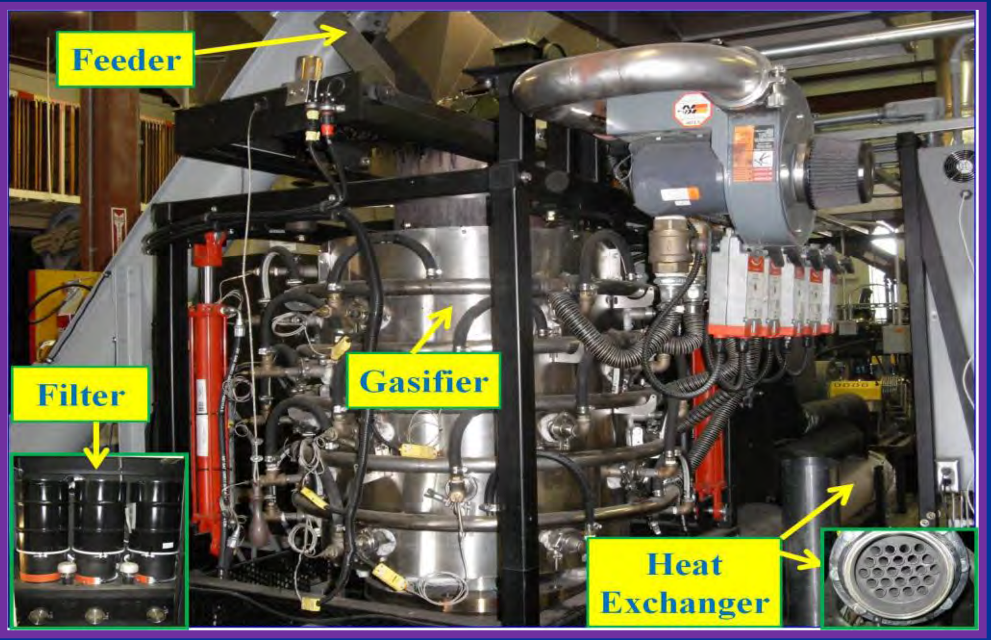
Lignin
- Lignin Upgrading → **Etherified gasoline**

Huber, G. W. and Dumesic, J. A. 2006. *Catal. Today.* 111:119-132.

MSU Syngas to Fuel System

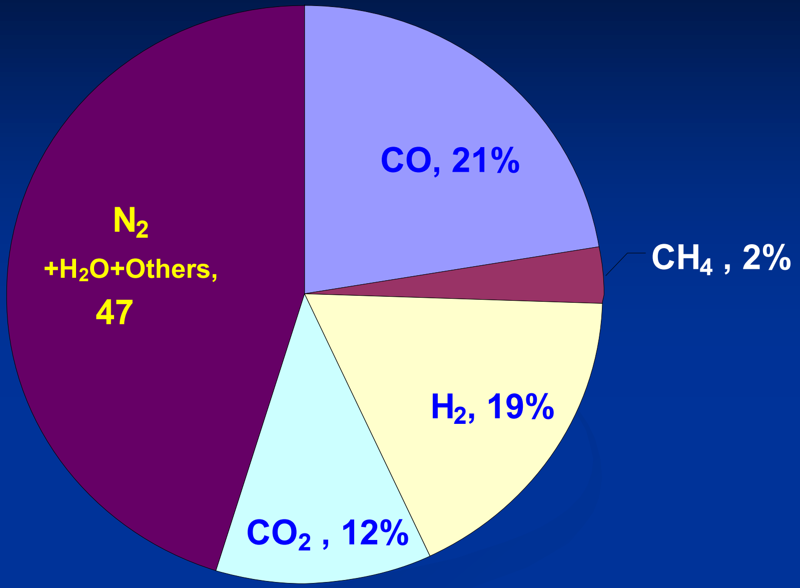


1 Biomass Gasification



Downdraft Gasifier (BioMax25) in MSU-Pace Seed Lab

(60-120 m^3/hr syngas production).



Average Composition of Syngas

Gasifier Type	Particulate (mg/Nm³)	Tar (mg/Nm³)
Downdraft	**10-500**	**10-1,000**
Updraft	100 – 1,000	20,000 – 100,000
Fluidized-bed	2,000 – 20,000	1,000 – 15,000

Wei L. et al. 2009. *Transactions of the ASABE.* 52:1649-1659.

Reaction Describing Biomass Gasification

Biomass + Air (O_2 or H_2O)

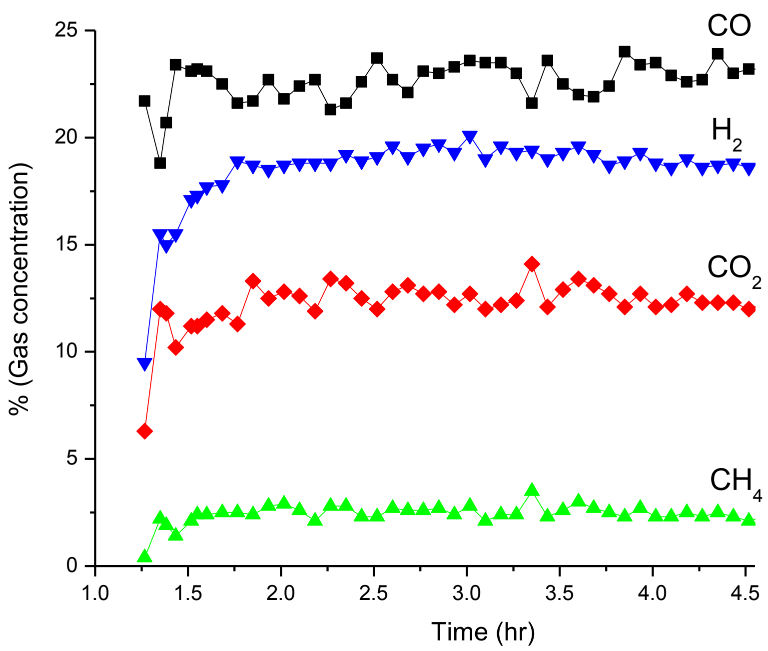
$\rightarrow$ CO, CO_2, H_2O, H_2, N_2, CH_4 + other hydrocarbons

$\rightarrow$ tar + char + ash

$\rightarrow$ NH_3 + H_2S + COS + O_2

Syngas from a biomass gasifier typically contains 10,000-15,000 ppm of tars, 2000-4000 ppm of ammonia, 0.1~2% oxygen, and 100-500 ppm of H_2S

Syngas Production from Wood Chips



Typical syngas composition monitored by a portable gas analyzer.

Feedstock: Oak tree chips

Typical syngas composition

Components	H_2	**CO**	CO_2	CH_4	N_2
Concentration (%)	**18.4**	**21.0**	**11.6**	**1.7**	**47.3**

- Gas **composition ASTM D1945**
- **S compounds ASTM D5504**
- **Tar An European Standard (CEN) Draft**
- **Trace Oxygen in Gases by Gas Chromatography UOP759-76**
- Trace of ammonia by ion selective electrode or ion chromatography ASTM WK6527

Equations for Material Balance and Energy Balance Analysis

Material balance

$$\text{Carbon Conversion Rate} = \frac{\Sigma \text{Carbon Content}_{gas} * \text{Weight}_{gas}}{\text{Carbon Content}_{wood\ chip} * \text{Weight}_{wood\ chip}} \text{ X } 100\% \quad (1)$$

gas = CO, CO2 or CH4

$$\text{Hydrogen Conversion Rate} = \frac{\Sigma \text{Hydrogen Content}_{gas} * \text{Weight}_{gas}}{\text{Hydrogen Content}_{wood\ chip} * \text{Weight}_{wood\ chip}} \text{ X } 100\% \quad (2)$$

gas = H_2 or CH4

Energy balance

$$\text{Energy Conversion Rate} = \frac{\text{LHV}_{syngas} * \text{Volume}_{Syngas}}{\text{LHV}_{wood\ chip} * \text{Weight}_{wood\ chip}} \text{ X } 100\% \quad (3)$$

$$\text{Waste Heat Energy} = \Sigma \int_{T_{room}}^{T_{hex\ in}} \text{Weight}_{gas} * C_{p,gas}\, dT \quad (4)$$

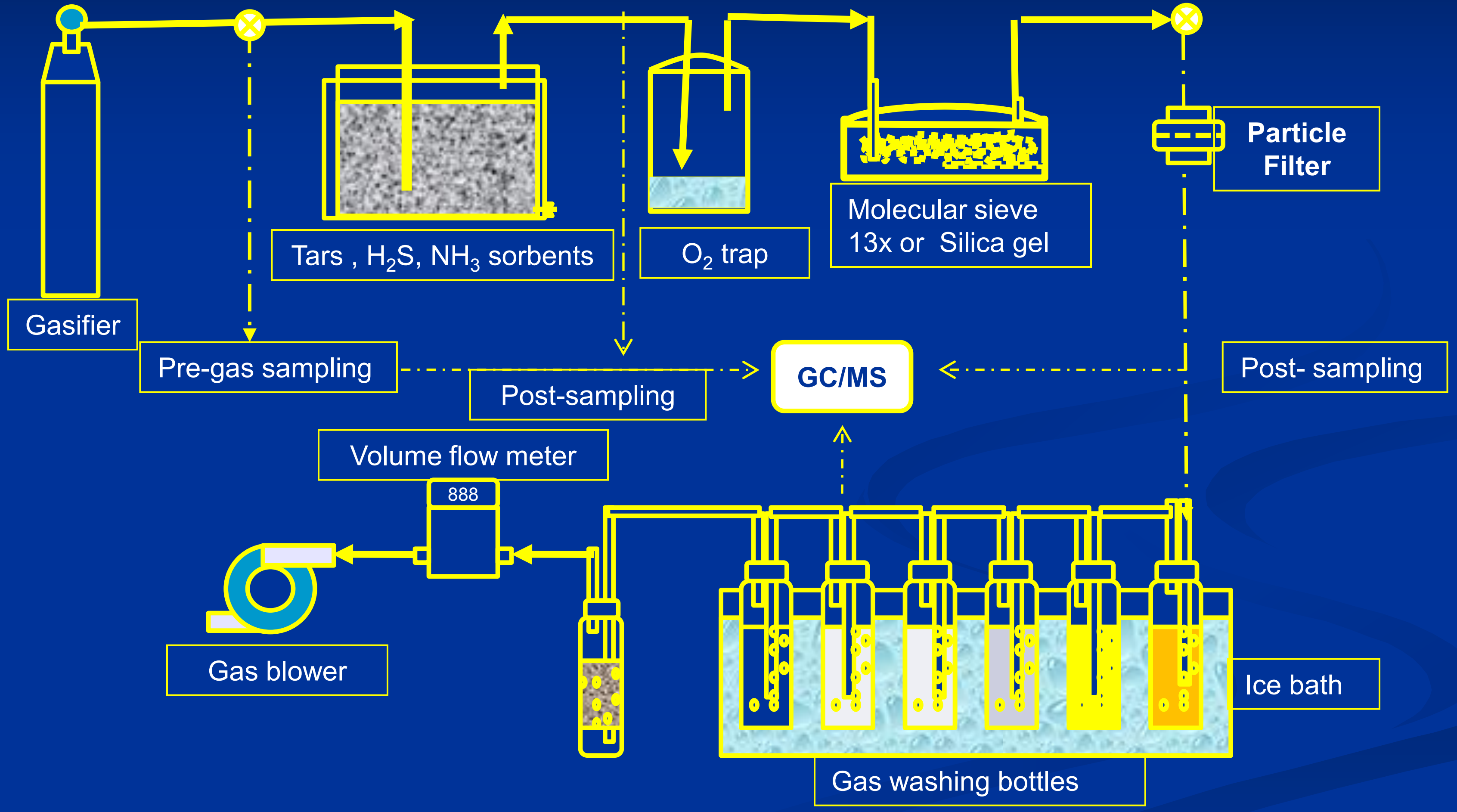
$$\text{LHV} = 12.622\, P_{CO} + 10.788 P_{H2} + 35.814 P_{CH4}$$

$T_{hex\ in,}$ the temperature of gases when getting in the heat exchanger

Material Balance and Energy Balance Analysis

	Run 1	Run 2	Run 3
Wood chip consumption rate (kg/h)	27.8	26.5	29.3
Moisture content of wood (%)	9.5	8.3	10.8
Syngas production rate (kg/h)	70.2	71.2	73.0
Sygngas yield (kg/kg wood) (Nm^3/kg wood)	2.5 (2.3)	2.7 (2.5)	2.5 (2.2)
Biochar/ash yield (g/kg wood)	7.7	10.5	7.6
Carbon conversion rate (%)	92.1	98.9	99.9
Hydrogen conversion rate (%)	67.5	75.4	71.4
Syngas LHV (MJ/Nm^3)	5.1	5.3	5.5
Energy conversion rate (%)	59.5	65.2	62.3
Waste heat energy rate (%)	10.4	11.9	11.0
Energy consumed by gasifier (%)	30.1	22.9	26.7

2 Biosyngas Cleaning



MSU Biosyngas Cleaning System

Deep Purification of Wood Syngas

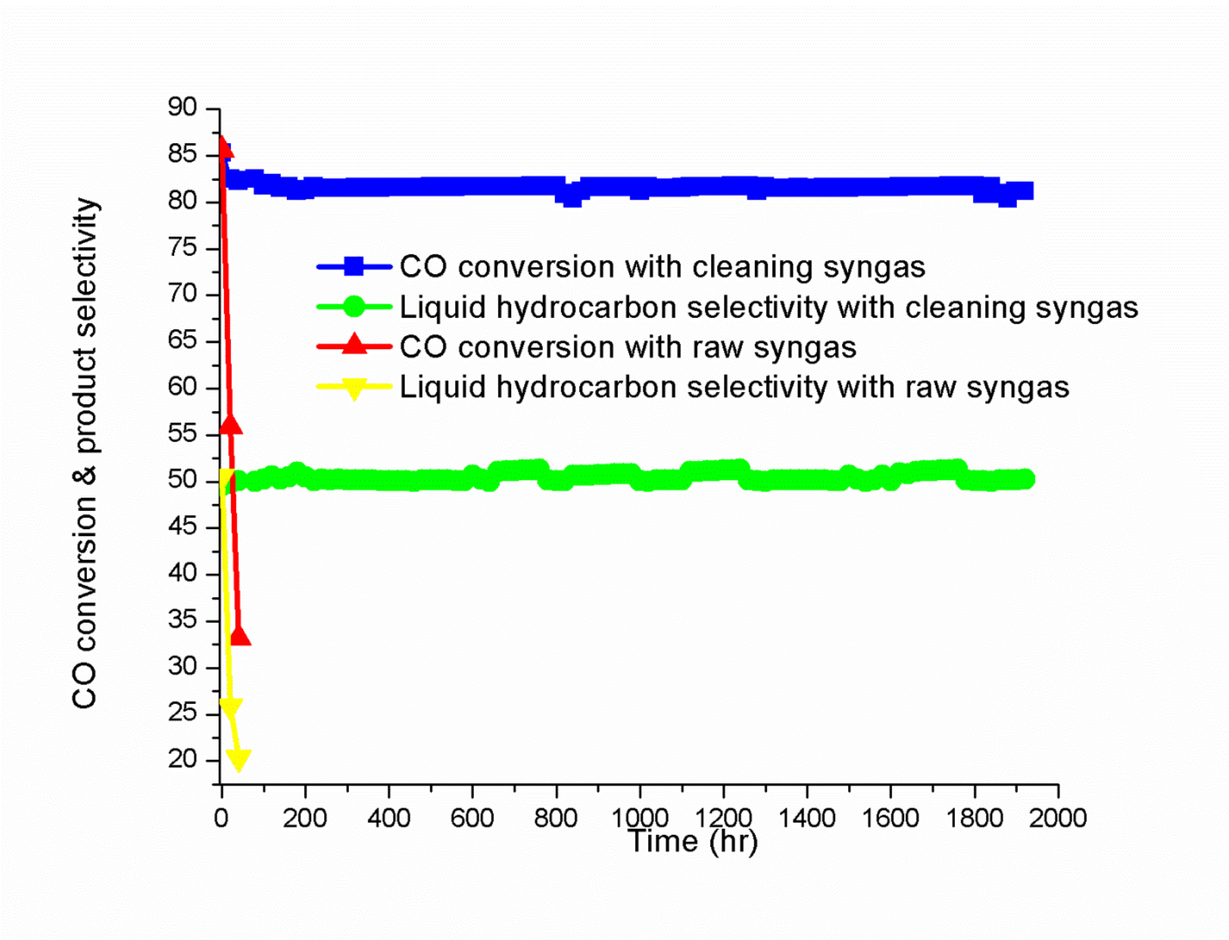
Bench-scale wood syngas cleaning system

Pilot-scale syngas cleaning system

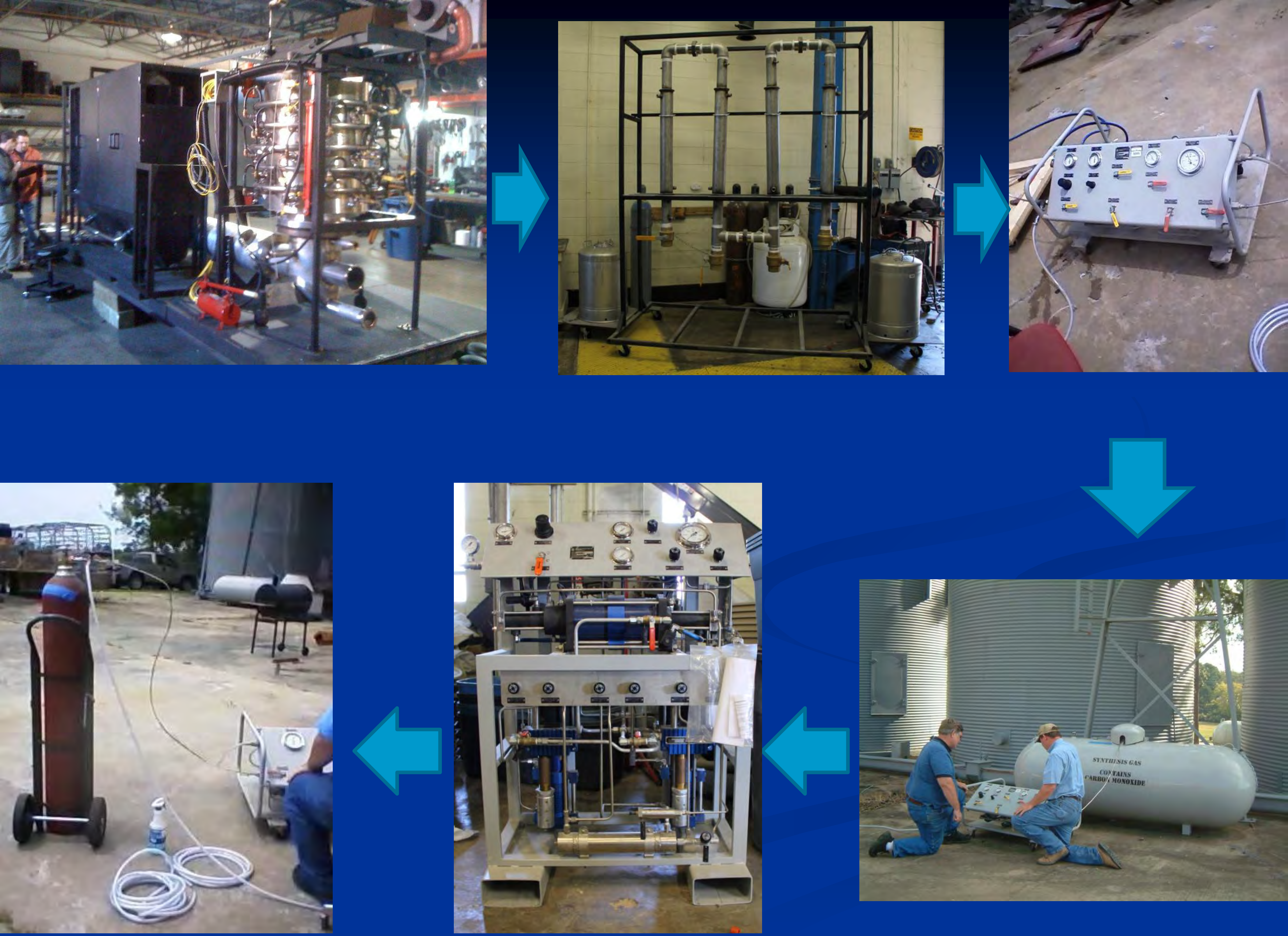
Impurities identified from wood syngas before and after cleaning

Components	Tar	Oxygen	NH_3	H_2S + COS
Before Cleaning	500-3000 ppm	0.1~2%	200-1000	200-400 ppm
After Cleaning	<1ppm	<0.1ppm	<1ppm	<1ppb

Effect of Syngas Cleaning on Catalyst Performance

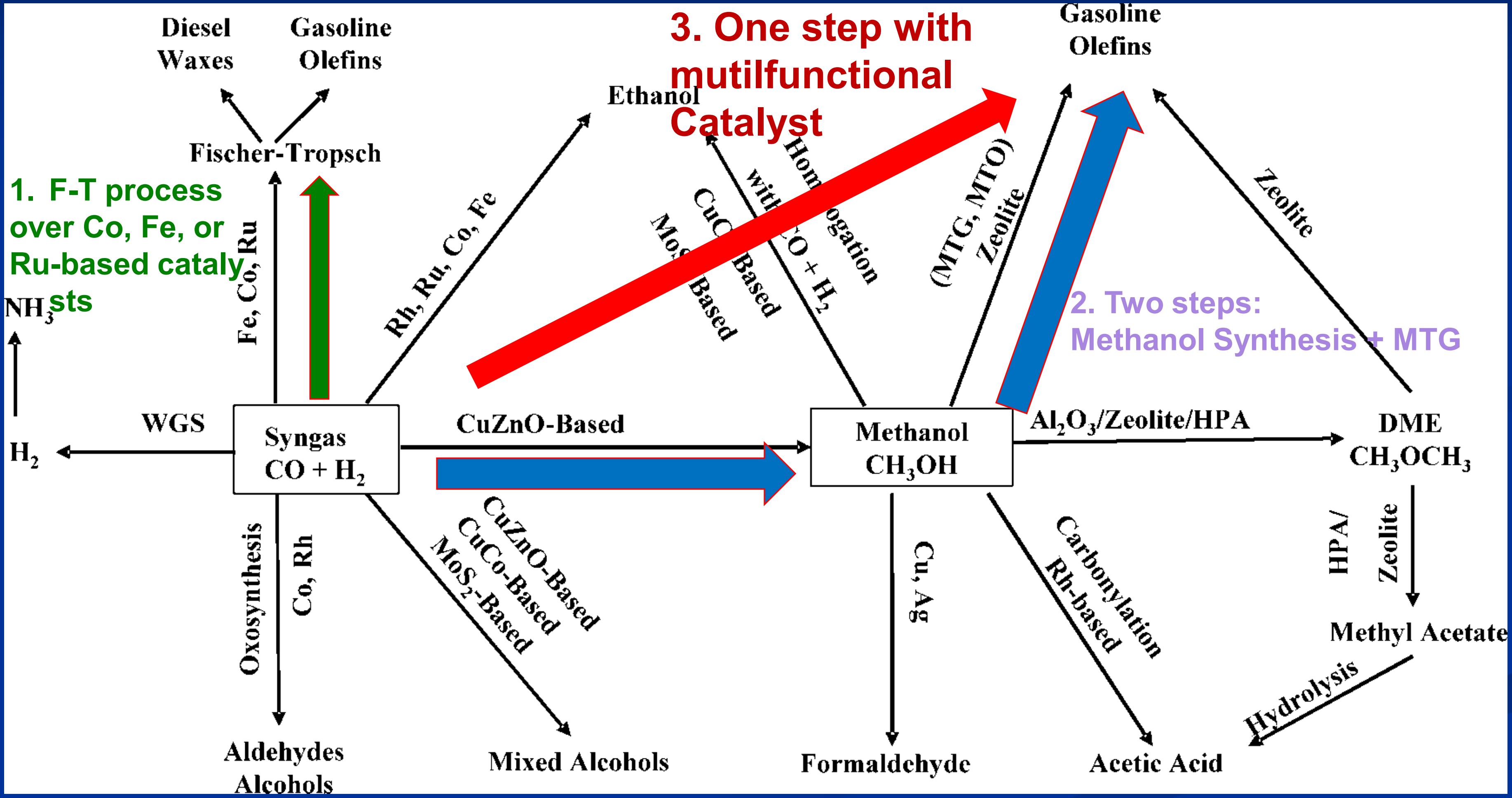


Time on stream of CO conversion, light hydrocarbon and liquid product selectivity on the catalyst at 260^{o}C, 1000 psig, 3000 h^{-1} with purified and raw syngas.


SYNTHESIS GAS
CONTAINS
CARBON MONOXIDE

3 Catalytic Conversion

Opportunities for Catalytic Conversion of Syngas to Fuels and Chemicals



1. F-T process over Co, Fe, or Ru-based catalysts

2. Two steps: Methanol Synthesis + MTG

3. One step with mutilfunctional Catalyst

Subramani V. and Gangwal S.K. *2008. Energy & Fuels. 22:814–839.*

Jet Fuels

- C8 to C17 hydrocarbon compounds
- Usually from petroleum products
- Mainly derived from the kerosene fraction of petroleum distillation
- Paraffins, isoparaffins, cycloparaffins/naphthenes, aromatics, and olefins
- Current art of status from syngas: FTS followed by multistep upgrading wax products to desired range of hydrocarbons by hydrotreating/cracking/hydrocaracking
- Cost increased and overall efficiency decreased due to multiple processes.

Multi-functional Transition Metal-Acid Oxide/Zeolite Catalysts

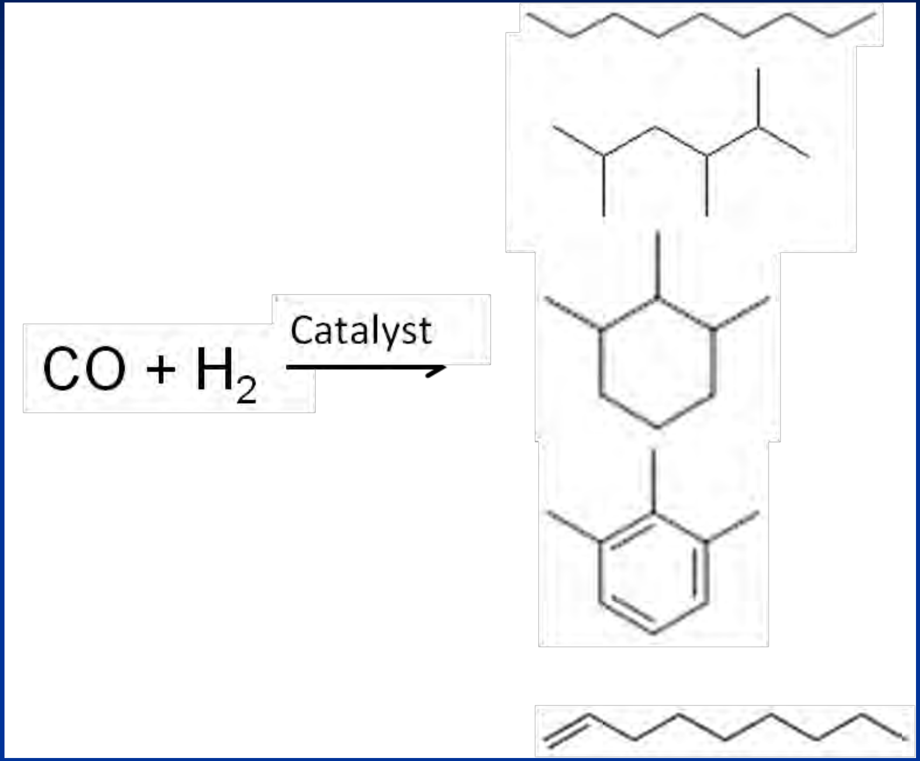
Traditional catalysts:

- FT (Fe, Co, Ru)
- CO hydrogenation (Cu, Cu-Co, Co, Co-Mo, Rh)
- Alcohol Dehydrogenation (SiO_2-Al_2O_3, SiO_2 , Al_2O_3)
- Isomerization (zeolites, SiO_2-Al_2O_3, SiO_2 , Al_2O_3)
- Hydrotreating/Hydrocracking (Co–Mo/Al_2O_3, Ni–Mo/Al_2O_3, etc).
- Promoters: alkaline K, noble metals, Rh, Pd, and Ru

Our catalyst:

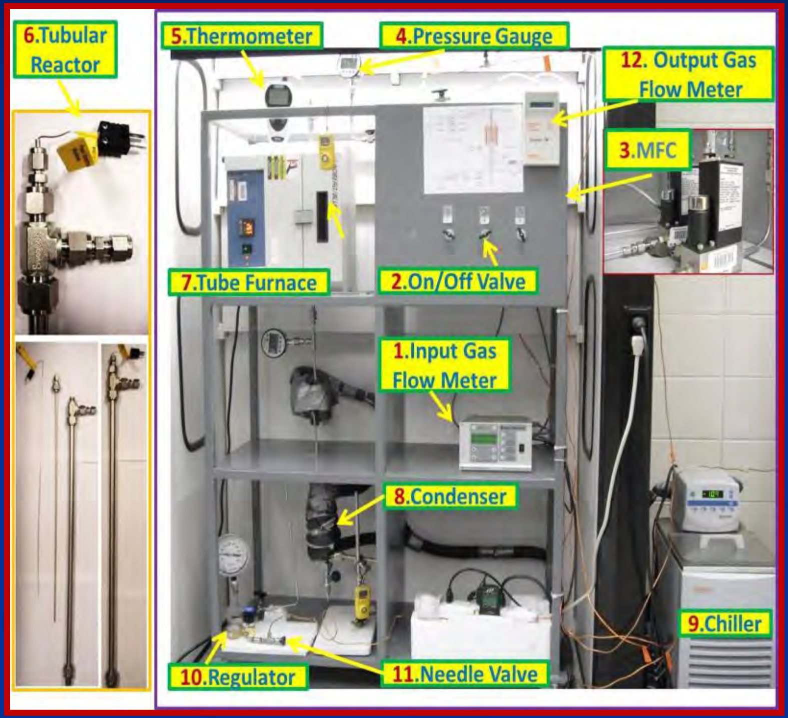
- K-Fe-Co-Mo/Al_2O_3

Catalytic Conversion



Catalyst: 4 wt% K-3 wt% Fe-3 wt% Co-5 wt% Mo/Alumina

Reaction Conditions:
wood syngas, T = 250-350°C, GHSV = 500~3,000h^{-1}, P= 500~1250 psig

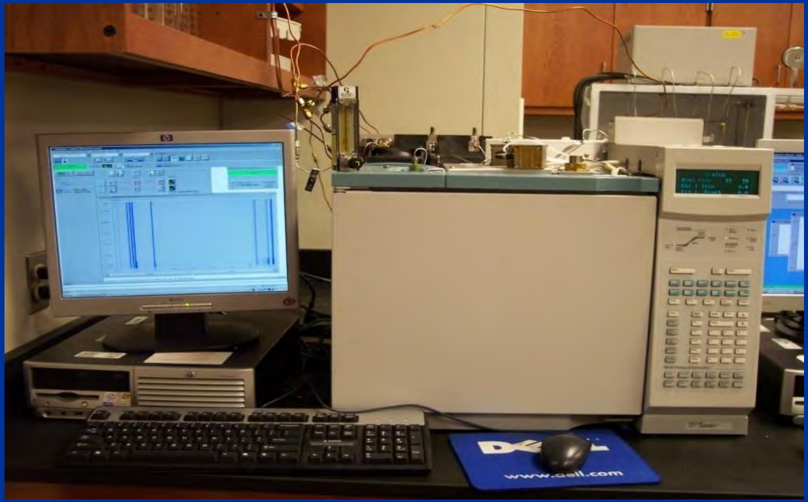


Lab Scale 1/2-inch Tubular Reactor

Sample Analysis

Sample analysis:

- Gas phase: On-line Agilent 7890 GC with TCD/TCD/FID.
- Liquid samples (PIANO method): A Perkin Elmer Clarus 680 GC with a FID using ASTM D 5134-92 but uses a 100-meter capillary column instead of a 50-meter column. Limited to compounds with carbon numbers less than 14. Another Agilent 6890 GC–MS is also used for liquid sample analysis (qualitative).
- Both mass and carbon balance were performed.

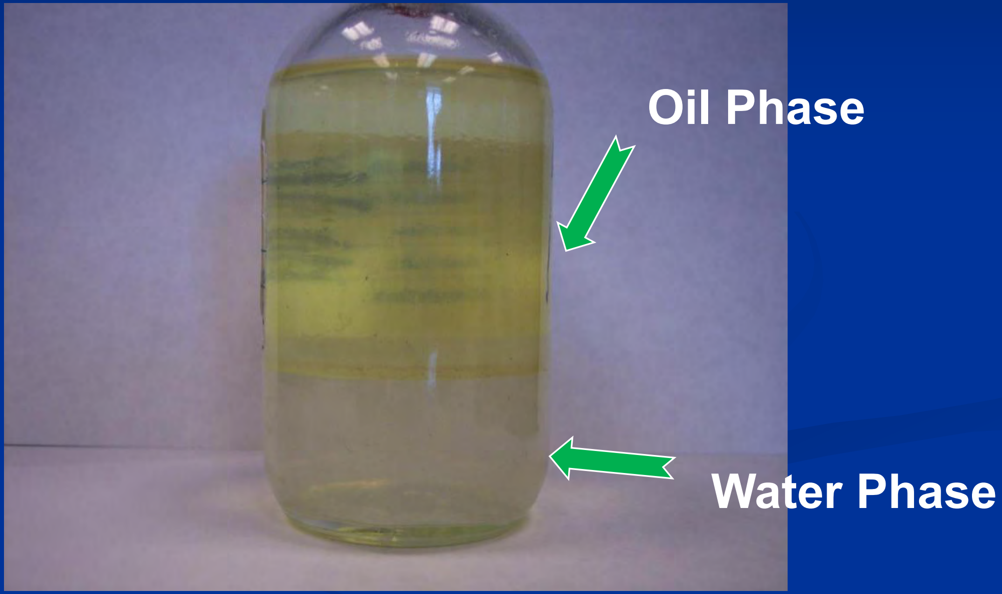


On-line Agilent 7890 gas chromatograph system

Agilent 6890 GC-MS

Catalytic Conversion

Catalyst samples

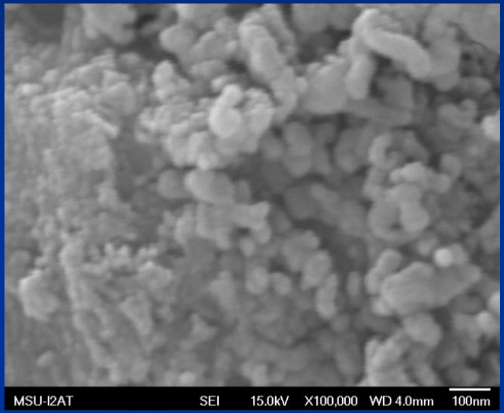


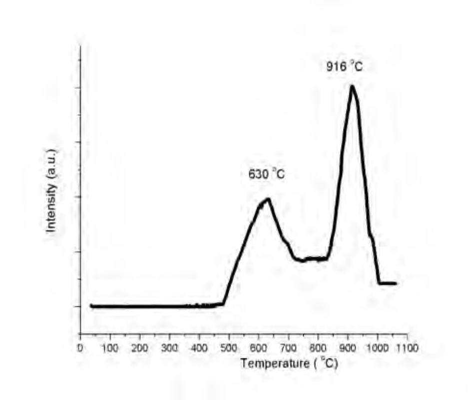
Liquid Sample

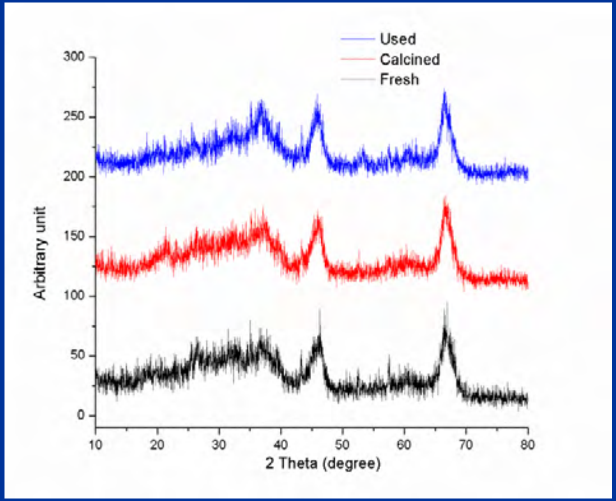
Characterization of Catalyst

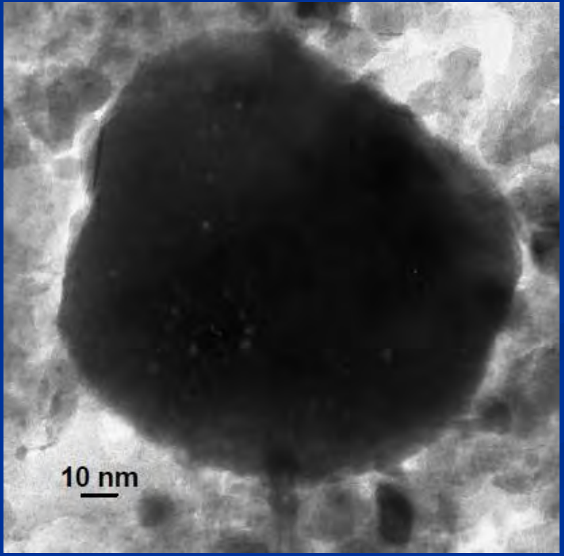
Physical properties of the catalysts

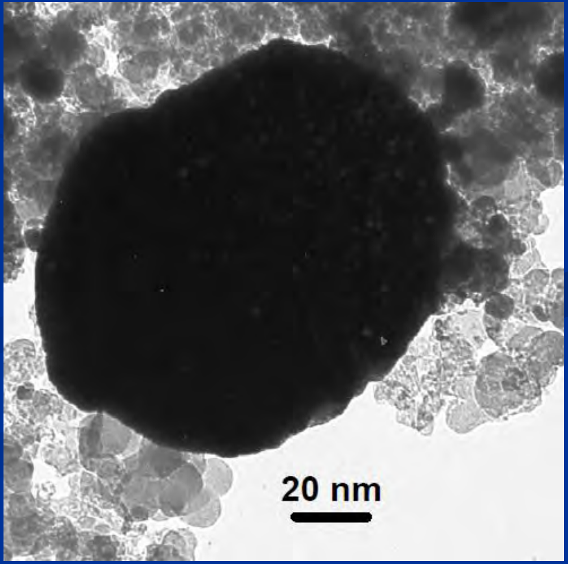
Catalyst	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore diameter (μm)
Support	246	0.92	0.109
Fresh	95.2	0.50	0.103
Used	86.3	0.349	0.095



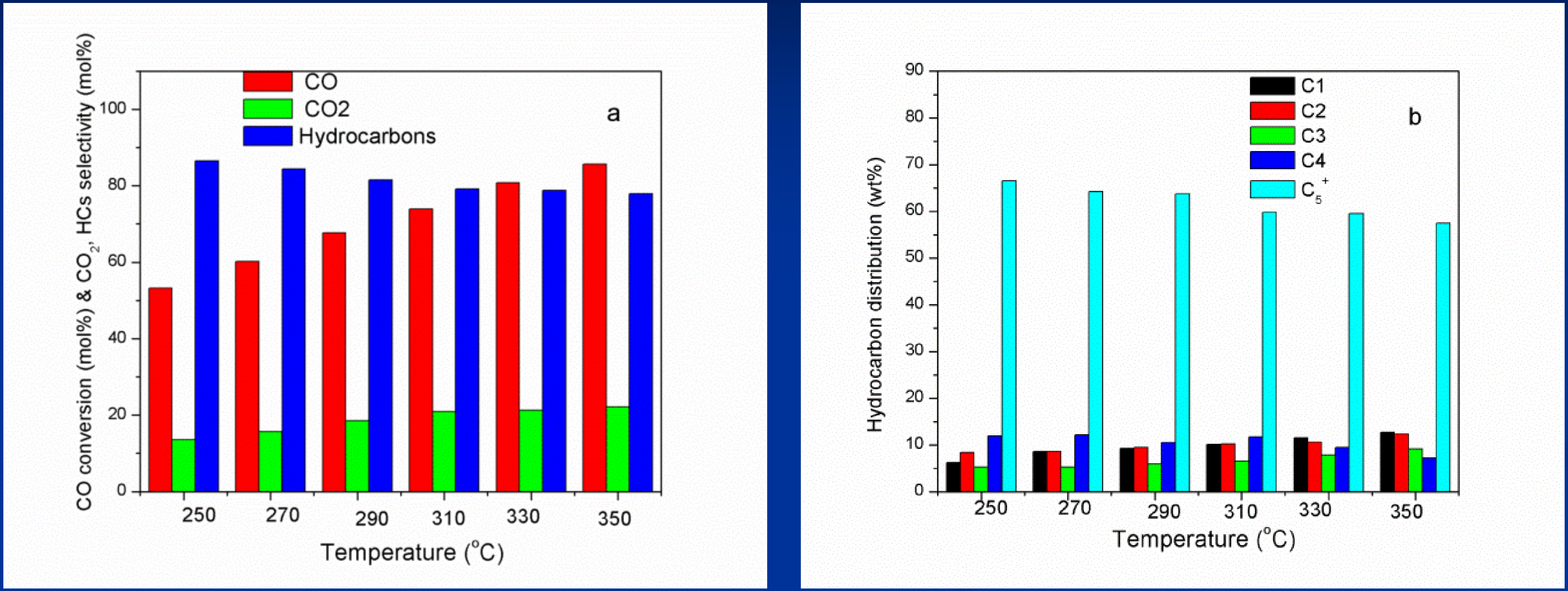






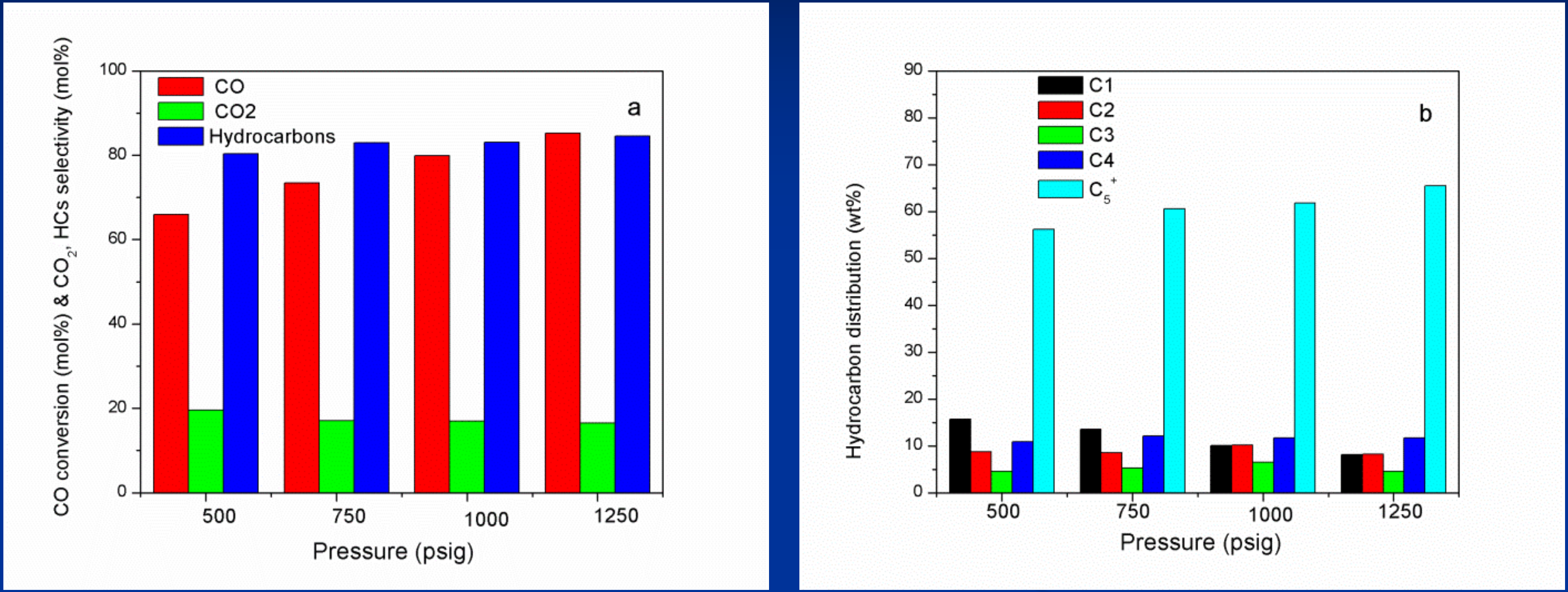


Catalytic Conversion



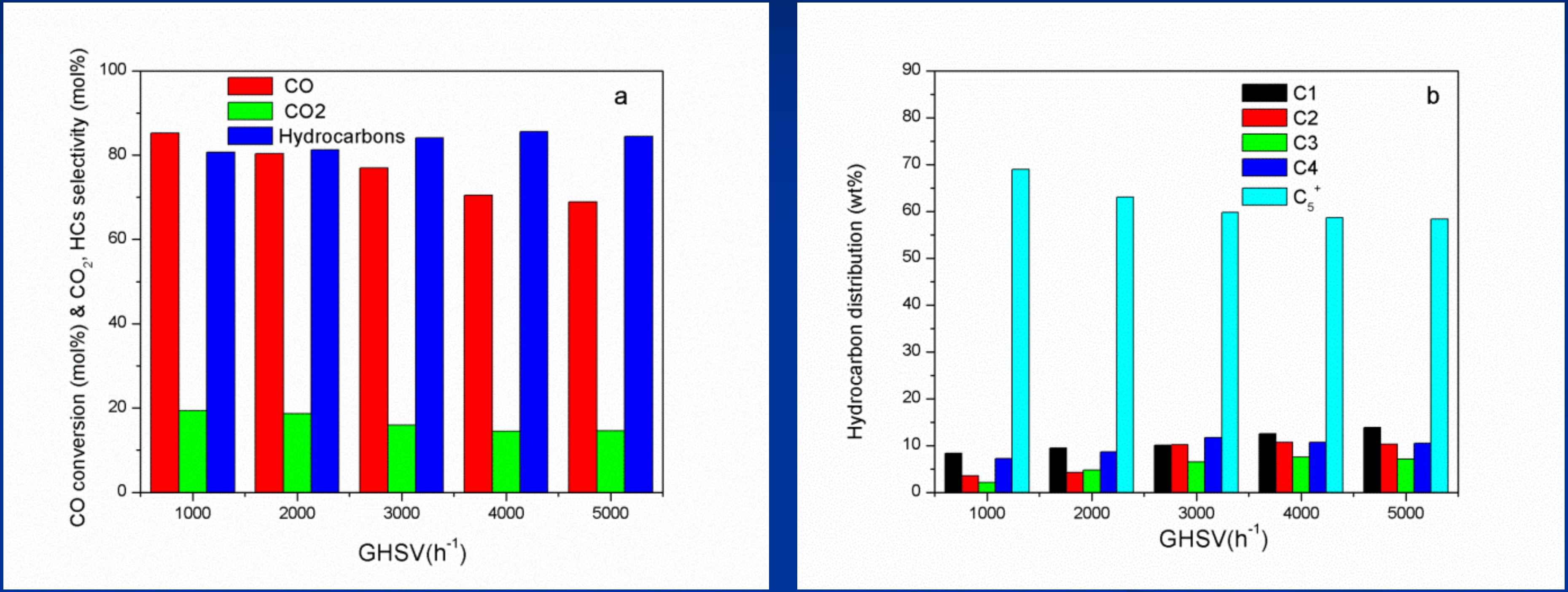
Effect of temperature on (a) CO conversion, CO_2 and hydrocarbon selectivity, (b) hydrocarbon distribution, at 1000psig, with wood syngas of 18.0% H_2, 21.0%CO, 12.0%CO_2, 1.921%CH_4, balance N_2, GHSV of 3000 h^{-1}; 3 g of catalyst was used in the reaction. Time on stream of 48-100 h.

Catalytic Conversion



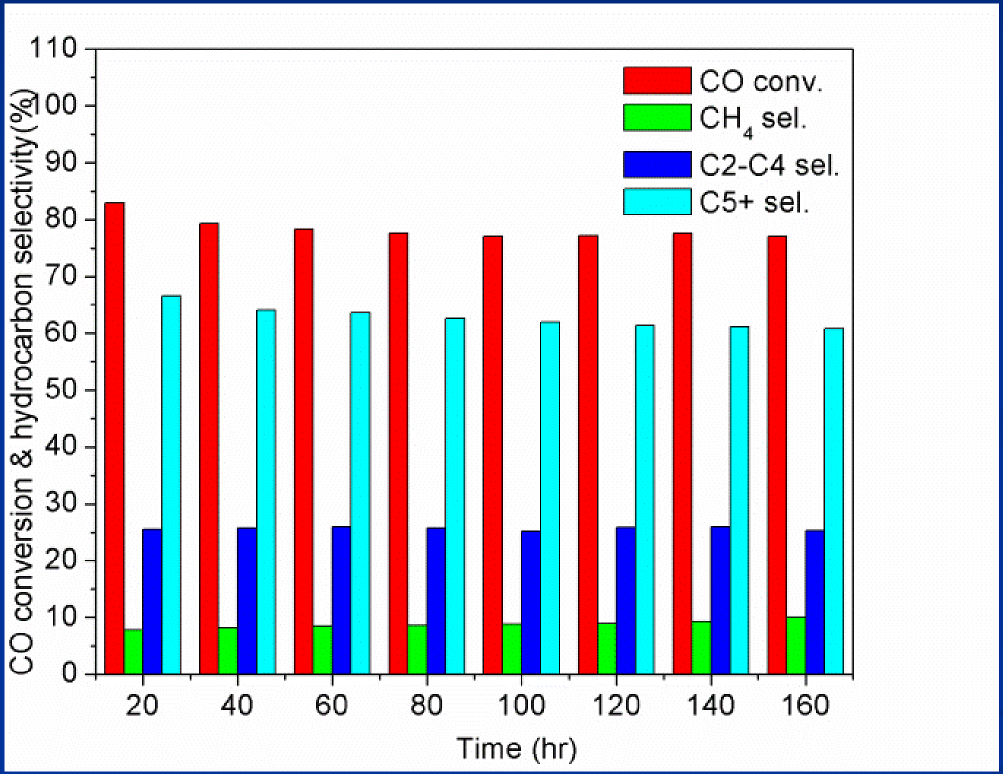
Effect of pressure on (a) CO conversion, CO_2 and hydrocarbon selectivity, (b) hydrocarbon distribution, at 320 °C, with wood syngas of 18.0%H_2, 21.0%CO, 12.0%CO_2, 1.921%CH_4, balance N_2, GHSV of 3000 h^{-1}; 3 g of catalyst was used in the reaction. Time on stream of 48-100 h.

Catalytic Conversion



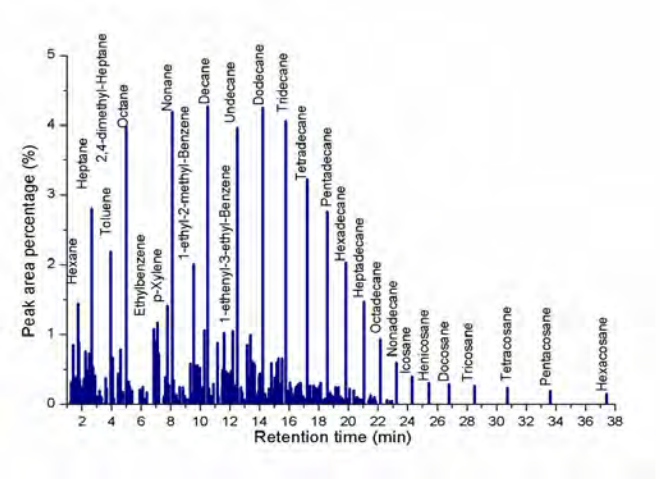
Effect of GHSV on (a) CO conversion, CO_2 and hydrocarbon selectivity, (b) hydrocarbon distribution at 320 °C, 1000 psig, with wood syngas of 18.0%H_2, 21.0%CO, 12.0%CO_2, 1.921%CH_4, balance N_2; 3 g of catalyst was used in the reaction. Time on stream of 48-100 h.

Time-on-stream performance



Time on stream of CO conversion, hydrocarbon selectivity and distribution on the catalyst at 310^{o}C, 1000 psig, 3000 h^{-1} with wood syngas.

Syncrude from Wood Syngas

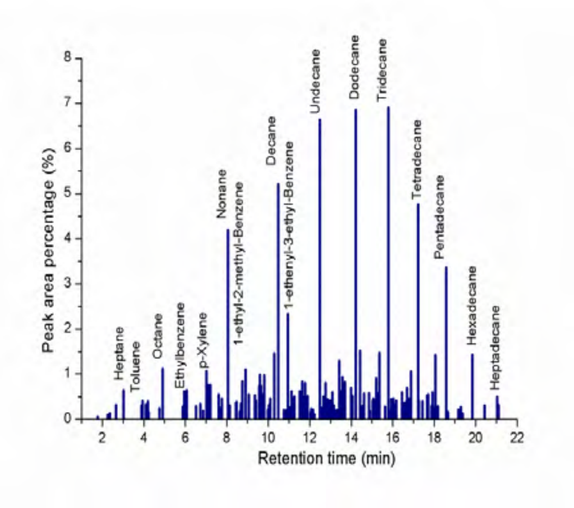


Typical GC-MS of unrefined fuels from wood chips derived syngas.

Typical product distribution of the C_5+ liquid fraction of the syncrude by group type & carbon number (in mol percent)

	Paraffins	I-Paraffins	Olefins	Napthenes	Aromatics	Unknowns	Total
C5	0.07	0	0.67	0	0	0	0.74
C6	1.1	0.025	4.68	0	0	0	5.81
C7	2.28	0.33	10.37	1.41	0.5	1.03	15.92
C8	2	0.79	1.26	1.5	0.61	9.12	15.28
C9	2.5	7.38	5.07	4.16	1.55	2.34	23
C10	2.92	4.23	0.5	0.77	13.78	0.81	23.01
C11	1.07	1.84	0.15	0.2	1.91	0.32	5.49
C12	0.50	0.41	0.032	0.012	1.99	3.01	5.96
C13	0.5	0.02	2.1	0	0	2.51	5.13
Total	12.94	15.02	25.33	8.05	19.84	19.74	81.18

Distillation of Syncrude



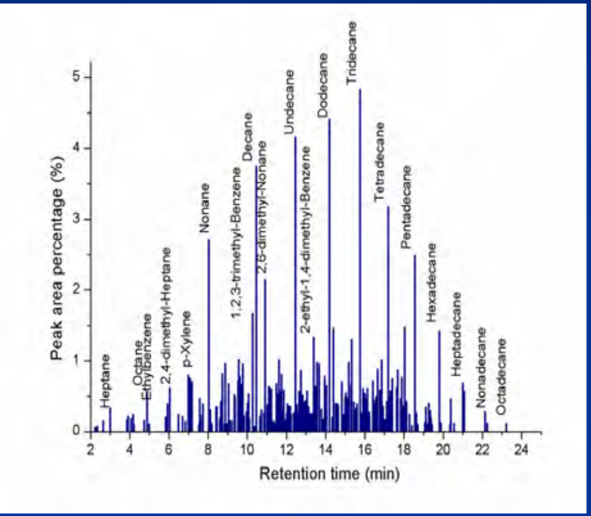
Typical GC-MS of the distillation

Typical product distribution of the C_5+ liquid fraction of the distillation by group type & carbon number (in mol percent)

	Paraffins	I-Paraffins	Olefins	Napthenes	Aromatics	Unknowns	Total
C5	0.03	0	0.02	0	0	0	0.05
C6	0.05	0.01	0.3	0	0	0	0.36
C7	1.3	0.1	0.88	0.92	0.95	0.3	4.45
C8	2.1	0.93	0.68	1.84	1.14	2.46	9.15
C9	1.52	2.8	2	5.46	2.04	5.18	19
C10	3.15	9.58	0.19	5.89	12.74	1.28	32.83
C11	2.59	4.06	0.36	0.4	2.96	3.77	14.14
C12	2.27	2.06	0.06	0	2.33	7.44	14.16
C13	1.1	0.09	2.74	0	0	7.11	11.04
Total	14.11	19.63	7.23	14.51	22.16	27.54	77.64

Since hydrocarbons in Jet fuels are mainly C8~C17, the syncrude from wood syngas was distilled to remove both lighter hydrocarbons and wax components. The production sample was collected by distillation with a range of boiling points between 110 °C and 310 °C.

A Commercial Jet Fuel (Jet A) Sample



Typical GC-MS of the commercial Jet A sample

Typical product distribution of the C_5+ liquid fraction of the commercial Jet A sample by group type & carbon number (in mol percent)

	Paraffins	I-Paraffins	Olefins	Napthenes	Aromatics	Unknowns	Total
C5	0.01	0	0.01	0	0	0	0.02
C6	0.01	0	0.17	0	0	0	0.18
C7	1.01	0.1	0.48	0.64	0	0.01	2.24
C8	0.7	0.93	0.58	1.8	1.18	2.22	7.41
C9	2.3	7.11	0.78	5.9	2.05	1.34	19.48
C10	3	7.1	0.23	2.08	19.22	2.1	33.73
C11	2.58	3.65	0.39	0.77	3.02	4.31	14.72
C12	1.23	1.95	0.02	0	2.05	5.66	10.91
C13	2.11	1.1	0.96	0	0	7.33	11.5
Total	11.95	21.94	3.62	11.19	27.52	22.97	74.55

Properties of Syncrude, Distilled Fuels, and Jet A

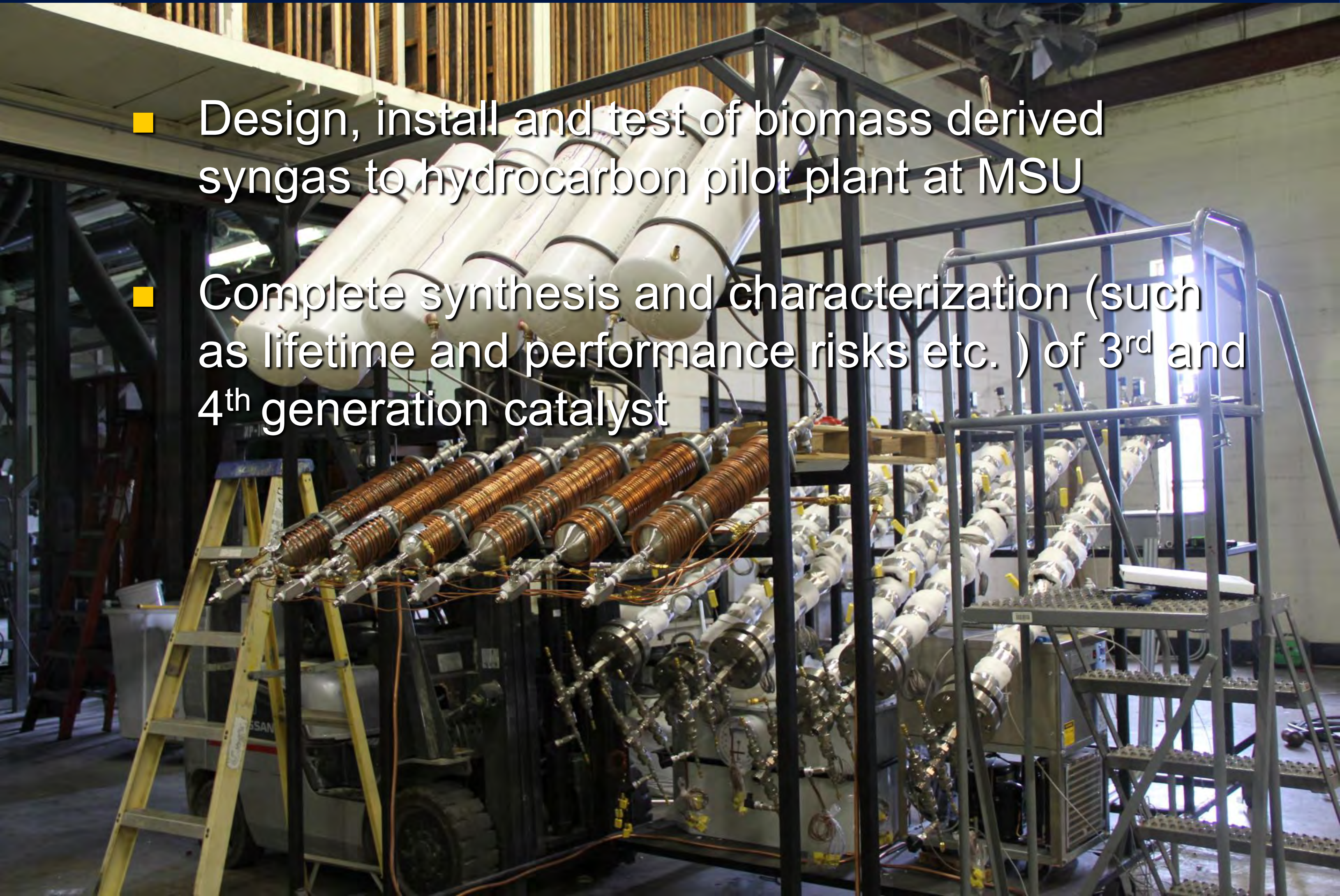
Properties	Syncrude	Distilled fuel	Jet Fuel JPA
Average Molecular Weight	125.50	137.98	140.65
Relative Density	0.804	0.810	0.815
Reid Vapor Pressure @ 100 F(37.8 C)	0.55	0.16	0.04
Percent Carbon	86.58	86.61	86.95
Percent Hydrogen	13.29	13.36	13.05
Bromine Number (Calc)	26.16	6.12	3.18
Total Oxygen Content (mass %)	0.12	0.025	0.0044
Freeze point (°C)	-28.5	-37	-40

Liquid samples were dried using sodium sulfate and subjected to test of relative gravity by ASTM D287, distillation range (ASTM D86) and Reid vapor pressure (D323 - 08).

Summary

- **Developed and Demonstrated a continuous process to produce** synthetic aviation turbine fuels (SATFs) from wood chips.
- **Produce wood syngas from oak chips through a commercial downdraft gasifier with main components of** 47% N_2, 21% CO, 18% $H_{2,}$ 12% $CO_{2,}$ 2% CH_4 .
- **Designed and tested a synags cleaning system to purify wood syngas, and** the cleaned syngas meets the requirements for the following step of catalytic conversion to liquid fuels.
- **Developed and tested multifunctional catalysts for converting wood syngas to** synthetic aviation turbine fuels (SATFs).
- **Characterized syncrude and it's distillation, the properties of the distillation was similar to Jet A.**

Future Work



- Design, install and test of biomass derived syngas to hydrocarbon pilot plant at MSU
- Complete synthesis and characterization (such as lifetime and performance risks etc.) of 3rd and 4th generation catalyst

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- Sustainable Energy Research Center at Mississippi State University and is supported by the Department of Energy under Award Number DE-FG3606GO86025.
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Thank You !