Fischer-Tropsch Catalyst for Aviation Fuel Production

As the oil supply declines, there is a greater need for cleaner alternative fuels. There will undoubtedly be a shift from crude oil to non-petroleum sources as a feedstock for aviation (and other transportation) fuels. The Fischer-Tropsch process uses a gas mixture of carbon monoxide and hydrogen which is converted into various liquid hydrocarbons; this versatile gas-to-liquid technology produces a complex product stream of paraffins, olefins, and oxygenated compounds such as alcohols and aldehydes. The Fischer-Tropsch process can produce a cleaner diesel oil fraction with a high cetane number (typically above 70) without any sulfur and aromatic compounds. It is most commonly catalyzed by cobalt supported on alumina, silica, or titania or unsupported alloyed iron powders. Cobalt is typically used more often than iron, in that cobalt is a longer-active catalyst, has lower water-gas shift activity, and lower yield of modified products. Promoters are valuable in improving Fischer-Tropsch catalyst as they can increase cobalt oxide dispersion, enhance the reduction of cobalt oxide to the active metal phase, stabilize a high metal surface area, and improve mechanical properties. Our goal is to build up the specificity of the Fischer-Tropsch catalyst while adding less-costly transition metals as promoters; the more common promoters used in Fischer-Tropsch synthesis are rhenium, platinum, and ruthenium. In this report we will describe our preliminary efforts to design and produce catalyst materials to achieve our goal of preferentially producing C_8 to C_{18} paraffin compounds in the NASA Glenn Research Center Gas-To-Liquid processing plant. Efforts at NASA Glenn Research Center for producing green fuels using non-petroleum feedstocks support both the Sub-sonic Fixed Wing program of Fundamental Aeronautics and the In Situ Resource Utilization program of the Exploration Technology Development and Demonstration program.

Fischer-Tropsch Catalyst for Aviation Fuel Production

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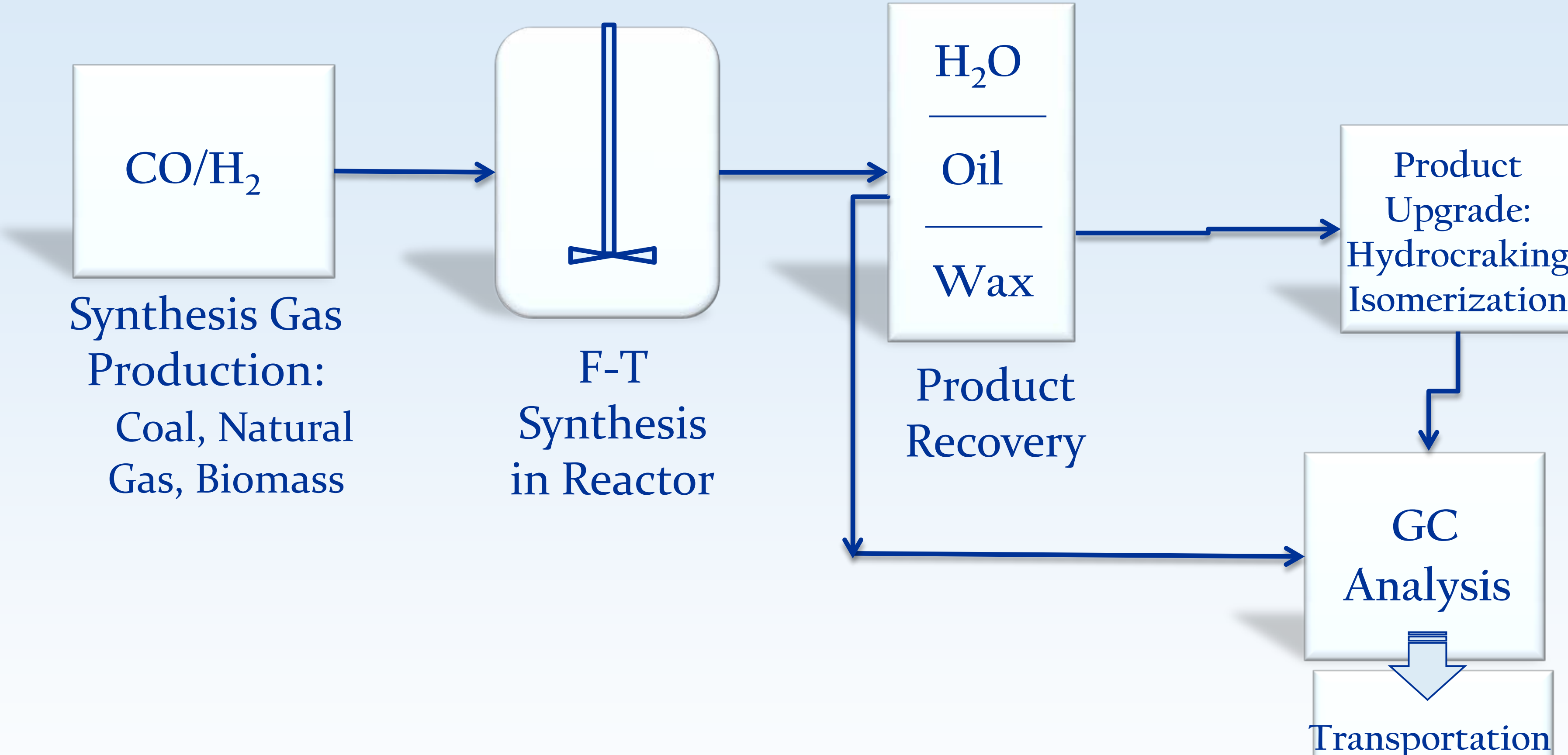
Fischer-Tropsch Process Overview



$$(2n{+}1)\ H_2 + n\ CO \Rightarrow C_nH_{(2n+2)} + n\ H_2O$$

$\Delta H = -\ 49$ kcal/mol

FTS Research Objectives at NASA GRC

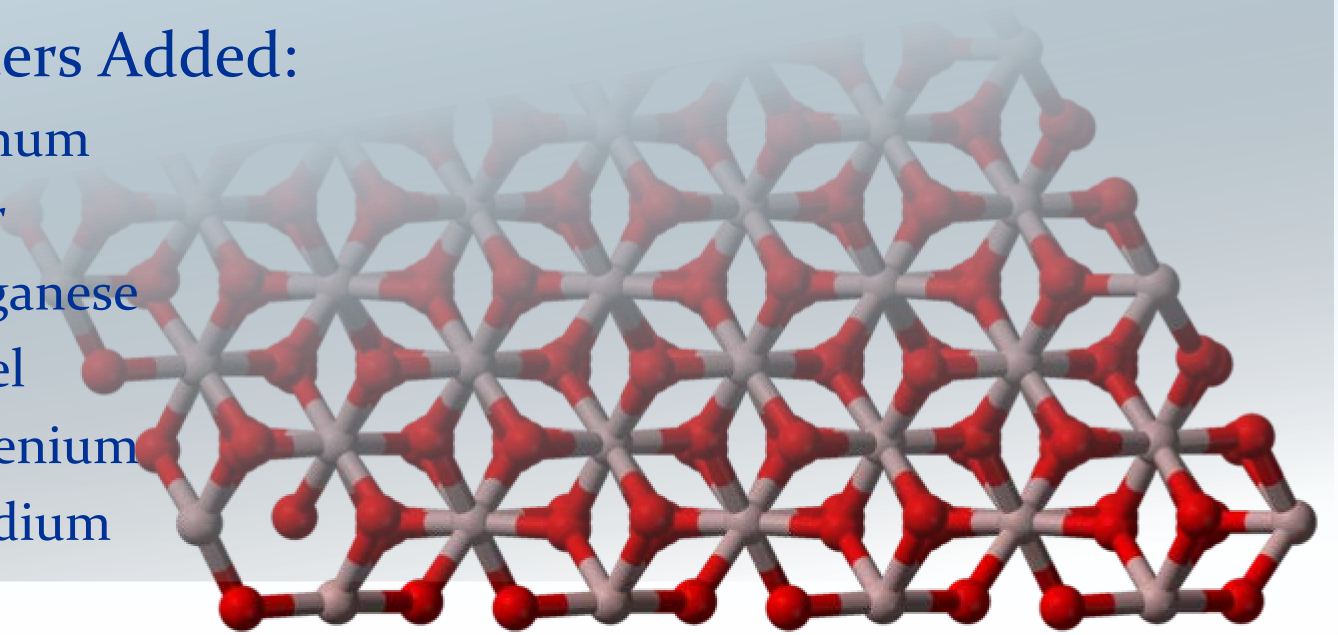
- Synthesize Cobalt Catalysts (supported on alumina) for Longer-chain Hydrocarbon Production
  - Increase dispersion of Co on Alumina
- Examine the Promoter Effects on Catalytic Activity
  - Ag, Pt, Cu, etc.
- Compare the Catalyst Morphology and Function
  - SEM/EDS
- Look for Opportunities to Develop Processes for ISRU
  - Use other gas feedstocks relevant to atmospheres
  - Catalysts related to other feedstocks/products (CH_4)

Projects

- Synthesis of Catalyst
  - Cobalt on Alumina
  - Noble metal promoted catalyst
- Catalyst Characterization
  - Brunauer Emmett Teller (BET) Surface Area Measurements
  - Temperature Programmed Reduction (TPR)
  - Scanning Tunneling Microscopy
  - Energy Dispersive Spectroscopy
  - Inductively Coupled Plasma – Atomic Emission Spectroscopy
- Use of Catalyst for Fuel Production
  - Fischer-Tropsch Synthesis

Cobalt on Alumina

- $Co(NO_3)_2 * 6H_2O$
- Al_2O_3
- Slurry impregnation
  - Multiple additions increase the loading of the cobalt nitrate onto the alumina
- Promoters Added:
  - Platinum
  - Silver
  - Manganese
  - Nickel
  - Ruthenium
  - Palladium



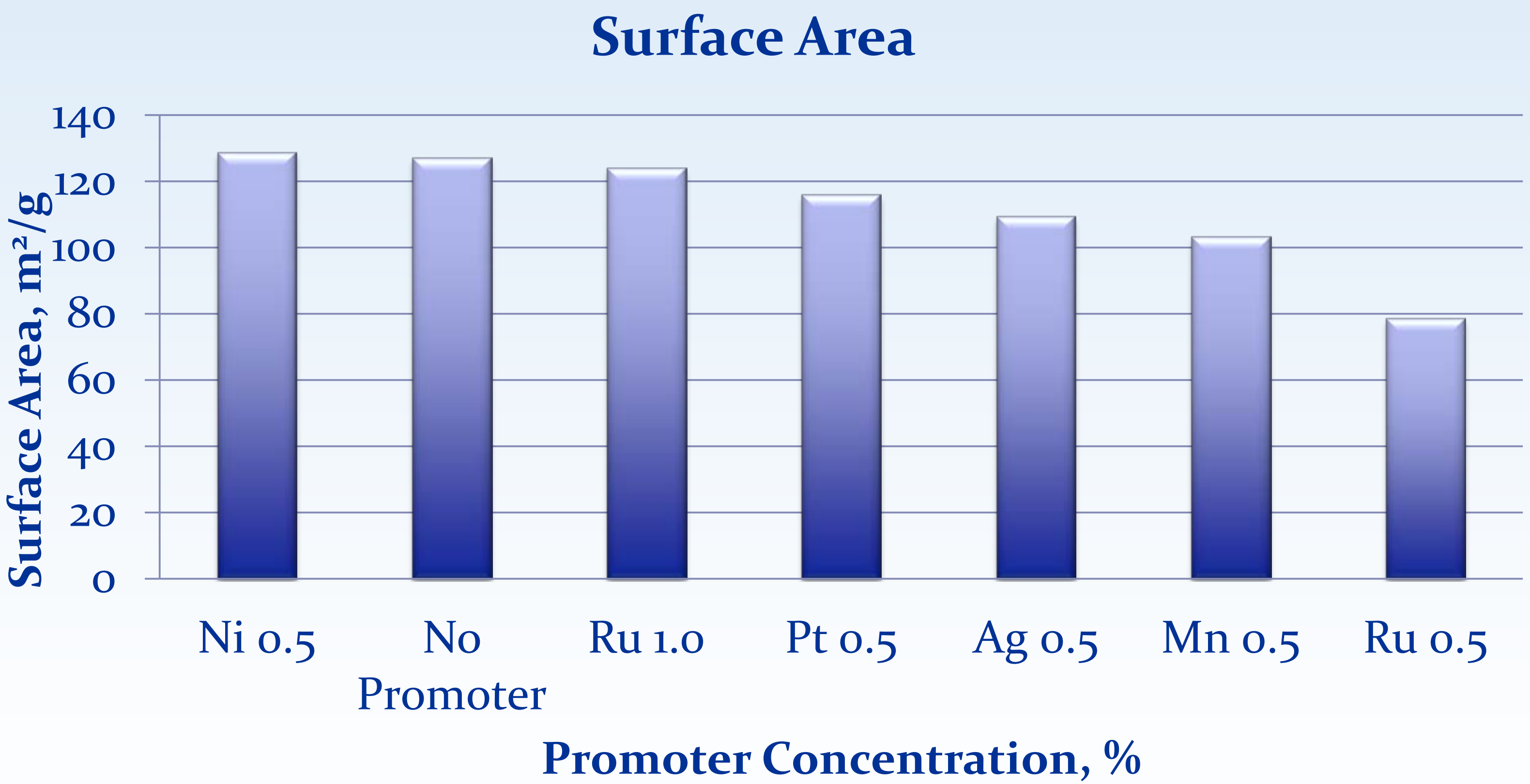
Characterization

❖ Catalyst Synthesized

Sample #	Co Loading %	Promoter%	ICP-AES Elemental Analysis	Surface Area (m^2/g)	Reduction Temp (°C)
1	25	No Promoter		127.135	350
3	25	Ag 0.5	23.6 / 0.278	109.35	369
4	25	Mn 0.5	25.7 / 0.592	103.17	366
5	25	Ni 0.5	23.8 / 0.891	128.66	348
6	25	Ru 0.5	25.5 / 1.26	78.57	322
7	25	Pt 0.5	24.8 / 0.459	115.93	265
8	25	Ru 1.0	23.0 / 2.20	123.85	264
9	15	Mn 0.5	13.8 / 0.572	101.01	354
10	15	Pd 0.5	14.1 / 0.429	111.37	229

Characterization

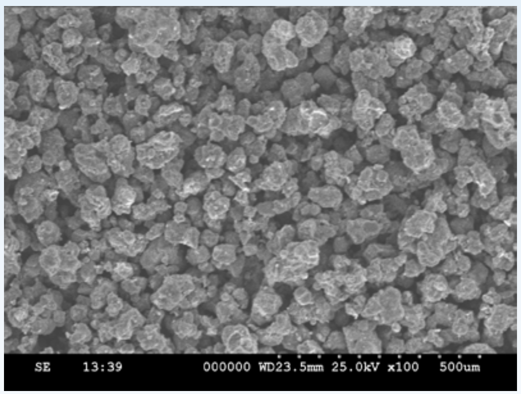
❖ BET – Brunauer Emmett Teller Results

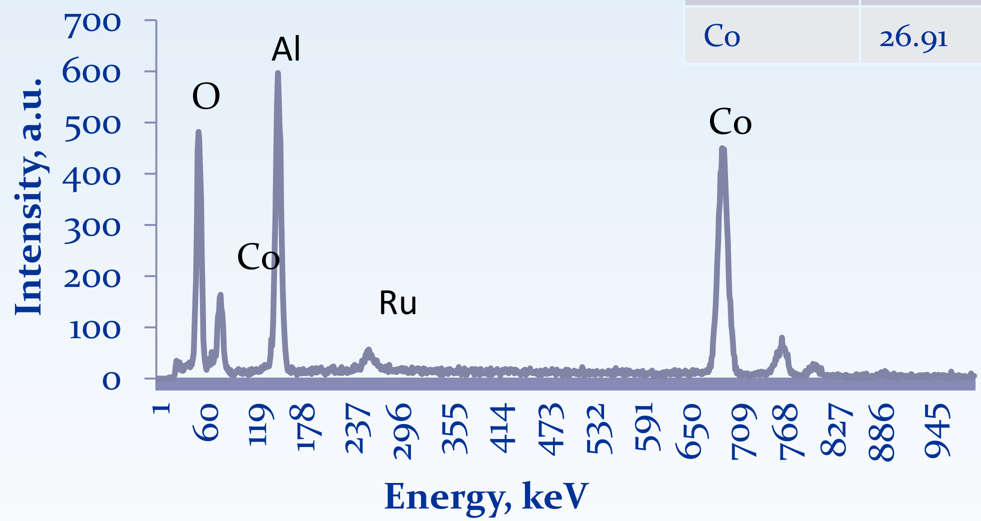


Characterization

- Scanning Electron Microscopy
- Energy Dispersive Spectroscopy

Element	Wt %
O	43.14
Al	28.29
Ru	1.15
Co	26.91

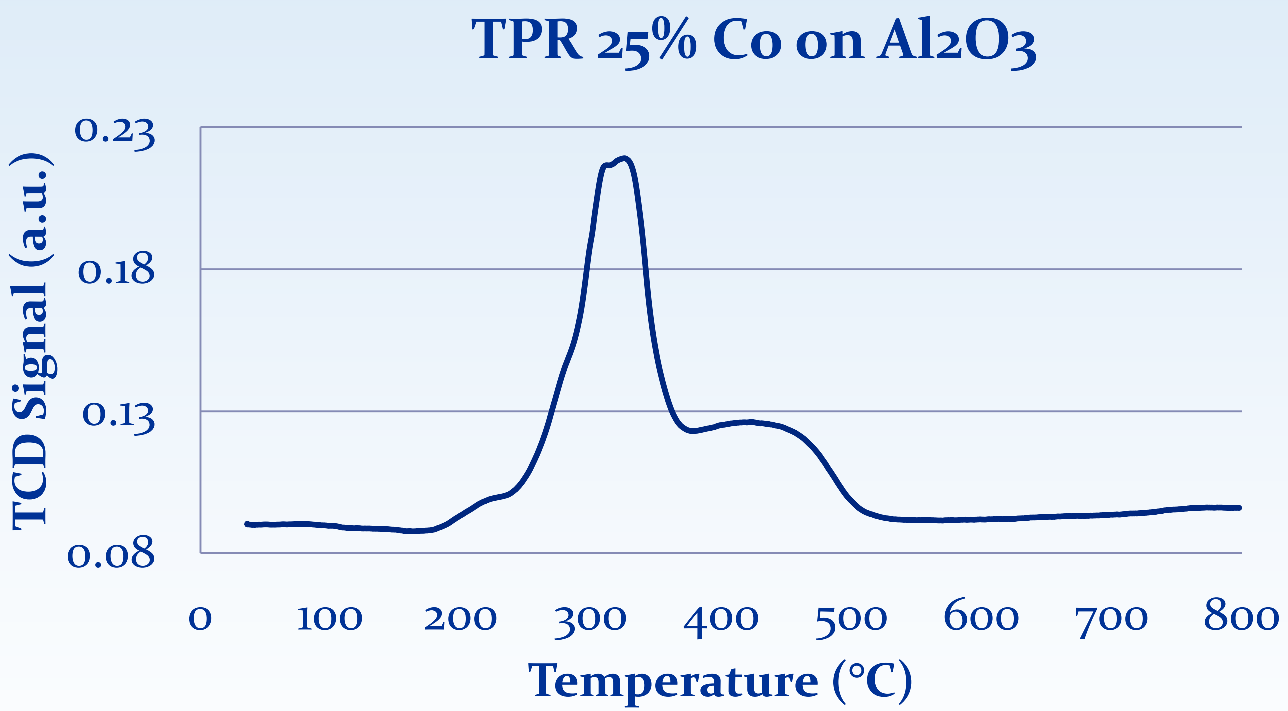




SEM image of 1.0% Ru and 25% Co on Alumina.
100X magnification, catalyst made by slurry impregnation.

Characterization

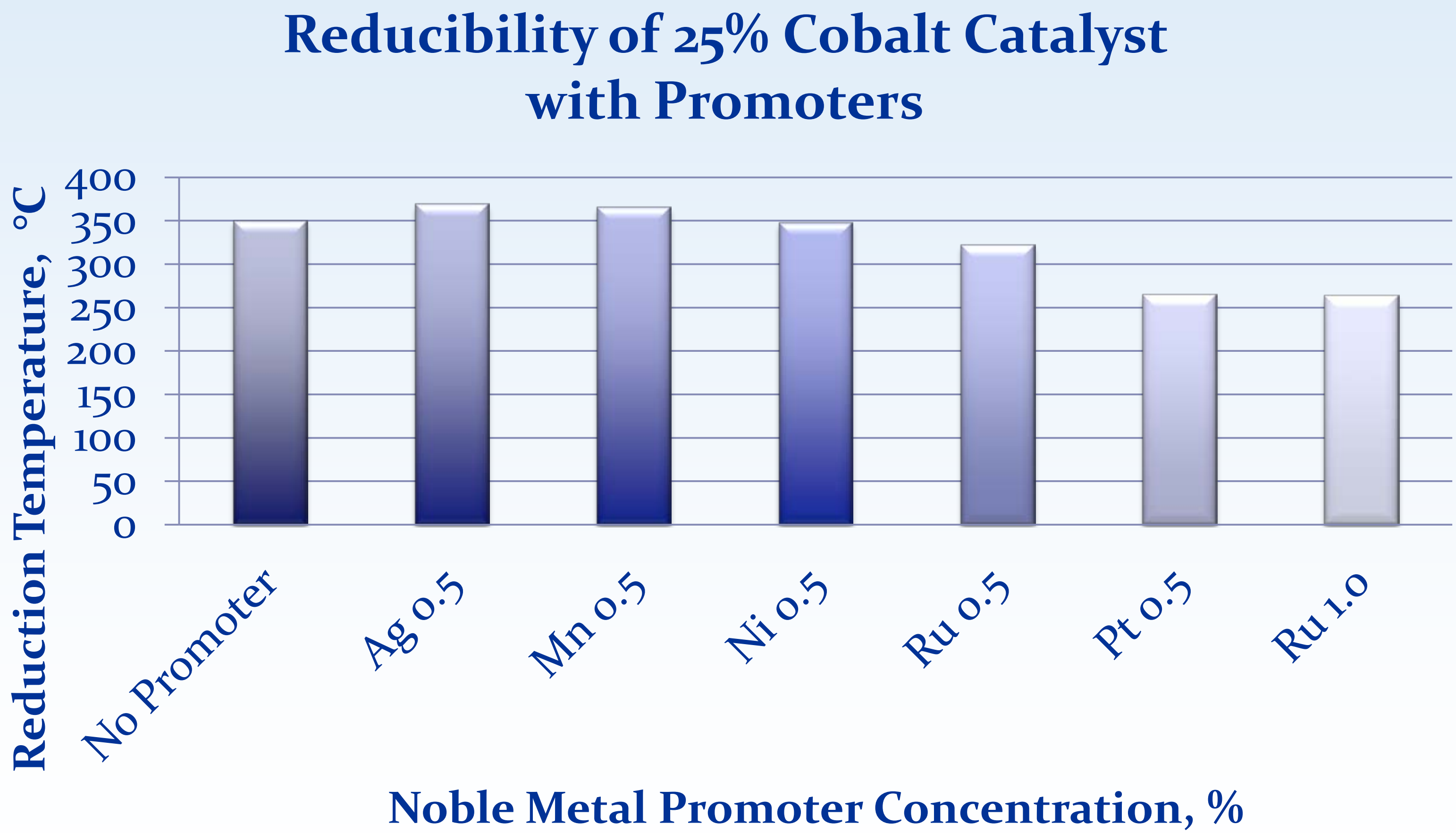
- Temperature Programmed Reduction



$Co_3O_4 \rightarrow CoO \rightarrow Co^o$

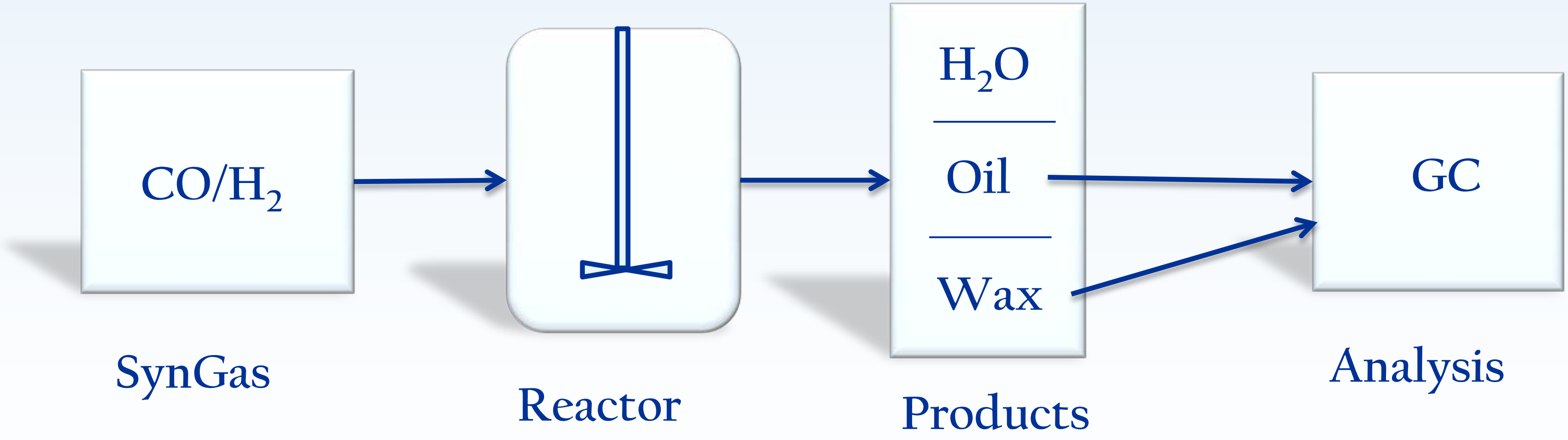
Characterization

- ❖ Temperature Programmed Reduction



Fuel Production

- Fischer-Tropsch Synthesis
  - Three 1-Liter continuous Stirred Tank Reactors (CSTR)
  - Converts synthesis gas (CO/H_2) to fuel by running at high pressures and temperatures



Research Objectives of F-T Fuels

- Improve reactor yield, reduce energy input, and reduce CO_2 by-product by conducting bench scale Fischer-Tropsch reactor screening experiments with innovative catalysts
  - Investigate FT product distributions
  - Identify the effects of critical parameters (T, P, H2:CO Ratio, catalyst) on F-T reactor product distribution with respect to aviation fuel yields, compositions and physical properties

Fischer-Tropsch Reaction
Over View Chemistry & Testing

$$(2n+1)\ H_2 + n\ CO \Rightarrow C_nH_{(2n+2)} + n\ H_2O$$

Paraffins	$(2n+1)\cdot H_2 + n\cdot CO \Rightarrow C_nH_{2n+2} + n\cdot H_2O$
Olefins	$2n\cdot H_2 + n\cdot CO \Rightarrow C_nH_{2n} + n\cdot H_2O$
Water gas shift rxn	$CO + H_2O \Leftrightarrow CO_2 + H_2$

Catalysts	Pressure	Temperature
Cobalt	180 – 450 psig	180 – 270 °C
Iron	180 – 450 psig	330 – 350 °C

Feed conditions / test variables (typical)

H_2:CO ratio	0.6 – 2.5	
H_2 / CO flow rates	20 – 100 SLPH	(Max design 120 SLPH – H_2/CO/Ar)
Argon mol %	10 – 50 (inert carrier gas)	
Space velocity	1,000 to 10,000 hr^{-1} at STP	
Catalyst Type	Co or Fe; promoted/unpromoted; supports Al_2O_3, SiO_2, TiO_2	

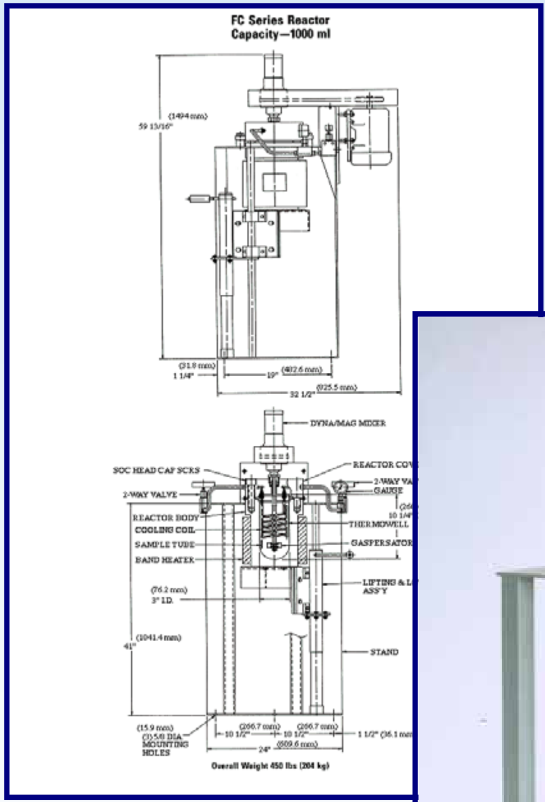
Fischer-Tropsch Autoclave Reactor – 1 liter

❖Reactor capacity

- ❖ 1 liter (internal volume)
- ❖ 6000 psig @ 650 °F (ASME rated)
- ❖ 316 SS
- ❖ Agitator – Dynamag mixer
- ❖ Jacket heater (electric – 2.4 kW)

❖Operating Conditions

- ❖ Max Operating Pressure: 500 psig
- ❖ Max Operating Temperature: 842° F
- ❖ (450 ° C)
- ❖ Reactors have safety relief valves set to 750 psig
- ❖ Normal test conditions range from 180-450 psig and 356-518° F (210- 270 ° C)



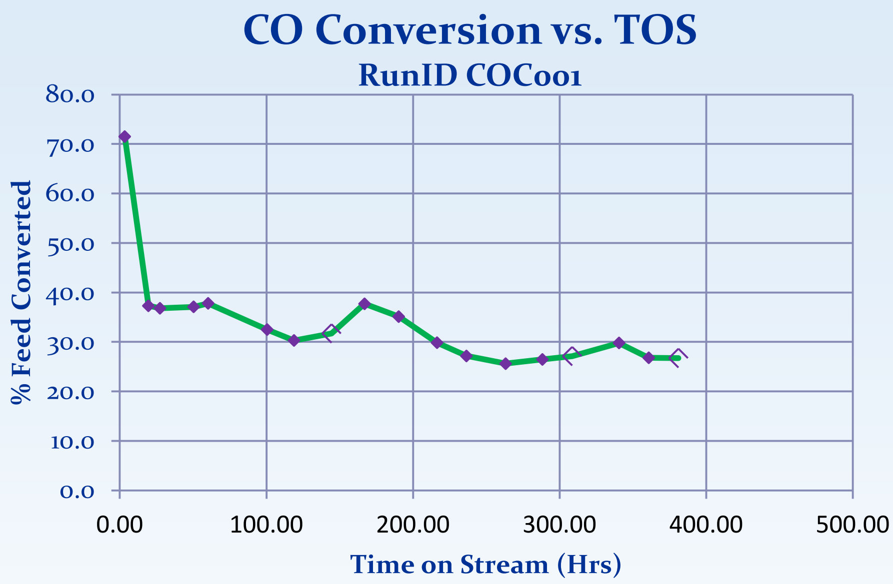
Catalyst Performance:

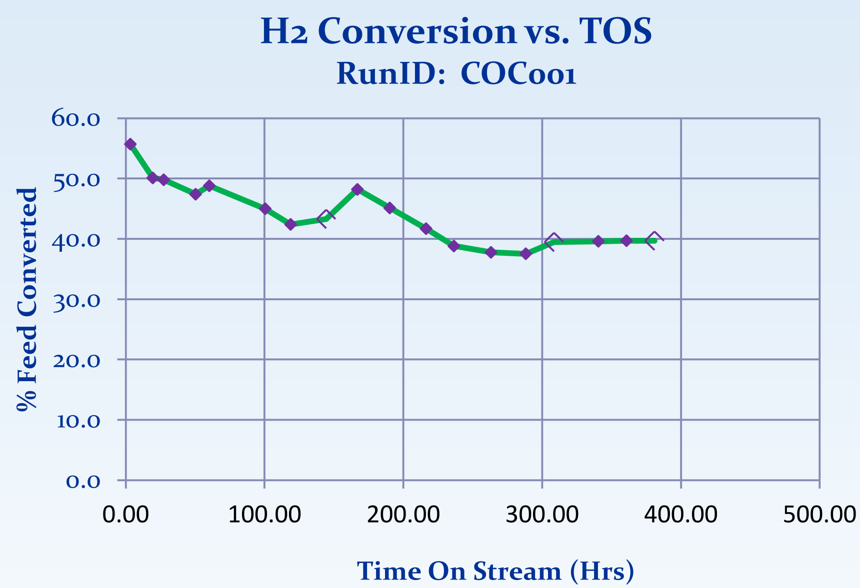
Catalyst 0.5% Pt, 15% Co on Alumina Support

	GRC Run CoC-001
Reactor Temp (deg C)	220
Reactor Press (psig)	268
Space Velocity (SLPH/g-Cat *)	5.1
Feed H2: CO molar	2.02
CO conversion (mol%)	37.7 to 26.7
H2 conversion (mol%)	55.7 to 39.7
Total time on stream (hr)	381 (~16 days)
Product Gas (SLPH)	59.2 to 71.8, avg. 66.3
Product Water (g/day)	246.7 to 170.7, avg. 200.5
Product Liq Oil (g/day **)	76.3 to 62.9, avg. 70.2
Product ReWax (g/day ***)	239.1 to 153.6, avg 190.6

CO and H_2 Conversion

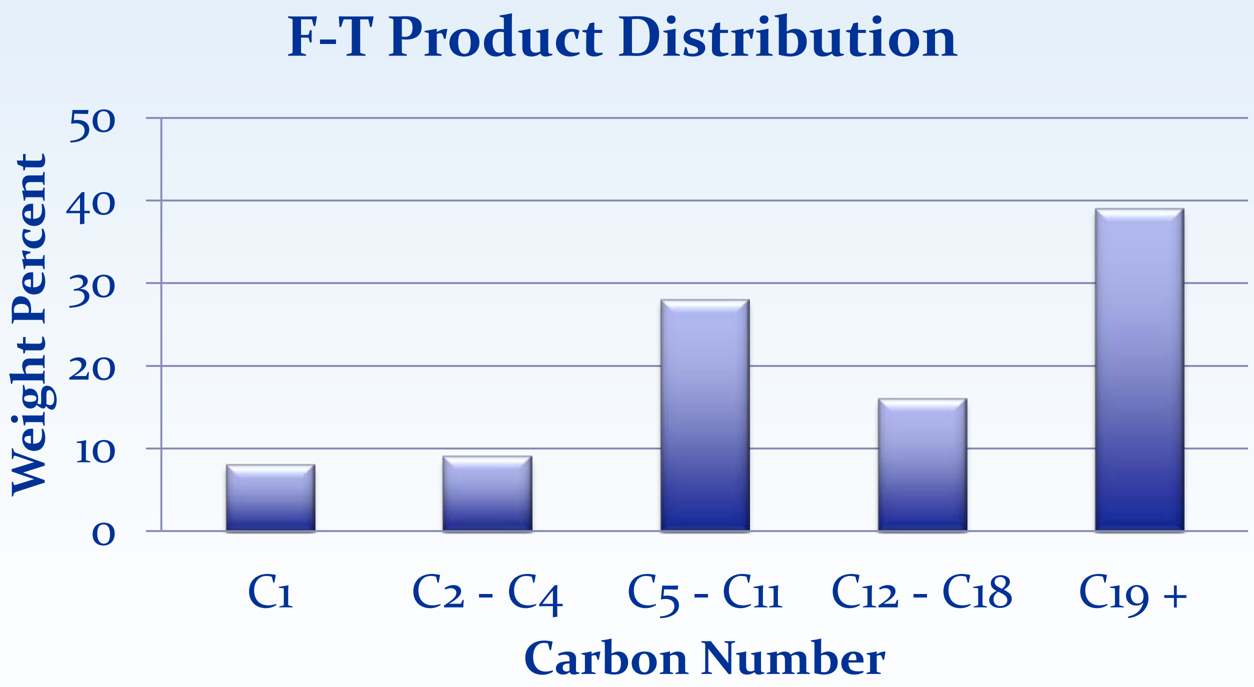
GRC Run CoC-001





Results

- Hydrocarbon production from catalyst
  - Cobalt on Alumina provides



Jet Fuel Types, Alternatives & Details

Jet fuels classified as kerosene-, naphtha-type, or other

- Kerosene-type jet fuels: Jet A, Jet A1, JP-5 and JP-8
  - Carbon range from C_8 - C_{16} (Kerosene is C_{12} - C_{15})
  - Standard fuel used for civilian or military aircraft
  - Conventional Jet-A:
    - Petroleum based distillate
    - Rely on foreign oil and refined fuels
    - Limited supply worldwide
  - Alternative Jet Fuels:
    - Fischer Tropsch Fuel from coal, natural gas, non-petroleum sources
    - Biofuels from renewable sources
- Naphtha-type ("wide-cut") jet fuels: Jet B and JP-4
  - Carbon range from C_5 - C_{15} (Petroleum Ether is C_7 - C_{11})
  - Enhanced volatility generally used for cold-weather climates

Sources of SynGas

- Pure Gas Feed System
  - Initially used to test variables and find optimal settings
  - Introduce impurities to simulate real systems
- Biomass
- Waste Processing

Alternative Feedstock Impurity Issues

Sources of Impurity Species from Polymer Feedstocks

Polymer	Monomer	Impurity Element	Weight Percent
Polytetrafluoroethylene	C_2F_4	Fluorine (F_2, HF)	75.98
Polybrominatedbiphenyl	$C_{12}H_{10}Br_2$	Bromine (Br_2)	50.91
Polyvinyl chloride	C_2H_4Cl	Chlorine (Cl_2, HCl)	55.86
Polyurethane	$C_{17}H_{16}N_2O_4$	Nitrogen (N)	8.97
Polysulfone	$C_{27}H_{22}O_4S$	Sulfur (S, SO_2, H_2S, CS_2)	7.25
Polydimethylsiloxane	C_6H_6OSi	Silicone (Si)	37.91

Conclusions

- Successfully Synthesized Catalyst for FTS
- Surface area was reduced by addition of promoters
- SEM/EDS confirmed uniform particles and composition of catalyst
- Promoters Pt and Ru reduced activation temperature
- CO conversion is comparable to published results

Future Goals:

- Cobalt/Promoter dispersion studies
- Non-Petroleum or Green Feedstocks
  - Biomass (non-edible plants, bio-oils, human waste)
  - Plastic Waste (discarded or non-recyclable)

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