SYNTHESIS, DECOMPOSITION AND CHARACTERIZATION OF FE AND NI SULFIDES AND FE AND CO NANOPARTICLES FOR AEROSPACE APPLICATIONS

J.E. Cowen[a,**], A.F. Hepp[b,‡], N.V. Duffy[c,‡], M.J. Jose[c], D.B. Choi[c], S.M. Brothers[c], M.F. Baird[c], T.M. Tomsik[b], S.A. Duraj[d], J.N. Williams[d], M.J. Kulis[e], and J.R. Gaier[b]

[a]Dept. of Materials Science, Case Western Reserve University, Cleveland, OH 44106
[b]NASA Glenn Research Center, Cleveland, OH 44135
[c]Department of Chemistry, Wheeling Jesuit University, Wheeling WV 26003
[d]Department of Chemistry, Cleveland State University, Cleveland, OH 44115
[e]National Center for Space Exploration Research, NASA GRC, Cleveland, OH 44135

Abstract: We describe several related studies where simple iron, nickel, and cobalt complexes were prepared, decomposed, and characterized for aeronautics (Fischer-Tropsch catalysts) and space (high-fidelity lunar regolith simulant additives) applications. We describe the synthesis and decomposition of several new nickel dithiocarbamate complexes. Decomposition resulted in a somewhat complicated product mix with NiS predominating. The thermogravimetric analysis of fifteen tris(diorganodithiocarbamato)iron(III) has been investigated. Each undergoes substantial mass loss upon pyrolysis in a nitrogen atmosphere between 195^o and 370^{o}C, with major mass losses occurring between 279^o and 324^{o}C. Steric repulsion between organic substituents generally decreased the decomposition temperature. The product of the pyrolysis was not well defined, but usually consistent with being either FeS or Fe_2S_3 or a combination of these. Iron nanoparticles were grown in a silica matrix with a long-term goal of introducing native iron into a commercial lunar dust simulant in order to more closely simulate actual lunar regolith. This was also one goal of the iron and nickel sulfide studies. Finally, cobalt nanoparticle synthesis is being studied in order to develop alternatives to crude processing of cobalt salts with ceramic supports for Fischer-Tropsch synthesis.

Corresponding authors:

Aloysius F. Hepp - Tel.: (216) 433-3835
Email: Aloysius.F.Hepp@nasa.gov

Norman V. Duffy - Tel.: (304) 243-4430
Email: nduffy@wju.edu

Mr. Jonathan C. Cowen is a graduate student presenter from CWRU.

Synthesis and Characterization of Fe and Ni Sulfides & Fe and Co Nano-Particles for Aerospace Applications

J.E. Cowen[a], A.F. Hepp[b], N.V. Duffy[c], M.J. Jose[c], D.B. Choi[c], S.M. Brothers[c], M.F. Baird[c], T.M. Tomsik[b], S.A. Duraj[d], J.N. Williams[d], M.J. Kulis[e], and J.R. Gaier[b]

[a]Department of Materials Sci. & Eng., CWRU, Cleveland, OH 44106
[b]NASA Glenn Research Center, Cleveland, OH 44135
[c]Department of Chemistry, Cleveland State University, Cleveland, OH 44115
[d]Department of Chemistry, Wheeling Jesuit University, Wheeling WV 26003
[e]National Center for Space Exploration Research, NASA GRC, Cleveland, OH 44135

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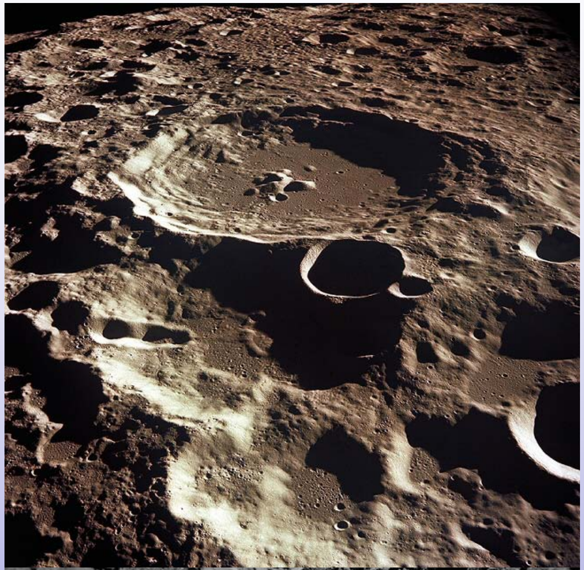
Outline

- Lunar Regolith
  - Background
- Fischer-Tropsch Catalysis
  - Background
  - NASA Facilities
  - Co nanoparticles
    - Synthesis
    - Characterization

Lunar Regolith



Regolith-is a layer of loose, heterogeneous material covering solid rock.

Rhegos-Greek-which means blanket

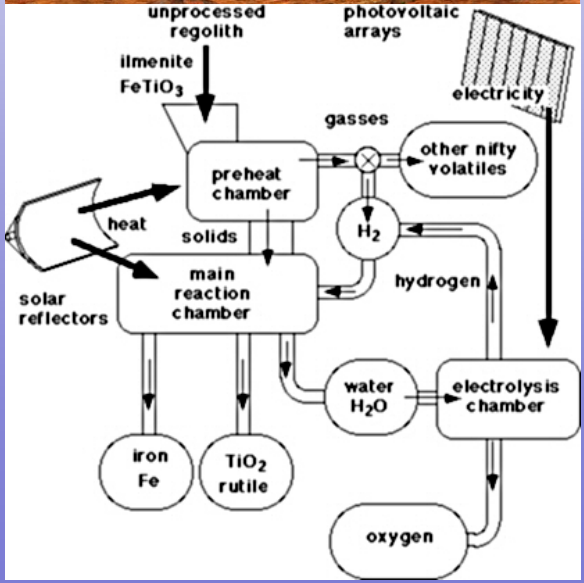
Lithos-Greek- which means rock

Literally translated-blanket of rocks

Lunar Minerals in High Fidelity Simulants

- Silicate minerals make up to 90% volume of lunar rocks
  - Pyroxene - $(CaFeMg)_2Si_{12}O_6$
  - Plagioclase feldspar – $(CaNa)(AlSi)_4O_8$
  - Olivine - $(MgFe)_2SiO_4$
- Oxide minerals make up to 20% volume of lunar rocks
  - Ilmenite – $(MgFe)TiO_3$
  - Spinel – $FeCr_2O_4$, Fe_2TiO_4, $FeAl_2O_4$, $MgTiO_4$
  - Armalcolite – $(MgFe)Ti_2O_5$
- Low abundance of native metals
  - Fe, Ni, Co
- Most sulfur contained in single mineral
  - Troilite – FeS
- Traces of many other minerals

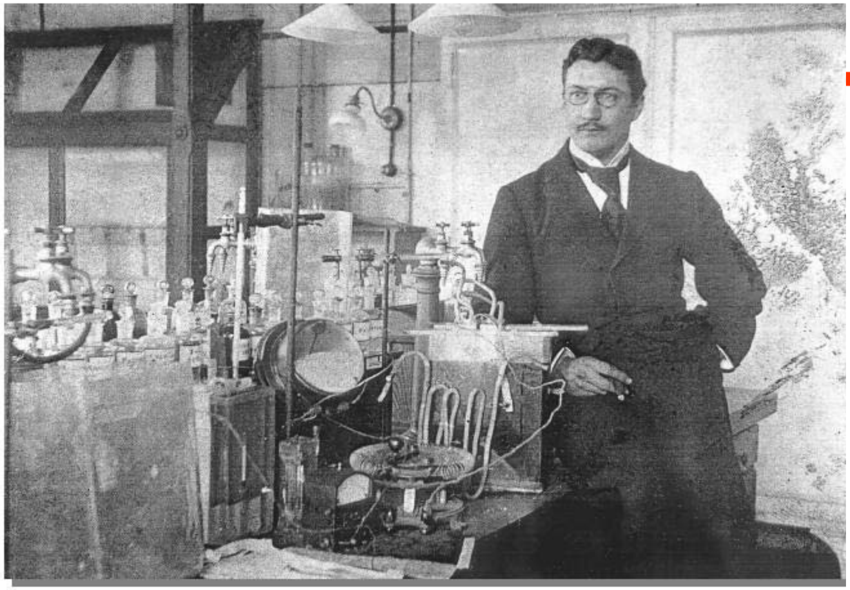
The Importance for High Fidelity Lunar Regolith Simulants



- Abrasion studies
- Thermal conductivity
- Solar attenuation
- Inherent chemistry

Fischer-Tropsch Catalysis

Franz Fischer at Work in 1918



Financial Mail, 2000

The Fischer-Tropsch Process

1) Synthesis Gas Formation

$$CH_n + O_2 \xrightarrow{\text{(Catalyst)}} \tfrac{1}{2}\, n\, H_2 + CO$$

2) Fischer-Tropsch Reaction

$$2n\, H_2 + CO \xrightarrow{\text{Catalyst}} -(CH_2-)_n- + H_2O$$

3) Refining

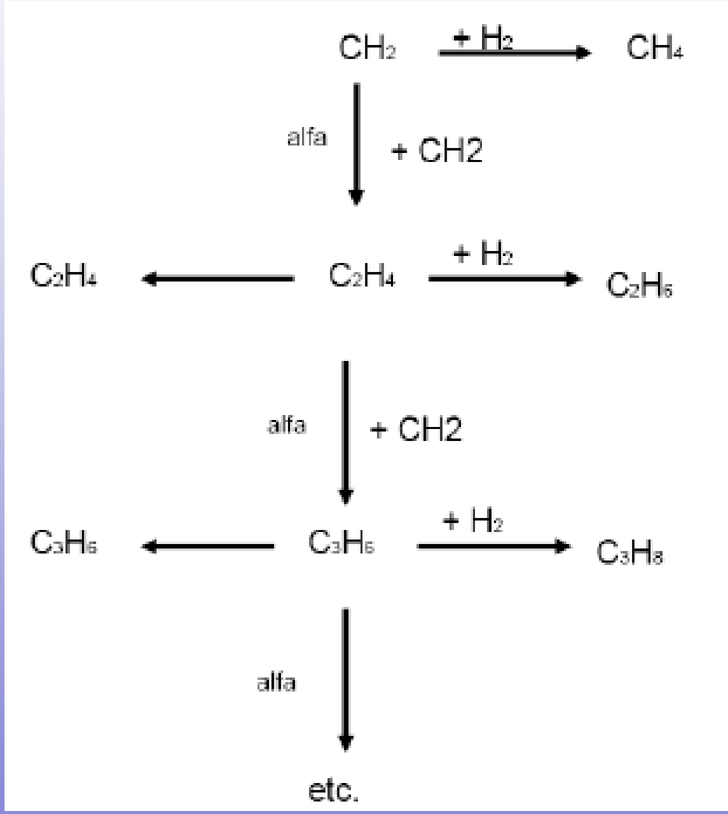
$$-(CH_2-)_n- \xrightarrow{\text{(Catalyst)}} \text{Fuels, lubricants, etc.}$$

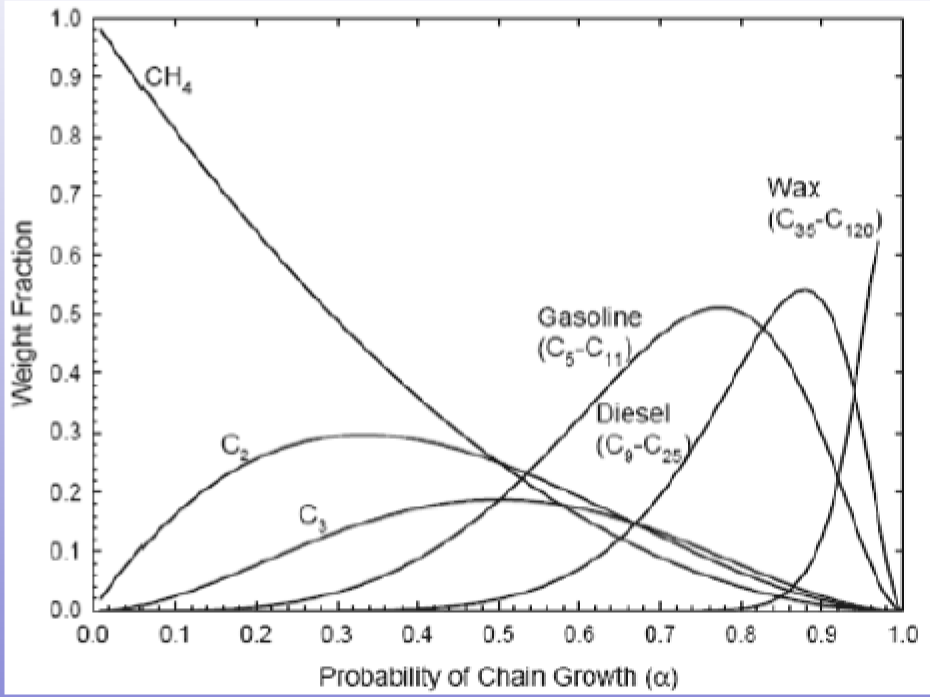
Syntroleum

History of FT Catalysis

- 1897 - Losanitsch and Jovitschitsch
  - Converted CO and hydrogen to liquid products using an electrical discharge
  - Primary product was formaldehyde
- 1902 – Sabatier and Senderens
  - Converted CO and hydrogen to methane over nickel catalyst
- 1923 – Fischer and Tropsch
  - Converted CO and hydrogen to liquid hydrocarbons using Catalysts used included CO, Fe, and Ru based catalysts
- 1925 – German patent issued on process
- 1936 – First commercial plant operates in Germany
- 1944 – Wartime FT-process production peak
  - Germany 16,000 barrels per day
  - Japan 1,500 barrels per day
- 1947 - 1952 US Synthetic Fuels Production
  - German plant moved to Louisiana, MO by Bureau of Mines
  - Texaco builds 120 bpd plant at Montebello, CA using NG feed
- 1950 – 1953 Hydrocarbon Res. Inc. builds 5,000 bpd Hydrocol Plant in Brownsville, TX – operates briefly
- 1953 - Koelbel/Ackerman operate full commercial scale FT slurry process plant in Germany using Fe catalyst
- 1955 – Sasol operates 8,000 bpd SASOL 1 plant in Sasolburg, SA using Fe catalyst and Fixed bed and CFB reactors

Alpha-probability of chain growth





Pros & Cons of Alternative Fuels

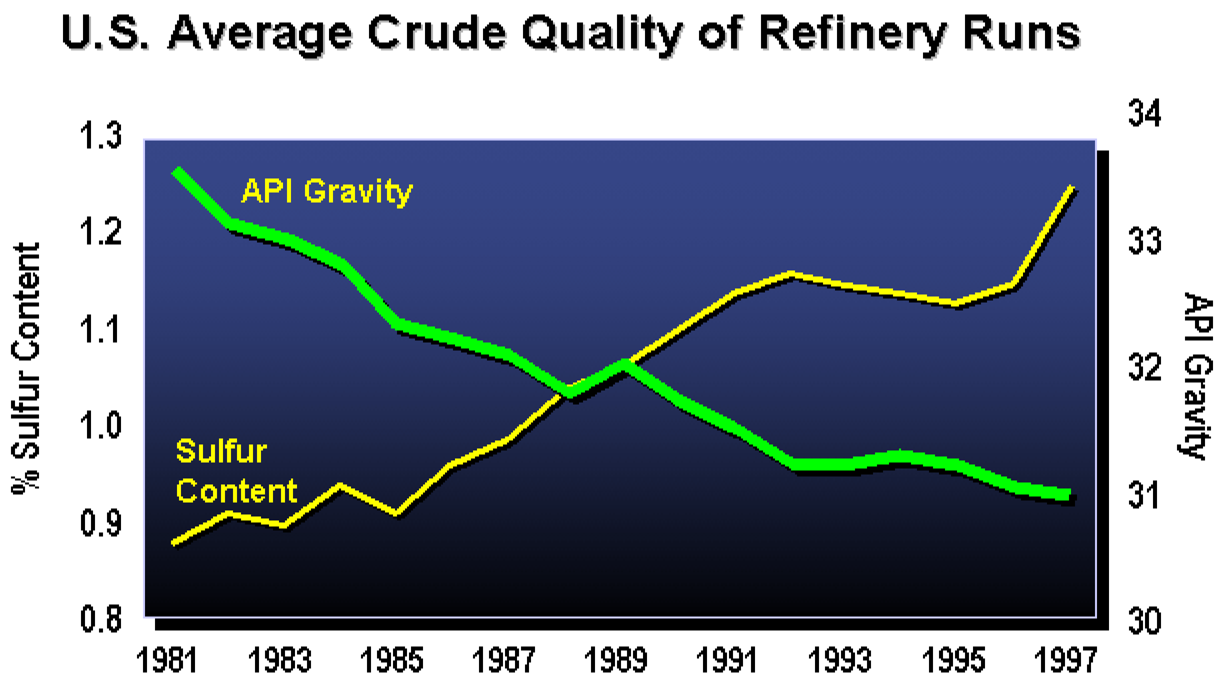
- **FT fuel advantages:**
  - **No sulfur**
  - **Reduced CO emission**
  - ***Reduced particulate matter (PM) emissions***
  - **Less toxic, no aromatics**

- **FT fuel Issues**
  - ***Low lubricity: new additives or blending (bio-fuel?)***
  - **Smaller particle size distribution in particulates emissions**

- **Bio-fuel Advantages**
  - **Clean burning as F-T fuel**

- **Bio-fuel Issues**
  - **High freezing point, gel problem**
  - **Heavier than Jet-A (C16-C18, vs. C12 avg.)**

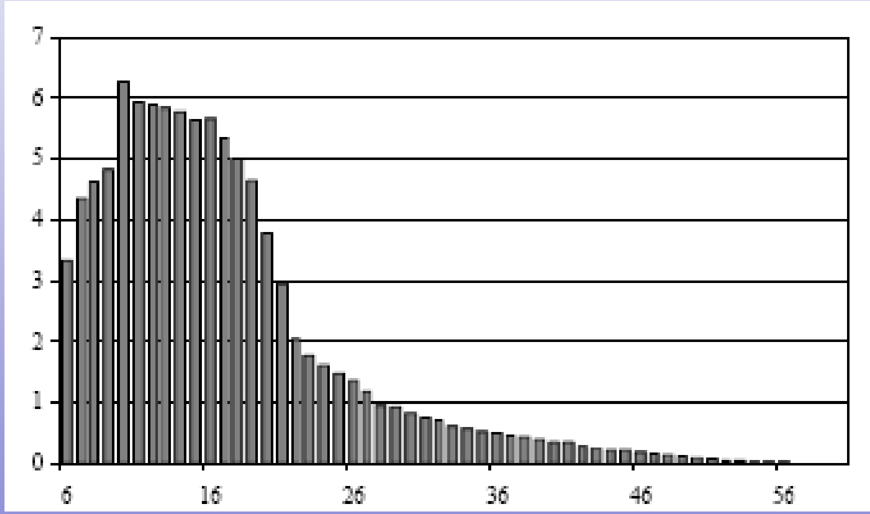
Clean Fuel Regs Run Counter to Oil Quality Trends



American Petroleum Institute (API>10 floats on water API<10 sinks in water)

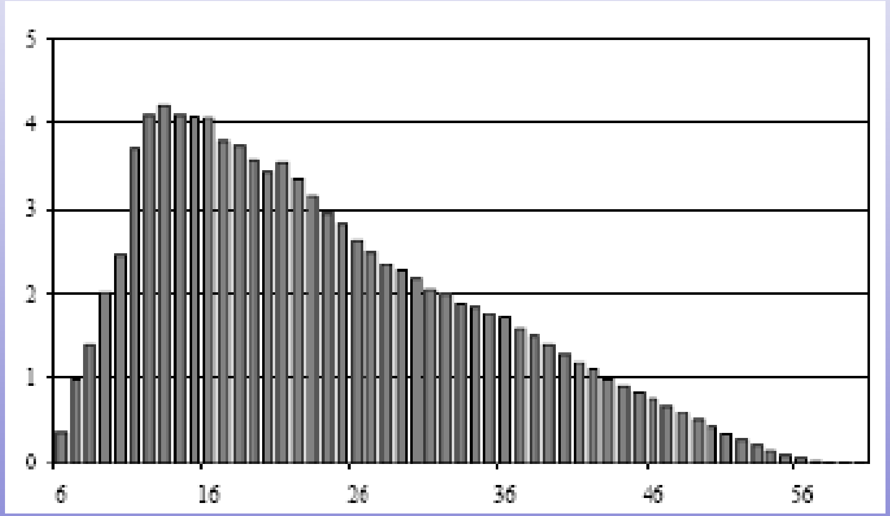
Product Selectivity Dependent on Catalysts Material

Fe catalyst distribution



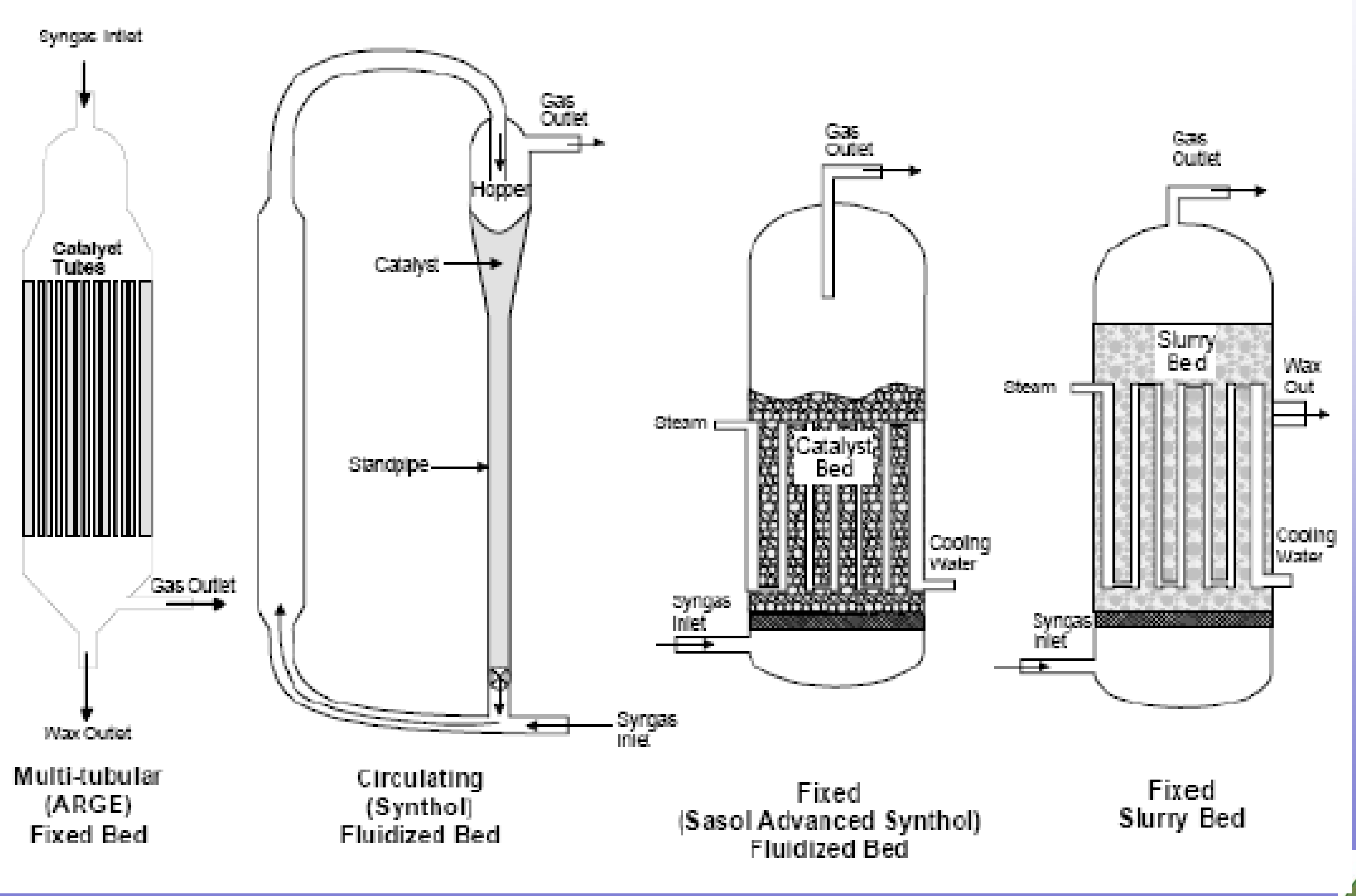
# of Carbon atoms

Co catalyst distribution



# of Carbon atoms

Main types of FT Reactors



Bldg 109 Test Facility

Control Room

Gas Chromatograph work area

Test Facility

Agilent 6890N Capillary GCs

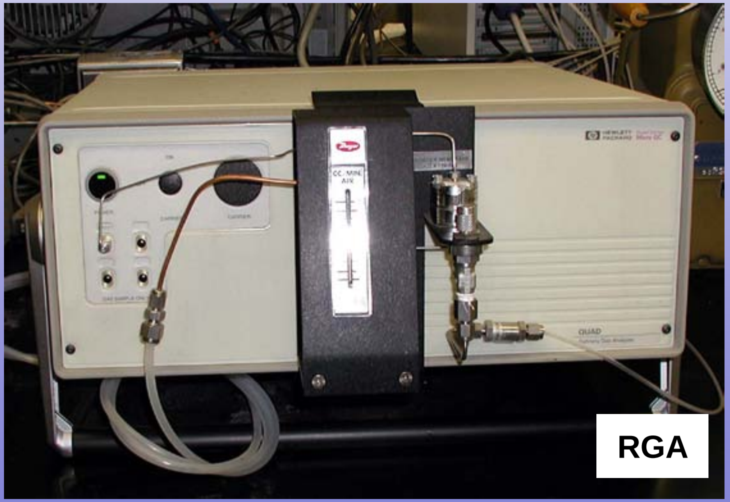
Oil + Wax Analysis

- Oils: C4 thru C44 Alkanes and Alkenes
  - Sample Prep – 0.2 ml Neat Injection (inj)
- Wax: C11 thru C80 Alkanes and Alkenes
  - Sample Prep – Dissolve w/O-Xylene (1 ml inj)
- FID – carrier gases H2, He & Zero-Air
- Data Acquisition – Cerity NDS Software

RGA (Refinery Gas Analyzer)

Agilent 3000A Micro GC

- CO, CO_2, H_2, N_2 & C1 thru C8 Hydrocarbons
- TCD detector w/4 columns – carrier gas He & Ar
  - Gas Samples – Continuous from reactors
- Data Acquisition – Cerity NDS Software



Fischer-Tropsch Reaction – Over View Chemistry & Testing

$2H_2 + CO \rightarrow -CH_2- + H_2O$ (exothermic)

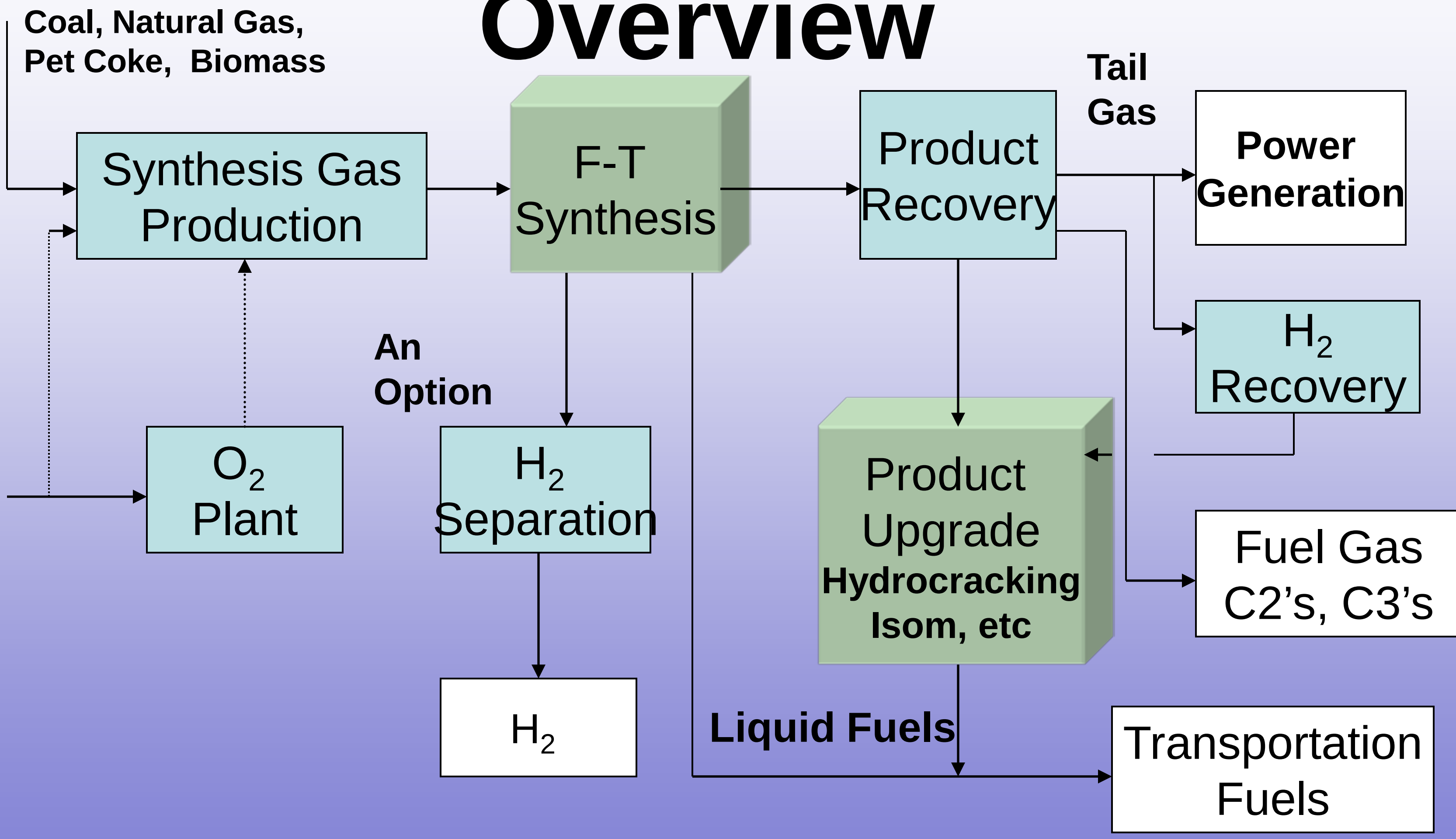
Paraffins	$(2n + 1)\cdot H_2 + n\cdot CO \Rightarrow C_nH_{2n+2} + n\cdot H_2O$
Olefins	$2n\cdot H_2 + n\cdot CO \Rightarrow C_nH_{2n} + n\cdot H_2O$
Water gas shift rxn	$CO + H_2O \Leftrightarrow CO_2 + H_2$

Catalysts	**Pressure**	**Temperature**
Cobalt	180 – 450 psig	210 – 240 ^oC
Iron	180 – 450 psig	240 – 270 ^oC

Feed conditions / test variables (typical)

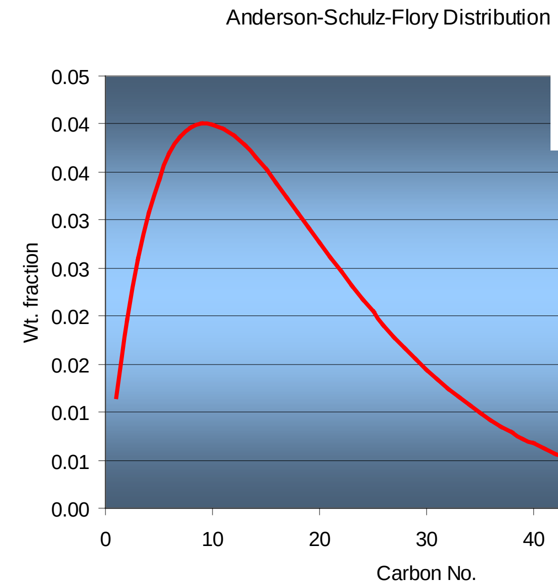
H_2:CO ratio	0.6 – 2.5
H_2 / CO flow rates	20 – 100 SLPH (Max design 120 SLPH – H_2/CO/Ar)
Argon mol %	10 – 50 (inert carrier gas)
Space velocity	1,000 to 10,000 hr^{-1} at STP (2 – 4 SLPH/gm-Cat)
Catalyst Type	Co, Fe, Ru; promoted/unpromoted; supports Al_2O_3, SiO_2, TiO_2

Fischer-Tropsch Process Overview

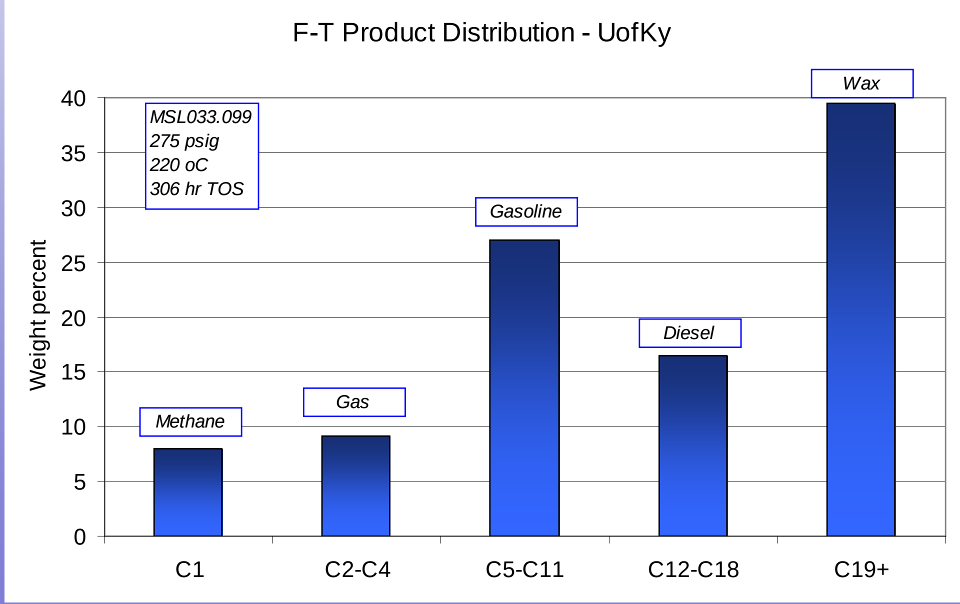


Fischer-Tropsch - Products of Reaction

Cobalt Catalyst Wax **Iron Catalyst Wax**



$$M_n = (1 - \alpha)\,\alpha^{(n-1)}$$
$$\alpha = 0.9$$

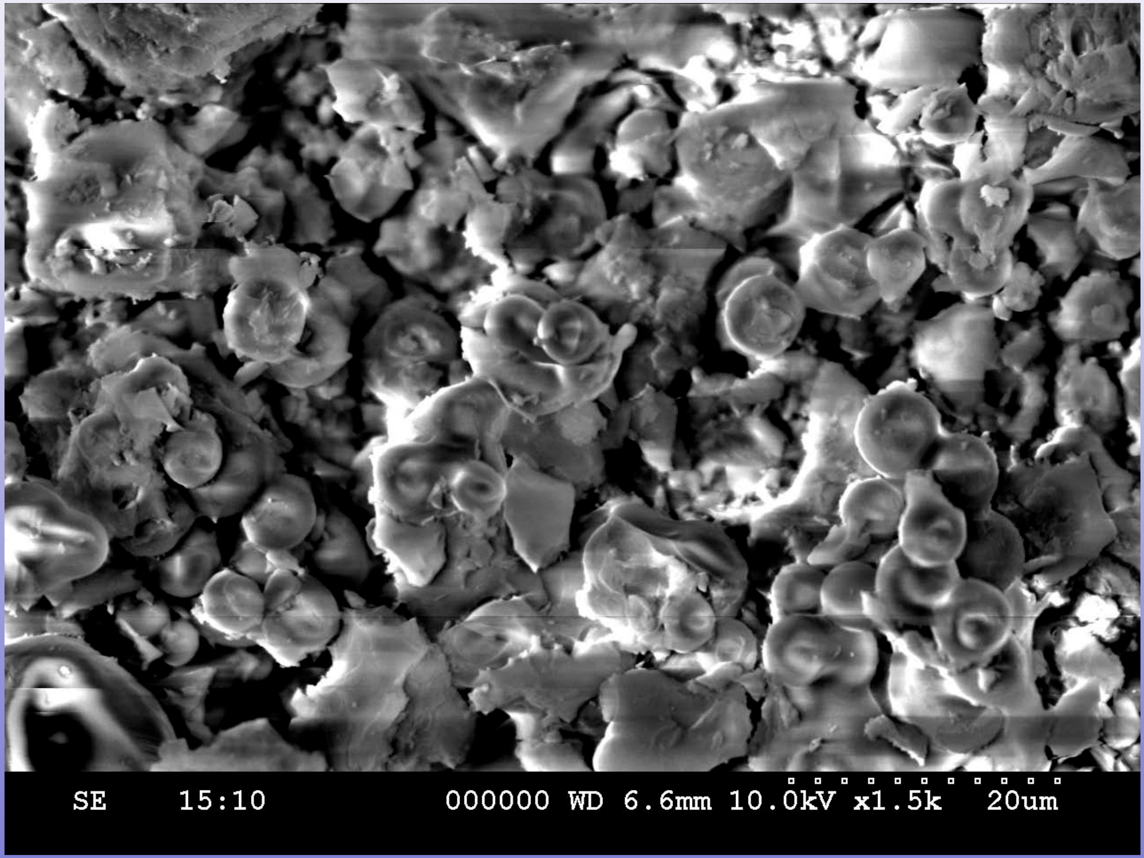


F-T Light Oil Product Sample

Synthesis of SiO_2 supports

$Si(OR)_4 + 4\ H_2O \rightarrow Si(OH)_4 + 4\ ROH$

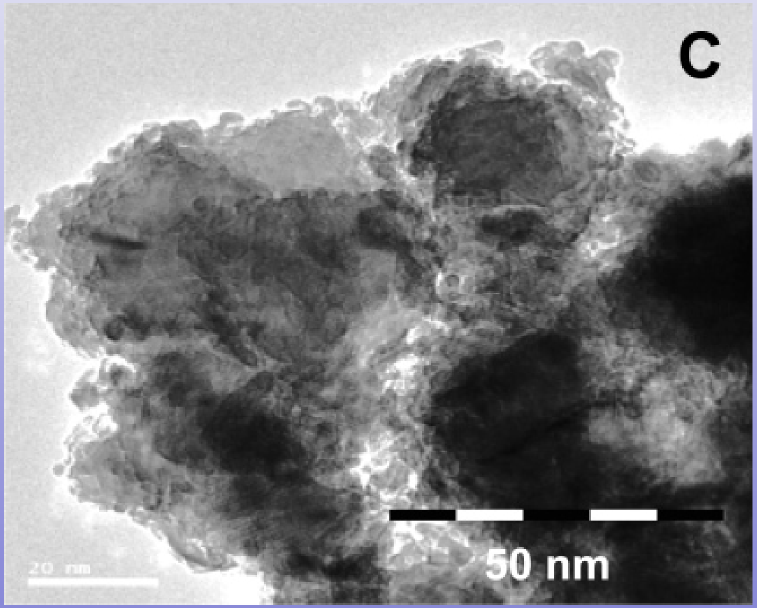
TEOS - tetraethylorthosilcate



Typical synthesis of Co loaded SiO_2 supports

- Cobalt is typically loaded onto commercially available supports.
    - Cobalt precursors are typically $CoCl_2 \cdot 6H_2O$ or $Co(NO_3)_2 \cdot 6H_2O$
    - Loading is typically ~ 10-20% by weight.
    - Loading is usually achieved through **chemical infiltration** or **Incipient wetness impregnation.**
- Often promoters are added to enhance the activation of the catalysts.
    - Common promoters include Pt, Re, Ru, Pd.
    - Loading of the promoters is typically ~ 0.5-3.0% by weight.

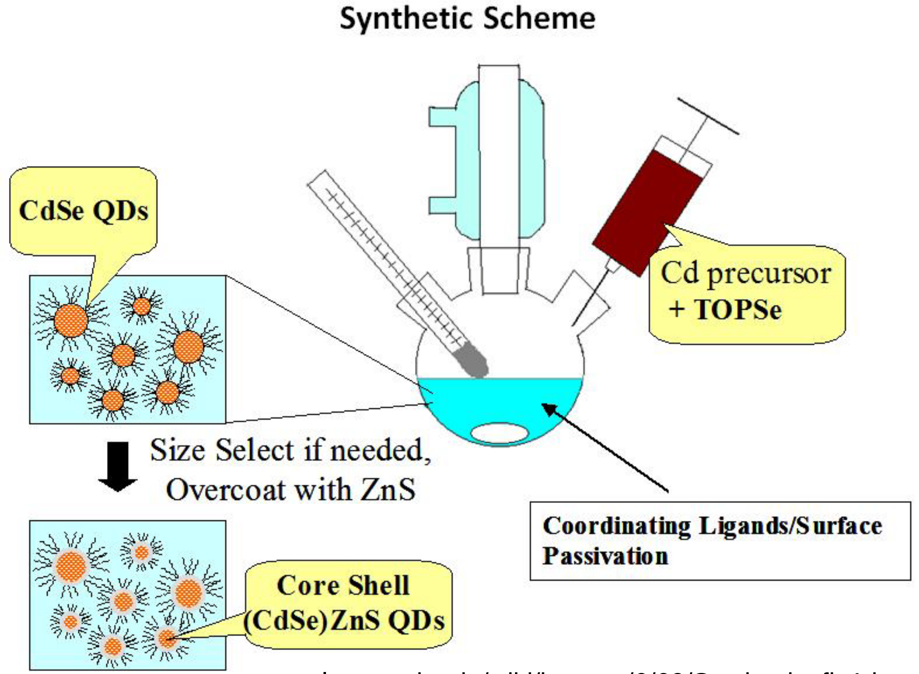
This type of deposition yields catalysts with much non-uniformity with regards to shape and size



X-ray absorption spectroscopy of Mn/Co/TiO2
Morales, Fernando; Grandjean, Didier; Mens, Ad; de Groot, Frank M. F.; Weckhuysen, Bert M. Journal of Physical Chemistry B (2006), 110(17), 8626-8639.

Synthesis of Co particles

- Co source is $Co_2(CO)_8$
- Capping group/Surfactant
  - TOPO
  - TOP
  - Oleic Acid
  - PPh_3
- Adjustable parameters
  - Temp
  - Time
  - Concentration/surfactant ratio

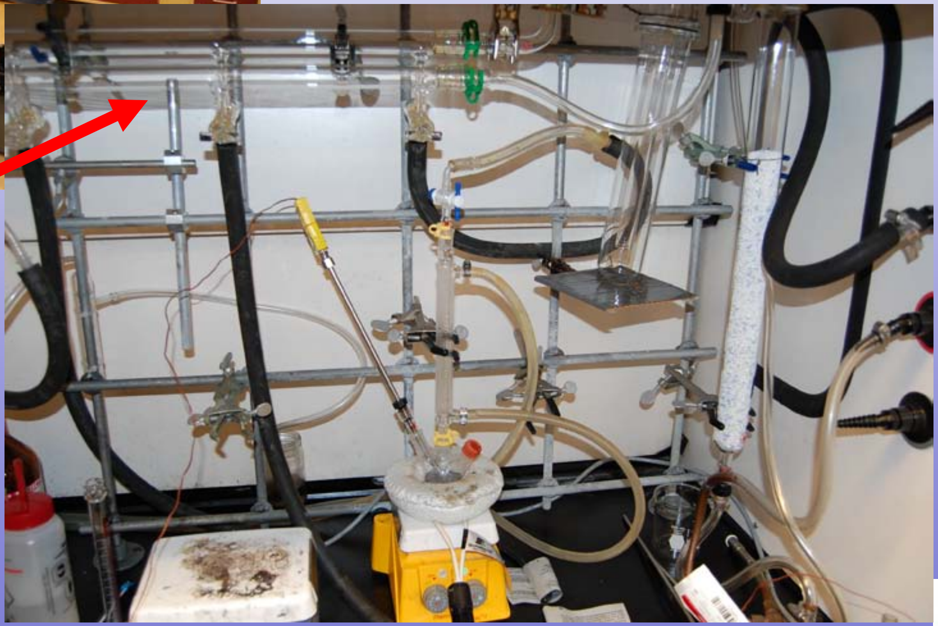


http://nanocluster.mit.edu/wiki/images/6/60/Synthesis_fig1.jpg

Synthesis Lab at NASA GRC

Reactions are carried out under inert atmosphere conditions

Glove box to store air sensitive materials

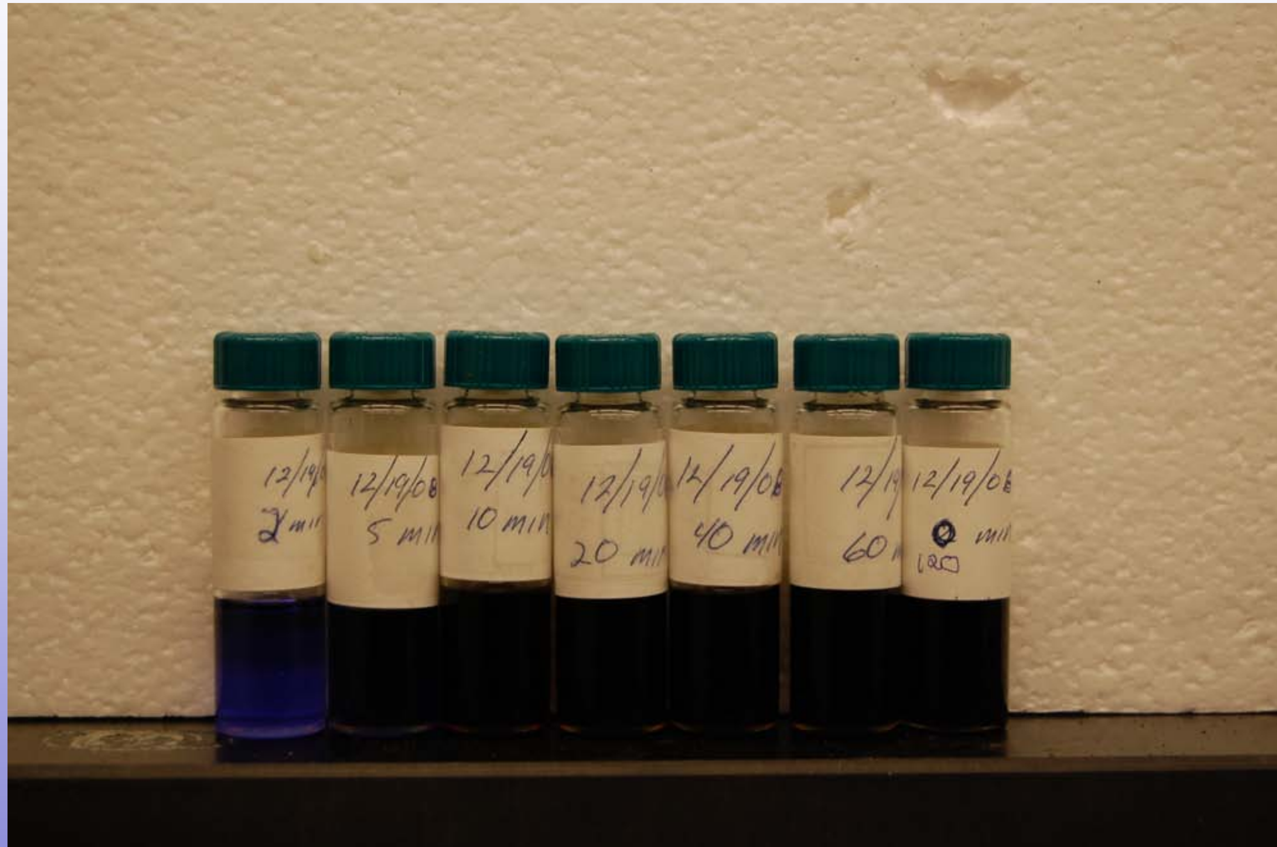


Schlenk line

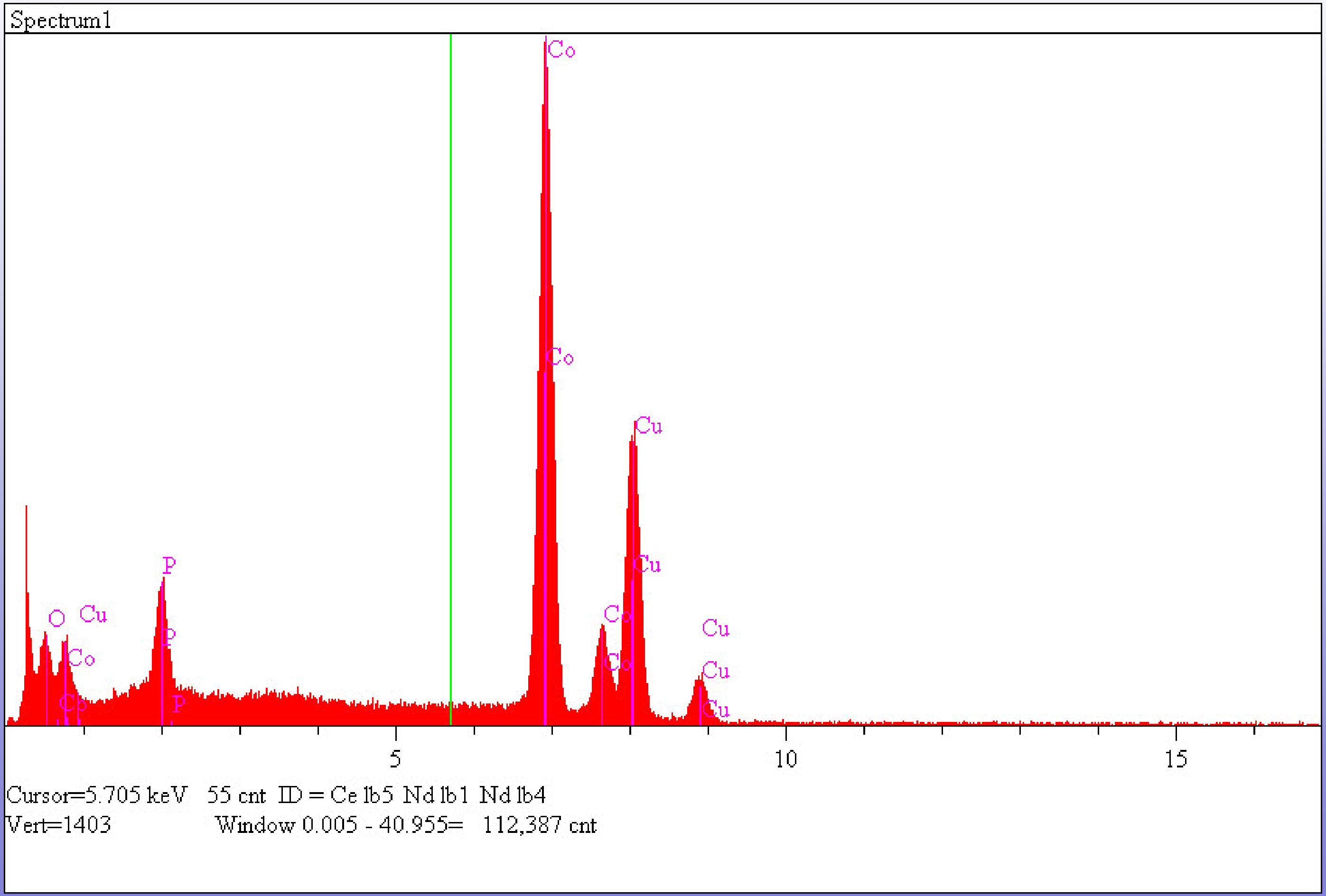
Reaction temperature controlled via programmable temperature controller

Synthesis Lab at NASA GRC

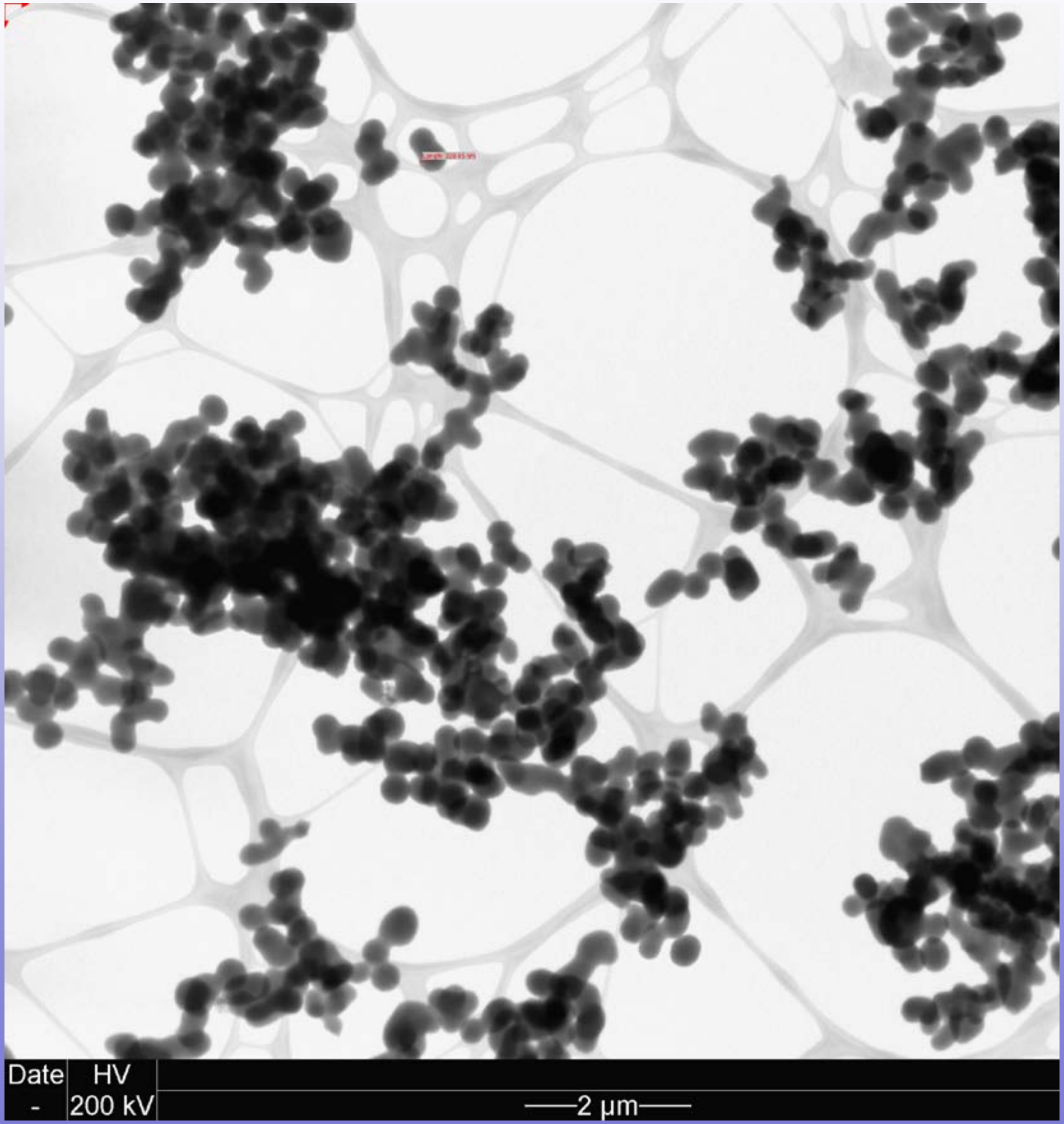
Co particles



EDS Spectrum of Co Particles



Co Particles



XRD Pattern of Co Particles