

PYROLYSIS-GCMS ANALYSIS OF SOLID ORGANIC PRODUCTS FROM CATALYTIC FISCHER-TROPSCH SYNTHESIS EXPERIMENTS. Darren R. Locke¹, Cyriah A. Yazzie², Aaron S. Burton³, Paul B. Niles³, Natasha M. Johnson⁴, ¹HX5 – Jacobs JETS Contract, NASA Johnson Space Center (darren.r.locke@nasa.gov); ²Diné College, Tsaile, AZ 86556; ³NASA Johnson Space Center; ⁴NASA Goddard Space Flight Center

Introduction: Abiotic synthesis of complex organic compounds in the early solar nebula that formed our solar system is hypothesized to occur via a Fischer-Tropsch type (FTT) synthesis involving the reaction of hydrogen and carbon monoxide gases over metal and metal oxide catalysts [1]. In general, at low temperatures (<200°C), FTT synthesis is expected to form abundant alkane compounds while at higher temperatures (>200°C) it is expected to product lesser amounts of *n*-alkanes and greater amounts of alkene, alcohol, and polycyclic aromatic hydrocarbons (PAHs) [2].

Experiments utilizing a closed-gas circulation system to study the effects of FTT reaction temperature, catalysts, and number of experimental cycles on the resulting solid insoluble organic products are being performed in the laboratory at NASA Goddard Space Flight Center [3]. These experiments aim to determine whether or not FTT reactions on grain surfaces in the protosolar nebula could be the source of the insoluble organic matter observed in meteorites. The resulting solid organic products are being analyzed at NASA Johnson Space Center by pyrolysis gas chromatography mass spectrometry (PY-GCMS). PY-GCMS yields the types and distribution of organic compounds released from the insoluble organic matter generated from the FTT reactions. Previously, exploratory work utilizing PY-GCMS to characterize the deposited organic materials from these reactions has been reported [4]. Presented here are new organic analyses using magnetite catalyst to produce solid insoluble organic FTT products with varying reaction temperatures and number of experimental cycles.

Instrumentation and Methods: The PY-GCMS measurements are being made in the Light Element Analysis Laboratory (LEAL) at the Johnson Space Center in Houston. The PY-GCMS system consists of a CDS pyroprobe (5200 model) coupled to a Thermo Trace-Ultra gas chromatograph with a Thermo DSQ II mass spectrometer. Organic compounds that can be identified with this method include both aliphatic and aromatic molecules. Aliphatic constituents may include normal, branched, and cyclic compounds, while aromatic constituents may include small one- to four-ring PAHs and associated alkylated compounds.

The pyrolysis procedure involves loading a small quantity of reacted FTT catalyst (10-20 mg) into a glass capillary with glass wool to contain the sample.

The loaded capillary is mounted into the pyroprobe platinum coil heater so that the coil windings encircle the entirety of the sample to be pyrolyzed. For these initial experiments, we have thermally desorbed volatile compounds and gently pyrolyzed macromolecular materials at 300°C for 10 minutes. During the duration of the heating, released compounds are trapped at room temperature, using a Tenax-TA sorbent tube. Following the heating, compounds adsorbed on the Tenax-TA are thermally desorbed and injected, in a single pulse, into the gas chromatograph for separation then detection by the mass spectrometer.

Results and Discussion: In general, the pyrolysis of solid organic materials produced by FTT experiments with magnetite catalyst released both aromatic and aliphatic organic compounds (Fig. 1). As anticipated, the FTT synthesis yields *n*-alkanes in the range of C6 (hexane) to C13 (tridecane). Surprisingly, these compounds were not the predominant products. The predominant products were aromatic, and were dominated by: toluene, xylene isomers, alkyl benzene isomers, naphthalene, and methyl and alkyl naphthalene isomers.

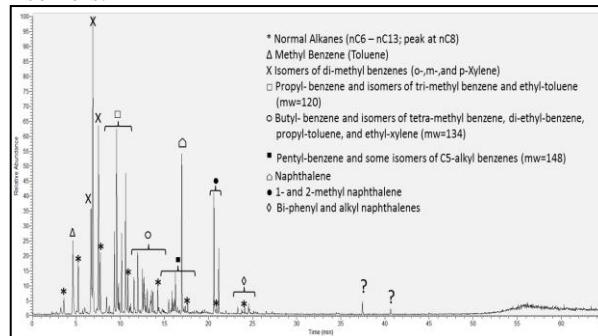


Figure 1 Gas chromatogram of organic compounds released by 300°C thermal desorption/pyrolysis of organic materials generated from an FTT experiment using magnetite catalyst at 400°C temperature.

The dominance of aromatic compounds over *n*-alkanes is likely due to the high thermal maturity of these samples, given that thermal maturity trends from aliphatic dominated products at low temperature to aromatic dominated products at higher temperatures. Typically, industrial FTT synthesis to generate long chain hydrocarbons are run at much lower temperatures (150°C to 300°C). The experiments that were performed here were at much higher temperatures

(>300°C) than the typical temperature range used for industrial processes, resulting in increased reaction rates, conversion of organics to methane gas, and generation of aromatic compounds dominated by small one- to four- ring PAHs and their alkylated derivatives. Larger PAHs may have been produced but are not detectable by this pyrolysis method due to their lower volatility.

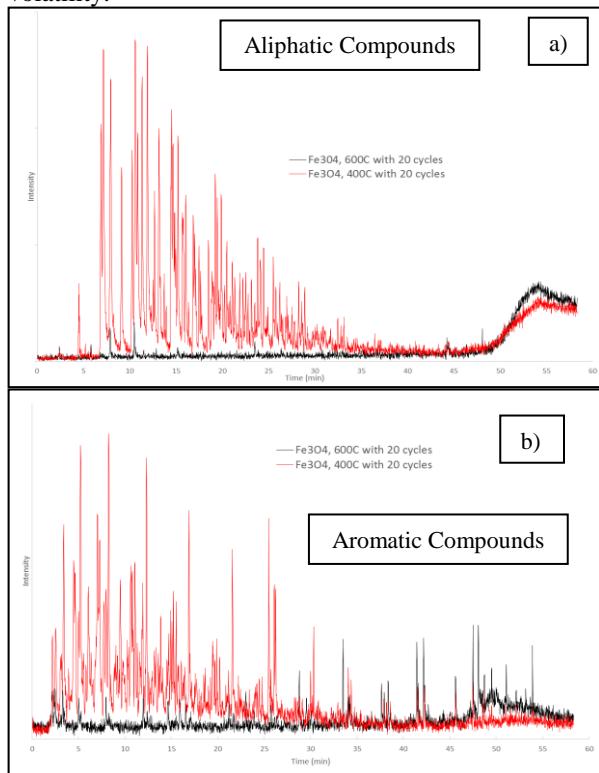


Figure 2 Extracted ion chromatograms showing the a) aliphatic and b) aromatic compounds present in FTT synthesis experiments with magnetite catalyst at 400°C and 600 °C.

The Effect of FTT reaction Temperature. The effect of FTT reaction temperature on organic compound generation with the magnetite catalyst has been investigated by performing the FTT reactions at 400°C and 600°C (Fig. 2). Both the aliphatic and aromatic compounds are far more abundant in the 400°C experiment. Further, the aliphatic compounds from the 400°C experiment tend to be lower molecular weight than the compounds produced at 600°C. Comparatively, the 400°C experiment yields abundant aromatic compounds while the 600°C experiments yields very little.

The Effect of FTT Cycles. The effect of the number of experimental cycles used to generate the solid organic materials has also been investigated (Fig. 3). The aliphatic compounds produced after 20 FTT reaction cycles with the magnetite catalyst at 400°C are more abundant and lower molecular weight than the

aliphatic compounds after one cycle. Surprisingly, aromatic compounds are not present in the one cycle sample while the 20 cycle sample has abundant aromatic compounds.

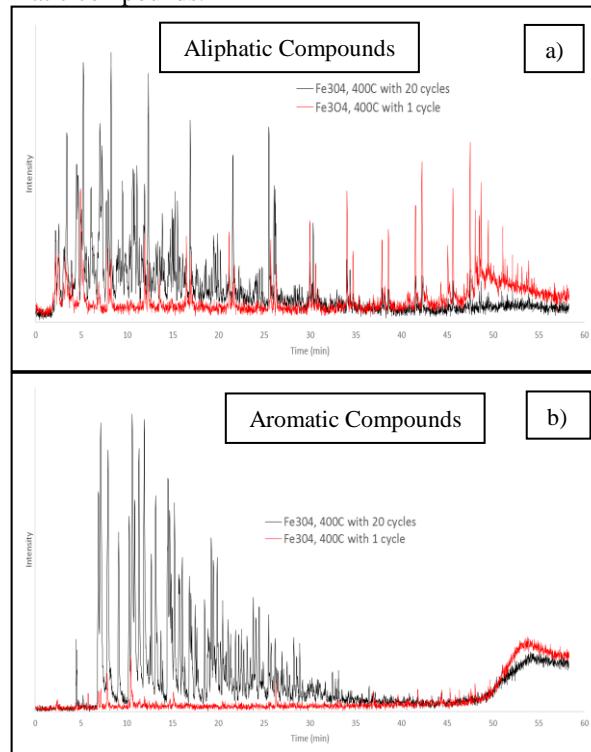


Figure 3 Extracted ion chromatograms showing the a) aliphatic and b) aromatic compounds present in FTT synthesis experiments with magnetite catalyst at 400°C after one and 20 experiment cycles.

Conclusions:

- Thermal desorption and gentle pyrolysis of solid insoluble organic materials deposited during FTT synthesis can be analyzed by PY-GCMS
- For magnetite catalyst, lower temperature FTT synthesis (400°C) favors abundant low molecular weight aliphatic compounds and abundant aromatic compounds while the higher temperature (600°C) favors low abundances of higher molecular weight aliphatic compounds and nearly no aromatic compounds.
- For magnetite catalysts, a greater number of experiment cycles (20) yield lighter molecular weight aliphatic compounds and abundant aromatic compounds that are nearly absent after only one cycle.

References: [1] Kress, M. E. and A.G.G.M. Tielens (2001), *Meteorit. Planet. Sci.*, 2001. **36**: p. 75-91. [2] Schultz, H. (1999), *Appl. Catalysis A: Gen.*, **186**: p. 3-12. [3] Hill, H.G.M. and J.A. Nuth (2003), *Astrobiol.*, **3**(2): p. 291-304. [4] Johnson, N.M., G.D. Cody, and J.A. Nuth III. (2004) *LPS XXXV*, Abstract #1876.