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*Aloysius F. Hepp and Michael J. Kulis*  
*Glenn Research Center, Cleveland, Ohio*

*Peter C. Psarras and David W. Ball*  
*Cleveland State University, Cleveland, Ohio*

*Michael T. Timko*  
*Worcester Polytechnic Institute, Worcester, Massachusetts*

*Hsi-Wu Wong and Jay Peck*  
*Aerodyne Research Inc., Billerica, Massachusetts*

*Russell R. Chianelli*  
*University of Texas at El Paso, El Paso, Texas*

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*Russell R. Chianelli  
University of Texas at El Paso, El Paso, Texas*

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Space Administration

Glenn Research Center  
Cleveland, Ohio 44135

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Cleveland State University  
Cleveland, Ohio 44115

Michael T. Timko  
Worcester Polytechnic Institute  
Worcester, Massachusetts 01609

Hsi-Wu Wong and Jay Peck  
Aerodyne Research Inc.  
Billerica, Massachusetts 01821

Russell R. Chianelli  
University of Texas at El Paso  
El Paso, Texas 79968

## Abstract

Transportation fuels production (including aerospace propellants) from non-traditional sources (gases, waste materials, and biomass) has been an active area of research and development for decades. Reducing terrestrial waste streams simultaneous with energy conversion, plentiful biomass, new low-cost methane sources, and/or extra-terrestrial resource harvesting and utilization present significant technological and business opportunities being realized by a new generation of visionary entrepreneurs. We examine several new approaches to catalyst fabrication and new processing technologies to enable utilization of these non-traditional raw materials. Two basic processing architectures are considered: a single-stage pyrolysis approach that seeks to basically re-cycle hydrocarbons with minimal net chemistry or a two-step paradigm that involves production of supply or synthesis gas (mainly carbon oxides and H<sub>2</sub>) followed by production of fuel(s) via Sabatier or methanation reactions and/or Fischer-Tröpsch synthesis. Optimizing the fraction of product stream relevant to targeted aerospace (and other transportation) fuels via modeling, catalyst fabrication and novel reactor design are described. Energy utilization is a concern for production of fuels for either terrestrial or space operations; renewable sources based on solar energy and/or energy efficient processes may be mission enabling. Another important issue is minimizing impurities in the product stream(s), especially those potentially posing risks to personnel or operations through (catalyst) poisoning or (equipment) damage. Technologies being developed to remove (and/or recycle) heteroatom impurities are briefly discussed as well as the development of chemically robust catalysts whose activities are not diminished during operation. The potential impacts on future missions by such new approaches as well as balance of system issues are addressed.

## Nomenclature

|                               |  |
|-------------------------------|--|
| BDE                           | bond dissociation energies   |
| BET                           | Brunauer Emmett Teller-surface area analysis method  |
| C1                            | generic term for single-carbon compounds or species (CO, CO <sub>2</sub> , CH <sub>x</sub> , etc.)             |
| C2                            | generic term for two-carbon compounds or species (CH <sub>3</sub> C(O)H, C <sub>2</sub> H <sub>x</sub> , etc.) |
| CH <sub>4</sub>               | methane (or natural gas)   |
| C <sub>2</sub> H <sub>4</sub> | ethylene, a starting material for polyethylene   |
| CO                            | carbon monoxide  |
| CO <sub>2</sub>               | carbon dioxide   |
| CSTR                          | continuously-stirred tank reactor  |
| E <sub>a</sub>                | activation energy for a reaction is reduced by the presence of a catalyst improving kinetics                   |
| EDS                           | energy dispersive spectroscopy (for elemental analysis)  |
| ΔH                            | enthalpy change, related to Gibbs free energy change: $\Delta G = \Delta H - T\Delta S$                        |
| FT(S)                         | Fischer-Tröpsch (synthesis)  |
| GRC                           | NASA Glenn Research Center   |
| H <sub>2</sub>                | molecular hydrogen   |
| H <sub>2</sub> O              | water  |
| ISRU                          | In Situ Resource Utilization (program)   |
| LOWR                          | lunar organic waste reformer   |
| LRR                           | logistics reduction and repurposing  |
| P25                           | commercial product, a mixed-phase (~75 percent anatase/25 percent rutile) TiO <sub>2</sub> powder              |
| PAG                           | plasma assisted gasification   |
| Syn-Gas                       | synthesis gas: H <sub>2</sub> /CO gaseous mixture, typical ratio is 2-3:1                                      |
| TiO <sub>2</sub>              | titanium dioxide (or titania), common phases: rutile (most stable), anatase and brookite                       |
| TMS                           | transition metal sulfide(s)  |
| TPR                           | temperature-programmed reduction, a chemi-sorption analysis method   |
| UV                            | ultraviolet light, roughly 400 to 800 nm   |
| UV-Vis                        | ultraviolet-visible (electronic absorption) spectroscopy   |
| WGS                           | water-gas shift reaction   |
| WTE                           | waste-to-energy technologies   |
| XPS                           | X-ray photoelectron spectroscopy, used to determine presence (and charge) of atoms on a surface                |
| XRD                           | X-ray diffraction  |

## Introduction

For a variety of economic, logistical, and technical reasons, transportation fuels production (including aerospace propellants) from non-traditional sources (gases, waste materials, and biomass) has been pursued for decades. These reasons include reducing terrestrial waste streams simultaneous with energy conversion, plentiful biomass, new low-cost methane sources made available by aggressive new extraction methods, and/or in-situ resource utilization of limited resources found in space (or extra-terrestrial surface); they each present significant technological and business opportunities being realized by a new generation of visionary entrepreneurs. In this summary work, we will discuss a series of issues to be addressed while developing technologies relevant to the production of aerospace (or transportation) fuels from non-traditional (non-petroleum) raw materials.

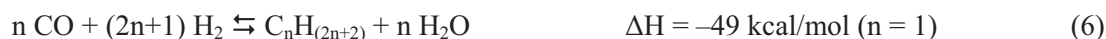
The rationale will be briefly outlined, aeronautics and related terrestrial fuels will be discussed; related needs for fuels for rocket travel will be delved into from the point of view of logistical issues and concerns, outlining the philosophy behind in situ resource utilization (ISRU). Finally, we will highlight follow-on discussions pointed towards new technologies intended to surmount the technical challenges inherent in developing alternative raw materials to produce transportation fuels. Previously, we have addressed ISRU from the point of view of analysis of available resources (Refs. 1 and 2), using solar concentrator technologies to process raw materials (Refs. 3 and 4), and compared methods of production for green aerospace fuels processing (Ref. 5) including a preliminary comparison of methods using a two-stage production paradigm (Ref. 6).

### Fundamental Considerations and Processing Architecture(s)

An important fundamental consideration begins with the thermodynamic energy balance of the chemical reactions at the heart of the various unit operations that comprise the processing steps and related hardware. Two fundamental architectures can be pursued depending upon the technical approach to processing: one begins with an endothermic breakdown step (with a positive  $\Delta H$ ) of the raw material(s) by a reforming reaction (see example Eqs. (1) to (3)) to yield simple inorganic “C1” feed materials, typically gaseous carbon oxides (CO or CO<sub>2</sub>) plus hydrogen (H<sub>2</sub>) (Refs. 5 to 7).



This step can be followed by an exothermic reaction to break C-O and H-H bonds, making C-C bonds and C-H bonds such as the Sabatier (Eq. (4)) (Ref. 8), methanation (Eq. (5)) (Ref. 9) or thermodynamically equivalent Fischer-Tröpsch (Eq. (6)) (Ref. 10) reactions; Figure 1 shows such an operational system combining a steam reformer and Sabatier reactor (Ref. 5).



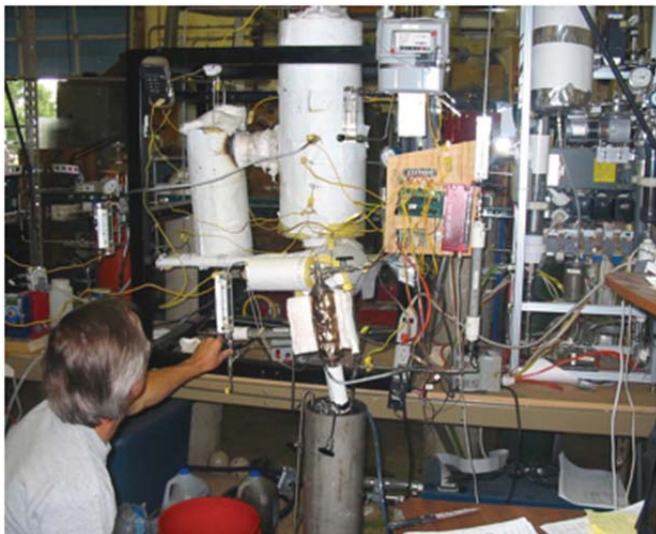


Figure 1.—Steam reformer/Sabatier reactor system delivered to GRC from SBIR Phase II contract.

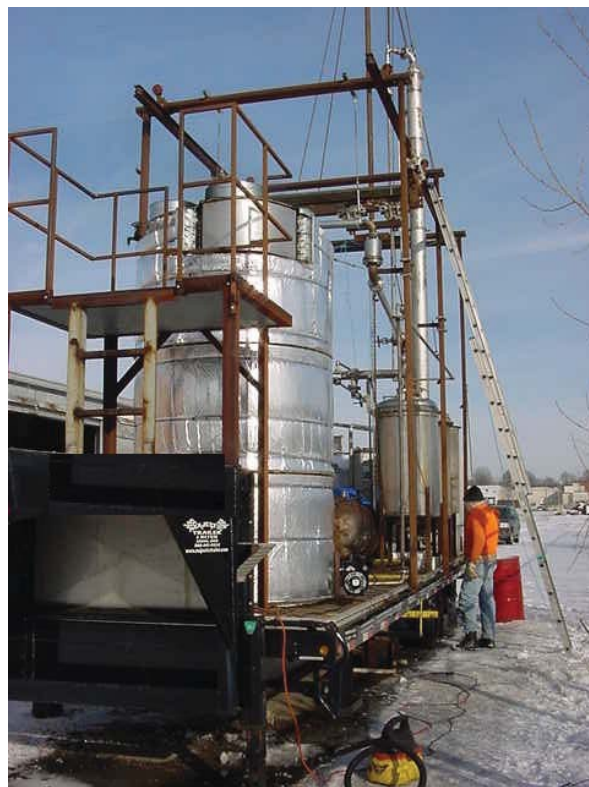


Figure 2.—Commercial pilot-scale reactor for chemical recycling.

Alternatively, a one-step approach can be pursued, typically relying on endothermic processes that can be fueled by heat supplied by combustion of volatile low-carbon by-products (C1-C4) that are not suitable as propellants; see Figure 2 showing an operational thermal cracking or pyrolysis unit (Ref. 5). These tertiary “cracking” reactions are also referred to as chemical recycling (Ref. 11) and are much simpler from a reaction engineering and system perspective but produce relatively large amounts of solid waste or char and are not suitable for a non-terrestrial or minimally-attended environments relevant for space exploration (Refs. 1 to 6).

### Fisher-Tröpsch Synthesis: Terrestrial Applications and Beyond

Fisher-Tröpsch synthesis (FTS) is a century-old gas-to-liquid (GTL) technology that commonly employs Co on an oxide support, or Fe either supported or unsupported. The raw material is a gas mixture of CO and H<sub>2</sub> (synthesis gas or syn-gas) typically produced by the slightly exothermic partial oxidation of methane (CH<sub>4</sub>) (Eq. (7)). Through FTS, a syn-gas feedstock is converted into various liquid hydrocarbons; see Equation (6) above (Ref. 12).



The actual product mix is actually quite complex, including aliphatic or saturated species, unsaturated (mainly olefins) hydrocarbons, and oxygenated species (ketones, aldehydes, and alcohols). The specific final product mix is controllable by adjusting reaction conditions (temperature, pressure, and flow rate) as well as choice of catalyst species, pretreatment, and substrate(s) (Ref. 13). A careful examination of Equation (6) reveals that FTS is essentially the reverse of the steam reforming of CH<sub>4</sub> and hence is an exothermic process.





Figure 3.—Example facilities for processing catalysts, characterizing, and screening fuel production catalysts; from upper left-hand corner: synthesis laboratory, instrument for TPR analysis, Alternative Fuel processing Facility, and continuously-stirred tank reactor.

FTS can produce a clean diesel oil fraction with a high cetane number (typically above 70) without any sulfur or aromatic compounds (Ref. 14). A long-term goal of the U.S. Department of Defense is to replace petroleum-derived fuels with synthetically-produced alternatives (Ref. 15). The U.S. Air Force has successfully tested 50/50 blends of standard jet fuels (JP-8) and FTS-processed synthetics for various aircraft (C-17, B-1, and F-15) (Ref. 16). In a recently-concluded research effort at NASA GRC, the capability to manufacture FTS catalysts (Ref. 17) and fuels was demonstrated in support of a cross-section of successful fuel tests conducted by the Center and Agency.

In order to facilitate more rapid progress in developing optimized catalysts for aerospace propellants, an in-house effort to apply density functional theory to model the interaction of small carbon and metal cluster species on oxide supports was initiated several years ago (Ref. 5). That effort has since migrated to a local university and is now under the guidance of Professor David Ball, in the Department of Chemistry at Cleveland State University and is described in detail below. In summary, our efforts at developing optimized catalysts for aviation fuel production has resulted in two capabilities: catalyst manufacturing and characterization and first principles calculations that can be applied to numerous problems for NASA involving challenging propellant production scenarios given scant raw materials. Figure 3 shows several infrastructural resources in place at GRC for catalyst and green fuels processing (Refs. 5 and 17).

### **In-Situ Resource Utilization and Space Exploration**

ISRU is an approach for human exploration based upon utilization of scarce resources (and anthropogenic material(s)) derived from extra-terrestrial bodies (surface and extant atmosphere) including planets, moons, and asteroids. NASA GRC has a 25-year legacy developing technologies to contribute to this technically challenging exploration architecture. The work pioneered and supported by GRC includes concept proposals, mission studies, hardware (including by contractors) development, and technology demonstrations to produce propellants (and other expendables) using extra-terrestrial resources for the



Figure 4.—Two example ISRU technologies at GRC—(left) Mars CO propellant production plant and (right) solar concentrator for processing regolith simulant.

exploration of the Moon, (Refs. 2 to 4) Mars, (Refs. 1, 18, and 19) and beyond (Refs. 20 and 21). Another important aspect of the NASA GRC effort is the variety of individual collaborations fostered, organizational partnerships formed, and students educated and brought into the aerospace community as a result of the technical work.

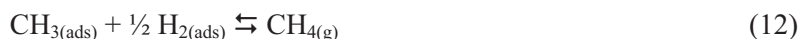
“Living off the land” imposes severe constraints for utilization of power, propellants, and other expendables. The normal rigors (mass, space limitations and environmental challenges) imposed by space travel are magnified by a resource-limited situation. On the other hand, enhanced energy efficiency and minimal launch mass will simplify missions (and increase successful outcomes) by resultant limitations to planned activities. Thus the technical hurdles and challenges alluded to above will stimulate development of technology solutions for space exploration that can be spun off to solve terrestrial problems for defense, dual-use, and commercial transportation, power generation, and efficient resource utilization (Ref. 22). The remainder of this paper discusses new technologies and/or applications for materials processing, hardware engineering, and systems integration to enable technological solutions for the challenging technical hurdles of space exploration and green energy conversion. Figure 4 shows examples of available NASA GRC ISRU facilities and capabilities.

## First Principles Studies for Catalyst Design and Optimization

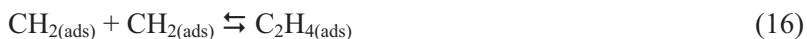
The role of (precious-)metal promoters in FTS is well documented (Refs. 12, 23 to 26). A deeper understanding of the electronic environments associated with  $\text{CH}_4$  selectivity is a useful insight to facilitate the design of more efficient FT catalysts. Evidence has suggested that a Brønsted-Evans-Polanyi (BEP) relationship exists between the effective barrier to methanation and carbon binding strength (Ref. 27). A volcano curve illustrates the catalytic activity as a function of a certain catalytic parameter (binding strength, for example). Plotting against  $\text{CH}_4$  selectivity reveals an important consideration akin to the Sabatier principle: catalytic surfaces should not bind the adsorbate too weakly nor too strongly as the adsorbate species is either non-activated or acts as a removal surface poison, respectively. Naturally, a tightly-bound surface species may reduce  $\text{CH}_4$  selectively but the trade-off is unfavorable: catalytic poisoning and, in the case of FTS, surface carbide build-up. The role of a promoter is to shift the parent surface (through changing the local electronic structure) to more favorable portions of the volcano curve, with higher activity/lower  $\text{CH}_4$  selectivity. We describe on-going work in the Chemistry Department at Cleveland State University to develop theoretical insights into surface reactions involving C1 and C2 species that can be exploited to design FTS catalysts to optimize the product mix for targeted fuels.

## Surface Chemistry

Within this study, the effect of late transition metal promotion with Cu, Ag, Au, and Pd on three active FT catalytic surface analogs (Ni(111), Fe(100), and Co(0001)) is investigated. Adsorption data for two sets of adsorbates is presented; species involved in surface carbide hydrogenation (Eqs. (8) to (12));



and species involved in four competitive C-C coupling pathways (Eqs. (13) to (16)).



## Computational Methodology

All geometry optimizations and frequency calculations for the reactants, products, and transition states are performed using wave function based density functional theory (DFT) in the Gaussian 03/09 platform. All calculations are processed on the Oakley Cluster at the Ohio Supercomputing Center in Columbus, Ohio, project PFS-0213. The exchange-correlation term is treated with the Becke 3-parameter formulation (Ref. 28) using Perdew and Wang (B3PW91) hybrid functionals (Ref. 29). The exchange functional is defined as a linear combination of Hartree-Fock, local, and gradient-corrected exchange terms; this functional is then mixed with the PW91 correlation functional of Perdew and Wang. This functional is chosen for its superior performance when compared to many non-hybrid DFT functionals, its accuracy in predicting geometries, and its appearance in similar studies (Refs. 30 and 31). Electronic orbitals are described with the LANL2DZ basis set (Ref. 32). This basis includes relativistic effects required for larger atoms ( $Z > 36$ ) and treats core electrons with a non-explicit effective core potential (ECP). The efficiency of calculation is greatly enhanced by treating core electrons (not involved in bonding) by only their collective effect on valence electrons.

Seven-atom clusters are used to approximate local surface-adsorbate interactions. Each cluster is designed based on experimental crystal structures for the most active surface for each considered FT catalyst: Ni(111), Fe(100), and Co(0001). Promoters are inserted as a substitute for a perimeter atom (Fig. 5). Clusters are allowed to optimize within the aforementioned basis and level of theory. All clusters are tested for proper spin configuration, where the correct spin state multiplicity  $Z$  ( $Z = 2S + 1$ , where  $S = 1/2$  times the number of unpaired electrons) corresponds with the lowest single point energy.

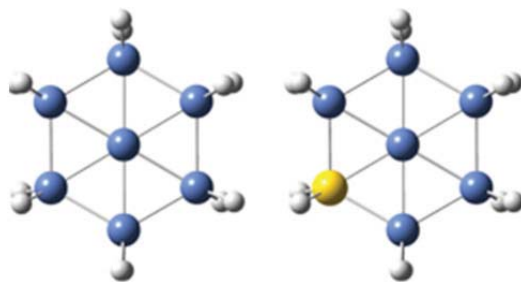


Figure 5.—Seven-atom surface analog: (left) pure metal and (right) with promoter substitution.

TABLE 1.—CALCULATED ADSORPTION ENERGIES (kJ/mol) FOR C ON FT SURFACE ANALOGS

| Metal  | $\Delta E_{\text{ads}}$ (kJ/mol) |        |        |        |        |
|--------|----------------------------------|--------|--------|--------|--------|
|        | Un-doped                         | +Cu    | +Ag    | +Au    | +Pd    |
| Nickel | -384.0                           | -368.7 | -381.5 | -365.1 | -364.9 |
| Cobalt | -415.8                           | -419.3 | -434.3 | -439.6 | -434.9 |
| Iron   | -557.7                           | -556.7 | -642.4 | -537.5 | -553.6 |

### Carbon Chemisorption

Results for C chemisorption are displayed in Table 1. Promoters weakened the C-surface bond on Ni in all cases, suggesting that  $\text{CH}_4$  selectivity is increased on promotion, though perhaps with a concurrent decline in catalytic activity. Cobalt was favorably promoted in all cases, with strengthening of the C-surface bond versus pure  $\text{Co}(0001)$  ( $-415.8$  kJ/mol). Strongly-binding Fe already exhibits lower  $\text{CH}_4$  selectivity than Co and Ni, though weakening the Fe-C bond should increase catalytic activity and possibly reduce the build-up of detrimental surface carbide. Traditionally, Cu is used as a promoter on Fe. Our results show a slight decrease ( $\sim 1$  kJ/mol) in C binding strength on  $\text{Fe}_6\text{Cu}$  over pure  $\text{Fe}(100)$ . Our results also suggest that Ag does not favorably influence C binding strength on Fe, with an 84.7 kJ/mol increase.

### Reaction Barriers

Aside from the BEP assumptions employed on the chemisorption of C, there were no observable trends linking thermodynamic and kinetic behavior. To understand the effect of promotion on the three surfaces under study, activation energies for the steps of hydrogenation (reactions 9 to 12) and for competitive C-C coupling (reactions 13 to 16) were compared; activation energies ( $E_a$ ) are summarized in Table 2. Results are considered relative to  $E_a$  for the hydrogenating and coupling steps on the pure surface. No catalyst was considered unanimously effective nor ineffective over the eight reactions considered (Eqs. (9) to (16)). Rather, good promoters generally favored a lowering of coupling barriers and/or raising of barriers to hydrogenation. Further, extent of change can be considered when results seem ambiguous, though reaction kinetics would suggest that elevation to coupling barriers should be considered more detrimental than reduction of hydrogenating barriers.

$\text{Ni}_6\text{Au}$  and  $\text{Ni}_6\text{Pd}$  were considered strong candidates because they both lowered all barriers to coupling while simultaneously raising the barrier to surface methyl hydrogenation to  $\text{CH}_4$  (reaction 12).  $\text{Ni}_6\text{Ag}$  could be considered moderately effective as it raised many barriers to methanation, and  $\text{Ni}_6\text{Cu}$  would not be recommended as it raised three of four coupling barriers by approximately 50 kJ/mol. Note that these findings are contrary to those based on the BEP assumption, where all catalysts appeared unsuitable for reduction of  $\text{CH}_4$  selectivity on Ni. Copper yielded unfavorable promotion on cobalt as well, with only three of eight reactions seeing favorable influence. Silver makes for an interesting case on Co as even though it reduced many barriers to methanation, coupling barriers were lowered substantially,

TABLE 2.—ACTIVATION ENERGIES ( $E_a$  - kJ/mol) FOR REACTIONS (9) TO (16)

| Cluster            | CH    | CH <sub>2</sub> | CH <sub>3</sub> | CH <sub>4</sub> | C <sub>2</sub> H | C <sub>2</sub> H <sub>2</sub> | C <sub>2</sub> H <sub>3</sub> | C <sub>2</sub> H <sub>4</sub> |
|--------------------|-------|-----------------|-----------------|-----------------|------------------|-------------------------------|-------------------------------|-------------------------------|
| Ni (111)           | 39.8  | 19.6            | 7.1             | 74.5            | 25.0             | 17.7                          | 51.8                          | 153.5                         |
| Ni <sub>6</sub> Cu | 31.6  | 28.1            | 82.7            | 34.0            | 88.0             | 65.6                          | 100.3                         | 5.8                           |
| Ni <sub>6</sub> Ag | 13.4  | 20.4            | 18.9            | 97.6            | 18.5             | 31.7                          | 34.6                          | 175.8                         |
| Ni <sub>6</sub> Au | 6.1   | 12.0            | 76.0            | 128.4           | 9.5              | 9.5                           | 25.5                          | 92.0                          |
| Ni <sub>6</sub> Pd | 1.5   | 9.0             | 2.9             | 134.1           | 24.7             | 1.6                           | 19.8                          | 16.0                          |
|                    |       |                 |                 |                 |                  |                               |                               |                               |
| Co (0001)          | 34.5  | 83.6            | 95.0            | 67.0            | 85.6             | 49.0                          | 0.4                           | 158.6                         |
| Co <sub>6</sub> Cu | 56.1  | 45.3            | 92.4            | 60.0            | 32.4             | 35.6                          | 44.2                          | 170.0                         |
| Co <sub>6</sub> Ag | 70.5  | 61.3            | 82.1            | 63.8            | 10.5             | 23.5                          | 8.7                           | 64.2                          |
| Co <sub>6</sub> Au | 45.6  | 61.9            | 110.2           | 84.1            | 62.6             | 30.0                          | 70.8                          | 85.8                          |
| Co <sub>6</sub> Pd | 15.3  | 13.7            | 80.0            | 130.4           | 19.9             | 72.7                          | 147.1                         | 89.7                          |
|                    |       |                 |                 |                 |                  |                               |                               |                               |
| Fe (100)           | 40.8  | 29.8            | 79.3            | 105.1           | 90.6             | 102.6                         | 119.8                         | 170.1                         |
| Fe <sub>6</sub> Cu | 27.5  | 57.4            | 100.6           | 243.4           | 70.2             | 69.6                          | 103.1                         | 157.2                         |
| Fe <sub>6</sub> Ag | 61.7  | 48.9            | 74.4            | 126.0           | 28.2             | 43.6                          | 88.5                          | 67.3                          |
| Fe <sub>6</sub> Au | 250.4 | 19.2            | 29.0            | 92.4            | 58.3             | 99.0                          | 84.9                          | 75.3                          |
| Fe <sub>6</sub> Pd | 128.7 | 36.3            | 41.0            | 91.5            | 0.0              | 36.5                          | 34.8                          | 91.5                          |

upwards of 75 kJ/mol. Co<sub>6</sub>Au was the only cluster to provide the desired simultaneous effects discussed above, with two exceptions (reactions 10 and 15). Co<sub>6</sub>Pd could be considered an ambiguous case with seemingly detrimental elevations to coupling barriers countered by highly favorable elevations to hydrogenation barriers.

As mentioned previously, elevation to coupling barriers should outweigh all other considerations. Fe<sub>6</sub>Cu displayed the best performance of any surface-promoter considered based on the aforementioned criteria, with favorable results in all but one reaction (reaction 9). All promoters on Fe lowered coupling barriers, though Fe<sub>6</sub>Ag, Fe<sub>6</sub>Au, and Fe<sub>6</sub>Pd lowered hydrogenating barriers as well. The extent of reduction to coupling barriers is greater for Ag and Pd than for Au, while Ag raised only one hydrogenating barrier, Pd two, and Au three. Based on these results, outside of the superior performance of Fe<sub>6</sub>Cu, promotion would seem to be favored in the order Fe<sub>6</sub>Ag > Fe<sub>6</sub>Pd > Fe<sub>6</sub>Au.

Plane wave calculations are being employed to study the band structure and density of states of the pure and promoted systems described above. The d-band center model will be used as it has been helpful in understanding the role of electronic structure changes on binding energies in other studies (Ref. 33). Use of Bloch's theorem allows us to take advantage of the periodic nature of bulk catalysts to get a truer sense of the electronic structure. The plane wave model can also validate the cluster and/or reveal its shortcomings. The Quantum Theory of Atoms in Molecules (QTAIM) (Ref. 34) will also be employed in further work to inventory charge transfer with special attention placed on the geometries at and about the transition state. In conclusion, practical use of theoretical studies described in this section confirmed the inclusion of Ag and Pd metal species for use in (co-)promoter studies, as discussed below.

## Catalyst Processing and Screening

We outline relevant aspects of the in-house efforts of several research teams at GRC and partners in catalyst processing, characterization and screening. While it is prudent to have control of a chemical process from “start to finish,” practical considerations sometimes come down in favor of vendor catalysts that have been carefully and reproducibly characterized, especially when the emphasis is upon hardware development or product optimization. Another desirable outcome, emphasized in projects with similar goals is the development of catalysts that have uses in multiple reactions, see following discussion in this section. Fuel production may be less than optimal for each specific individual reaction, the simplicity inherent in minimizing catalyst processing and/or handling can result in reduced hardware and infrastructure needs, enhancing odds of mission success or operational (economic) outcomes.

## Transition Metal(s) on Oxide-Based Catalyst Fabrication and Characterization

In industry, FTS is most often catalyzed by Co supported on alumina (Al<sub>2</sub>O<sub>3</sub>), silica (SiO<sub>2</sub>), or titania (TiO<sub>2</sub>) or unsupported alloyed Fe powders. Cobalt is typically used more often than Fe because Co is a longer-active catalyst, has less water-gas shift (Eq. (17)) activity, and lower production of oxygenated products such as alcohols, aldehydes, and ketones; (Ref. 35) these oxygenated materials are valuable commodity chemicals that can be preferentially produced using alternate catalysts, see the discussion below. While we focus herein on efforts at NASA GRC (see Table 3 for examples of Co catalysts fabricated during a recently concluded study), there is a significant worldwide effort to optimize FTS product streams for both transportation (petroleum) and chemical manufacturing markets (Refs. 10 to 17 and 23).



Several different fabrication methods were employed, both conventional (slurry impregnation (SI) and incipient wetness (IW)) as well as a method to enhance surface area (aqueous dispersion (AD)) for both promoted (Ag, Mn, Pd, Pt, and Ru) and un-promoted Co on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (Refs. 5 and 17). Temperature programmed reduction (TPR) and Brunauer Emmett Teller (BET) surface area analysis was used to screen the various catalysts; the bold numbers in the right-hand column were the lowest reduction temperature for each co-promoted (or un-promoted) sample. In general, lower Co loading resulted in higher surface area and lower reduction temperature, with the expectation of a more effective catalyst. However, the AD method resulted in equivalent screening performance for a higher Co loading. Higher concentrations of co-promoters, resulted in lower reduction temperatures, as has been previously observed (Refs. 14 and 23). As discussed above, Pd had some interesting properties during a DFT study, and in our synthetic studies had the lowest reduction temperature even for a low co-promoted loading (0.5 percent). AD-processed samples for 1 percent Ag and Pt had high surface area and low reduction temperatures; the use of Ag as a co-promoter has some theoretical precedence as discussed above.

The overall approach of the recently concluded effort at NASA GRC was to develop the capability to use theory to inform our efforts to fabricate and screen FTS catalysts to produce aviation fuels. While we are still in the early stages of combining theoretical studies with fabrication-characterization-screening

TABLE 3.—EXAMPLE PROMOTED/UN-PROMOTED CO/Al<sub>2</sub>O<sub>3</sub> CATALYSTS PREPARED AT NASA GRC

| Target cobalt loading, percent | Co-promoter metal and target loading | Processing method employed | ICP-AES elemental analysis, % Co/% PM | BET - Surface area, m <sup>2</sup> /g | Reduction temperature (°C) measured by TPR |
|--------------------------------|--------------------------------------|----------------------------|---------------------------------------|---------------------------------------|--|
| 10                             | None                                 | AD                         | 9.3/---                               | 142.4                                 | <b>335</b>                                 |
| 15                             | None                                 | SI                         | 14.3 /---                             | 123.0                                 | 351  |
| 20                             | None                                 | AD                         | 21.6 / ---                            | 126.3                                 | 350  |
| 30                             | None                                 | SI                         | 31.7 /---                             | 108.7                                 | 436  |
| 15                             | Mn – 0.5%                            | SI/IW                      | 13.8/0.572                            | 101.0                                 | <b>354</b>                                 |
| 15                             | Pd – 0.5%                            | SI/IW                      | 14.1/0.429                            | 111.4                                 | <b>229</b>                                 |
| 20                             | Pt – 0.5%                            | AD/SI                      | 20.9/0.397                            | 106.6                                 | 349  |
| 20                             | Ag – 1%                              | AD/SI                      | 21.0/0.806                            | 118.2                                 | <b>275</b>                                 |
| 20                             | Pt – 1%                              | AD/SI                      | 21.5/0.845                            | 123.7                                 | <b>254</b>                                 |
| 25                             | Ag – 0.25%                           | SI/IW                      | 23.6 /0.278                           | 109.4                                 | 369  |
| 25                             | Mn – 0.5%                            | SI/IW                      | 25.7 /0.590                           | 103.2                                 | 366  |
| 25                             | Ni – 1%                              | SI/IW                      | 23.8/0.891                            | 128.7                                 | <b>348</b>                                 |
| 25                             | Ag – 0.5%                            | SI/IW                      | 22.9/0.510                            | 117.6                                 | <b>337</b>                                 |
| 25                             | Ru – 1.0%                            | SI/IW                      | 25.5/1.26                             | 78.6                                  | 322  |
| 25                             | Pt – 0.5%                            | SI/IW                      | 24.8/0.459                            | 115.9                                 | 265  |
| 25                             | Ru – 2.0%                            | SI/IW                      | 23.0/2.20                             | 123.9                                 | <b>264</b>                                 |

efforts; it is clear that DFT can be a powerful tool to understand the fundamental interaction of small molecules on surfaces and to use these insights to design superior catalysts. The in-house continuously stirred tank reactors (CSTRs) located in the Alternative Fuels Laboratory are currently being re-purposed. However, the long-term goal of further developing this combined theoretical/experimental capability for broader application to answer fuel production needs of the Agency and the broader aerospace and transportation sector remains.

### Processing of Promoted-Titania Photocatalysts for Decomposition of Organic Wastes

Work is underway at NASA GRC and numerous other research laboratories worldwide to develop technologies based upon heterogeneous photocatalysis (typically employing oxides) to decompose organics and/or decontaminate wastewaters (Refs. 36 to 40). The presence of these contaminants in water could pose potential health and environmental problems in a controlled environment such as on a space station or during long-term manned missions. Conventional wastewater treatment techniques are usually ineffective in decontamination of these compounds. Thus developing energy efficient or “green” technologies to reduce or eliminate organic wastes has potential dual-use applications.

The basic principles concerning these catalysts are well understood: when a light source of sufficient energy illuminates a photocatalyst (such as TiO<sub>2</sub> or zinc oxide (ZnO)), electron/hole pairs will be produced as electrons, being promoted to the conduction band, leaving (positively-charged) holes in the valence band. Thus produced, electron/hole pairs induce a complex series of reactions that eventually result in the complete degradation of (organic) pollutants adsorbed on the semiconductor surface (Ref. 39). Transition metals serving as co-catalysts also trap free electrons, thus lowering the electron/hole pair-recombination rate resulting in an increase in the photocatalytic efficiency. Titania is the most commonly used photocatalyst due to its excellent optical properties and ability to facilitate very rapid light-induced reactions. Table 4 lists a series of metal promoted-TiO<sub>2</sub> (photo)catalysts fabricated and screened by decomposition of a dye (Rhodamine B (RhB)) recently at GRC.

As processed, the co-catalyst transition metals exist in either the metallic or oxidized state as determined by X-ray photoelectron spectroscopy (XPS) or XRD. A more detailed description of the processing and screening is available from a recent publication from our colleagues at University of South Florida and our group (Ref. 40). By following the trend of standard electrochemical potentials (Ref. 41) for the reduction of the metal-containing species (example reaction (Eq. (18))), there is a rough correlation between RhB decolorizing efficiency (reduction of the dye maximum peak in UV-Vis spectrum) and the

TABLE 4.—PROMOTED TiO<sub>2</sub>-BASED PHOTOCATALYSTS PREPARED AND SCREENED AT NASA GRC

| Co-promoter (Target load) | TiO <sub>2</sub> phase(s) <sup>a</sup> | BET - surface area, m <sup>2</sup> /g | Co-promoter analysis percent EDS/XPS | Chemical species detected <sup>b</sup>          | E° example reaction | Percent RhB reduction at 60 min <sup>d</sup> | Other reaction(s) Catalyzed                  |
|---------------------------|--|---------------------------------------|--------------------------------------|---|---------------------|--|--|
| Ag – 1%                   | Anatase                                | 8.38                                  | 1.11/2.0                             | Ag <sub>2</sub> O                               | 0.342               | 66   | Reduction of 4-nitrophenol (Ref. 43)         |
| Ag – 5%                   | Anatase                                | 7.52                                  | 3.78/3.3                             | Ag <sub>2</sub> O                               | 0.342               | 76   |  |
| Pt – 1%                   | P25                                    | 46.6                                  | 1.77/---                             | ---   | ---                 | 61   | Aromatization of n-hexane (Ref. 44)          |
| Pt – 1%                   | Anatase                                | 9.49                                  | 2.42/1.1                             | Pt; PtO <sup>c</sup>                            | 1.2                 | 72   |  |
| Au – 1%                   | Anatase                                | 8.54                                  | 3.17/---                             | Au  | ---                 | ---  | CO oxidation (Ref. 45)                       |
| Pd – 1%                   | Anatase                                | 8.75                                  | 1.40/0.8                             | PdO   | 0.95                | 74   | Oxidation of alcohols to aldehydes (Ref. 46) |
| Ru – 1%                   | P25                                    | 45.2                                  | 1.63/---                             | Ru <sup>0c</sup> ; RuO <sub>2</sub>             | 1.12                | ---  | Methanation of CO (Ref. 47)                  |
| Ru – 1%                   | Anatase                                | 9.26                                  | 1.95/---                             | Ru <sup>0</sup> ; RuO <sub>2</sub> <sup>c</sup> | 1.12                | 85   |  |
| Cu – 5%                   | P25                                    | 43.5                                  | 8.68/5.0                             | Cu <sub>2</sub> O <sup>c</sup> ; CuO            | -0.36               | 40   | CO-NO Reaction (Ref. 48)                     |
| Cu – 5%                   | Anatase                                | 8.35                                  | 6.31/3.6                             | Cu <sub>2</sub> O; CuO <sup>c</sup>             | -0.08               | 28   |  |

<sup>a</sup>P25 is a mixed anatase:rutile phase (3:1).

<sup>b</sup>XPS except for Au (XRD).

<sup>c</sup>Major phase.

<sup>d</sup>Reference 40.

potential relative to a standard hydrogen electrode,  $Ru > Pd \sim Pt > Ag \gg Cu$ ; Cu-containing materials are actually less effective than un-promoted  $TiO_2$ . A detailed analysis of electron transfer processes is beyond the scope of this overview and will be described in depth in future by our collaborator at University of South Florida (Ref. 42).



A further interesting aspect of all of these materials is that they are multi-functional and have activity for other catalytic reactions; see the right-hand column of Table 4. This multi-functionality could be exploited for space exploration to facilitate organic processing. Photocatalysis for the decomposition of organics in order to mitigate potential health and environmental problems in the controlled environment of a spacecraft or space station, particularly for long-term manned missions, provides an impetus to further develop and deploy technologies that exploit plentiful and cost-effective resources such as (ultraviolet) solar radiation.

### Sulfide Catalysis Research, Emphasizing Work at UTEP

The field of transition metal sulfide (TMS) catalysis began in earnest 100 years ago as a result of the need to develop processes to convert local raw materials (coal) into liquid fuels that would be invulnerable to geopolitics (Ref. 49). Paul Sabatier is considered the “Father of Modern Catalysis” for his work with TMS catalysts leading to a Nobel Prize in 1912. The literature concerning synthesis and characterization of sulfide materials (many mimic minerals found in nature) is overwhelming due to the stoichiometric flexibility inherent in sulfide bonding. For example, for the element nickel, sulfides exist in numerous stable phases (with relevant mineral names) ranging in stoichiometry from  $Ni_3S_2$  (heazlewoodite) through  $Ni_9S_8$  (godlevskite) and  $NiS$  (several phases), to  $Ni_3S_4$  (polymidite) and finally,  $NiS_2$  (vaesite) (Ref. 50). Given ternary phases and beyond, as well as (metal) doping or non-metal hetero(non-S)-atoms and multiple processing options, the possibilities are staggering in number.

Since World War II, TMS catalysis has played a major role in fuel upgrading, especially removal of nitrogen and sulfur pollutants from feedstock materials (Ref. 51). The major reactions catalyzed by TMS are: hydrogenation of olefins, ketones, and aromatics; hydrodesulfurization (HDS); hydrodenitrogenation (HDN); hydrodemetallation (HDM); hydrocracking; dealkylation; and ring opening of aromatics. But the TMS catalysts have many other uses as well, including: reforming, isomerization of paraffins, dehydrogenation of alcohols, FT and alcohol synthesis, hydration of olefins, amination, mercaptan and thiophene synthesis, and direct coal liquefaction (Ref. 52). Table 5 lists a few examples of sulfide catalysis that are germane to processes and reactions discussed in this paper (Refs. 53 to 59).

In 1989, R.R. Chianelli, working at Exxon Research and Engineering Corporate Research Laboratory in Linden New Jersey collaborated with Professor Kamil Clear and a graduate student. In their research they showed that the TMS catalytic materials could produce alcohols from  $CO + H_2$  (syn-gas or syn-fuel) using a FT-based process (Ref. 60). Very little work has been done in this area since. The higher surface area (and hence more active) UTEP catalysts are the subject of a current program with Professors Tracey Benson and David Cocke of the Chemical Engineering Department of Lamar University in Beaumont, Texas. An example of enhancing alcohol production activity begins with conventional  $MoS_2$ -based unsupported catalysts. These catalysts are treated with alkali metal promoters (i.e., K, Rb, and Cs). Further modifications are performed with additions of electronic promoters such as Co and Ni. In addition, combinations of alkali and electronic promoters are also being explored. Encouraging results already observed will be vastly improved and highly active catalysts will be obtained with control over alcohol chain length will emerge. These results should greatly interest chemical manufacturers. UTEP is in the process of commercializing these catalyst materials for petroleum refining with a commercial catalyst manufacturer, hence further details are not available.

A second current project involving UTEP TMS materials is the photo-catalytic  $CH_4$  reforming with  $CO_2$  producing liquid hydrocarbons and alcohols, beginning with solar-energy promoted reaction (2)



(above) followed by reaction (19) (Ref. 53). Note that while the overall  $\Delta H$  of the combined reactions is slightly negative ( $-2$  kcal/mol), thermodynamic considerations require a net energy input. This work was inspired, in part, by the work of Helmut Tributsch, who reported that the TMS were photo-catalysts for the dissociation of water ( $H_2O$ ) (Eq. (20)) (Ref. 61).



Many petroleum-producing wells flare  $CH_4$  and  $CO_2$  in approximately a 50/50 mixture. Satellite photographs of remote places such as Siberia show huge numbers of flare that are burning the  $CH_4$  because reforming is too energy intensive and liquefaction and transportation of  $CH_4$  is too expensive. A recent media report extrapolates from satellite data: every night such flares in Siberia consume more energy than used every day for transportation in the North East Coast of the United States (Ref. 62). These flares occur elsewhere in petroleum producing countries such as Nigeria. Photo-catalytic processes that inexpensively convert  $CH_4$  and reduce  $CO_2$  emissions are potentially valuable economically and environmentally. There are also potential applications for efficient utilization of waste gases in the presence of plentiful solar energy to develop a secondary source of liquid fuels for space exploration.

Using  $RuS_2$ , the UTEP group has observed production of alcohols using a photo-catalytic process; the UTEP laboratory results will be described in detail in future. Current research entails screening of a variety of TMS catalytic materials that are less expensive than  $RuS_2$ . Combinations of  $Co_9S_8$  and  $Ni_3S_2$  with  $MoS_2$  and  $WS_2$  are being explored as we have established that combinations such as these create active sites that mimic the electronic structure and active noble metal TMS catalytic materials; (Ref. 49) these catalysts will also be mixed with oxide materials that will enhance the capture of energy from sunlight. As discussed above,  $TiO_2$  and  $ZnO$  satisfy this criterion, and multiple combinations of mixed materials are being tested. The feedstock mixture, that is now 50 percent  $CH_4$  and 50 percent  $CO_2$ , can be modified to include reactive gases such as  $O_2$ . The purpose is to understand how such mixtures will affect the activity and selectivity of the reaction(s); Table 5 provides a glimpse into the wide array of catalysis opportunities available from utilizing sulfide catalyst materials (Refs. 49 and 52 to 59).

TABLE 5.—EXAMPLES OF RELEVANT PROCESSES CATALYZED BY METAL SULFIDES

| Material  | Processing method   | Reaction catalyzed                     | Details   | Text references |
|---|---|--|---|-----------------|
| $MoS_2/\gamma-Al_2O_3$                              | 1. $\gamma-Al_2O_3$ pellets soaked in Mo precursor solution<br>2. $H_2S$ sulfurization        | Alcohol (and Aldehyde) Synthesis       | $CO + 2 H_2 \rightarrow$ mostly ethanol and $CH_3C(=O)H$ ; some methanol and C1-C3 paraffins at 150 to 300 °C/~3 MPa; paraffins prominent at 300 °C | 53              |
| $FeS_2$ powder                                      | 1. Occurs in C<br>2. Finely ground  | Coal liquefaction                      | $Coal + CO + H_2 \rightarrow$ Oils + Asphaltenes (Polycyclic Aromatic Hydrocarbons)   | 54              |
| K- $MoS_2$ and K- $Mo_{1-x}Co_xS_2$ powders or on C | 1. $(NH_4)_2MoS_4$<br>2. Thermalized<br>3. K/Co added<br>4. Ground                            | Fischer–Tröpsch production of alcohols | $CO + H_2 \rightarrow$ C1 – C3 alcohols at 260 to 300 °C/~10 MPa  | 55              |
| $NiWS_x$ on zeolites (Si/Al = 18)                   | 1. Zeolites + Ni & cmpds. W in $H_2O$<br>2. Produce oxide<br>3. $CS_2 + H_2$ ; heat to 300 °C | Hydrocracking of Decane                | $C_{10}H_{22} \rightarrow$ mix of C3-C7 paraffins   | 56              |
| NiS on Ni   | 1. Ni wires/plates<br>2. + $H_2S$ at 300 °C   | Hydrogenation of Acetylene             | Acetylene ( $C_2H_2$ ) + $H_2 \rightarrow$ ethylene ( $C_2H_4$ ) and ethane ( $C_2H_6$ )  | 57              |
| $In_xCd_{1-x}S$ on ZnO                              | 1. $ZnO + MCl_x$<br>2. + $(CH_3)_2C=S$ (1 & 2 in $H_2O$ )<br>3. Heat to 350 °C                | Photocatalytic splitting of $H_2O$     | $H_2O \rightarrow H_2 + \frac{1}{2} O_2$  | 58              |
| $NiS/\gamma-Al_2O_3$                                | Commercial catalyst   | Steam reforming of $CH_4$              | $CH_4 + H_2O \rightarrow H_2 + CO + CO_2$ (3:1 ratio of $H_2O:CH_4$ ) at 700 °C and 0.15 MPa  | 59              |

## Catalyst Utilization and Novel Processing Approaches

It well known from basic chemistry and the processing industries: catalysts affect the kinetics but not the thermodynamics of reactions (Ref. 44). Thus it often not necessary for understanding the energetics of chemical reactions to include the presence of a catalyst. However, in a practical system, catalysts have a significant impact on reaction mechanisms and kinetics (Refs. 51 and 52). Hence, the product yield, energy efficiency, and materials utilization can be considerably improved by a judicious choice of catalyst, including the specific composition, amount, and physical form. Physical form concerns include: (nano-)particle size, formed shape with pores or channels, and heterogeneous interfaces and structures (core-shell (nano-)particles, zeolite structures, etc.). This section outlines practical concerns and issues connected with utilizing catalysts in real-world systems. Several of the processes discussed in this paper can be considered as primary for materials conversion to produce fuels from non-petroleum raw materials. After several years of effort at GRC, we have come to view catalytic wet air oxidation (CWAO) and photocatalysis as auxiliary processes to facilitate handling of reaction by-products and undesirable side-reactions. The relationship among the various technologies will be further elucidated in context in the concluding section.

### Catalytic Wet Air Oxidation and Photocatalytic Processing Research at NASA GRC

Catalytic methods such as wet air oxidation (Ref. 63) or photocatalysis (Refs. 37 to 40) may serve as the basis for a system of waste and trash processing, or more likely serve as part of a suite of supporting or auxiliary technologies to boost the hydrogen content of various gas streams, or in using energy-efficient methods to reduce the volume and/or increase the utilization of solid or by-product streams. CWAO is an attractive method for the treatment of waste streams that are too dilute to incinerate (<40 percent) (Ref. 64) and too concentrated for biological treatment (>1 percent) (Ref. 65). Heterogeneous catalysts (typically metal species on oxide supports) are used to oxidize carbon-containing compounds in the aqueous phase and produce desired products (mainly carbon oxides, CH<sub>4</sub>, and H<sub>2</sub>) in the gas phase. Typical conditions range from 200 °C and 2 MPa to 320 °C and 20 MPa.

GRC has recently investigated the feasibility of using CWAO to gasify waste plastic for logistics reduction and repurposing (LRR). The resultant gas mixture could then be further processed into fuels or used as a high-pressure propellant. Polyethylene terephthalate (PET or polyester) was used as a simulant as PET is estimated to make up a significant fraction of the waste stream generated by astronauts during a space mission. Tests were conducted using a 100 mL slurry reactor (Fig. 6) with 5 percent precious metal-containing supported catalysts (see Table 6). The reactor was loaded with 100 mg of PET shards from discarded water bottles in 30 mL of H<sub>2</sub>O and pressurized with 1.2 MPa air to provide a stoichiometric quantity of oxygen. After 24 hr of processing at 300 °C, 10 to 50 percent of the C was gasified into mainly CO<sub>2</sub> with smaller amounts of CH<sub>4</sub>.

The overall (complete or partial) oxidation of PET is given by reactions (21) and (22); these combustion reactions are quite exothermic (~5 kcal/g) (Ref. 66). The lack of overall CO production is likely due to an exothermic water-gas shift reaction (17); formation of CH<sub>4</sub> would occur by a methanation reaction (5). The Ru-containing catalysts were clearly the most active for PET decomposition. Also, given the known effectiveness of Ru for methanation (Ref. 47), approximately 1/8 of the total C1 product was CH<sub>4</sub> (Table 6). While C1 formation and departure from the catalytic surface is crucial, reaction kinetics may be dictated in part by such factors as surface tension, surface roughness, and gravity, where a practical understanding of bubble formation and departure may guide design of the final process under reduced gravity conditions. Work is ongoing to optimize CWAO and eventually integrate this valuable auxiliary process into a flight system.



TABLE 6.—CARBON GASIFIED INTO C1 GASES: RESULTS OF FOUR DIFFERENT CATALYSTS AT 300 °C FOR 24 HR

| Catalyst/Gas                         | CO <sub>2</sub> | CO  | CH <sub>4</sub> | Non-reacted |
|--------------------------------------|-----------------|-----|-----------------|-------------|
| 5% Ru/C                              | 44.0            | 0.1 | 6.0             | 49.9        |
| 5% Ru/Al <sub>2</sub> O <sub>3</sub> | 25.0            | 0.0 | 5.0             | 70          |
| 5% Pt/C                              | 8.0             | 0.0 | 0.5             | 91.5        |
| 5% Rh/C                              | 24.0            | 0.0 | 0.7             | 75.3        |



Figure 6.—(left) 100 mL stirred batch reactor, maximum temperature 500 °C, maximum pressure 5000 psi; (right) catalyst processing laboratory—facility for running CWAO reactor.



Figure 7.—Photocatalysis of phenol—(left) UV-Vis plot showing photodecomposition; (right) reactor.

Photocatalysis was also investigated as a recovery method for process H<sub>2</sub>O from steam reforming or CWAO. Phenol was used as model organic compound. Tests were conducted using a 15 mL photochemical reactor with a 5.5 W mercury gaseous discharge lamp. The reactor was loaded with  $6.0 \times 10^{-4}$  M aqueous phenol solution and 1 mg of Ru-promoted TiO<sub>2</sub>. Phenol was completely decomposed after 60 min of processing as evidenced by UV/Vis absorption spectra near 270 nm (Fig. 7). Finally, concentrated solar energy is being investigated as a thermal source (Refs. 3 and 4), thus photocatalysis could be employed as a supplementary method that could be used to split H<sub>2</sub>O in order to produce additional H<sub>2</sub> for CH<sub>4</sub> production (Refs. 58 and 61). Other processes that have been found to produce H<sub>2</sub> from H<sub>2</sub>O include “mechano-catalytic” H<sub>2</sub>O splitting; mechanical stirring of oxide slurries under elevated temperature and pressure has been found to produce H<sub>2</sub> under a variety of conditions (Ref. 67).

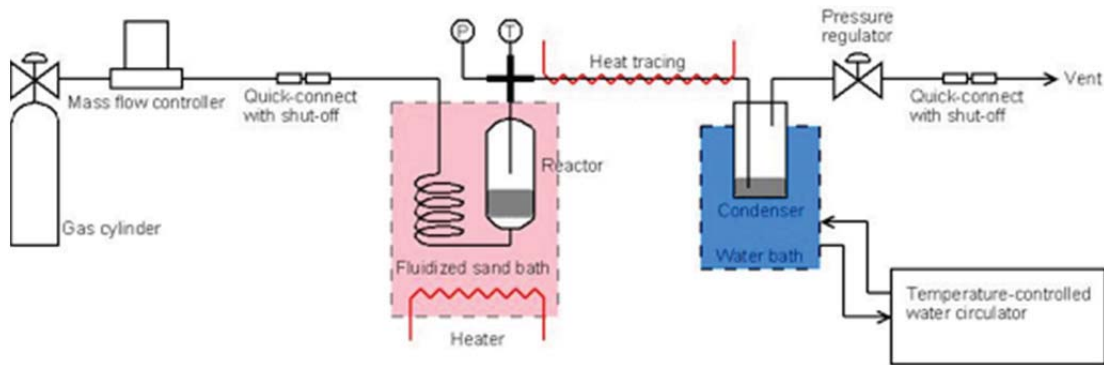


Figure 8.—Schematic of the Aerodyne flash pyrolysis process to convert waste plastics into usable liquid hydrocarbon fuels with tunable molecular weight distributions.

TABLE 7.—COMMON REACTOR TYPES FOR ISRU APPLICATIONS

| Reactor type   | Flow pattern          | Pressure drop | Heat/Mass transport | Catalyst attrition | Catalyst recovery |
|----------------|-----------------------|---------------|---------------------|--------------------|-------------------|
| Packed bed     | Plug-flow             | High          | Low                 | Low                | Difficult         |
| Fluidized bed  | Approaches well-mixed | Low           | High                | High               | Easy              |
| Slurry reactor | Well-mixed            | Low           | High                | Medium             | Difficult         |

### Flash Cracking of Plastic Waste at Aerodyne

Another process being studied is flash cracking of plastic waste into tunable molecular weight fuels. This technology, being developed by Aerodyne Research, Inc. under the support of NASA’s SBIR program, “flashes off” desired hydrocarbon products as they form (Fig. 8), thus preventing the over-cracking of the polymers into more volatile hydrocarbons. Key advantages of this innovation are 1) improved selectivity for low vapor-pressure hydrocarbons, which are easier to store as fuel in large quantities at low pressures; 2) tunable molecular-weight products by changing operating conditions for multiple applications. It has been demonstrated, both experimentally and using a pyrolytic model, that operating parameters, such as carrier gas flow-rate, can influence product distributions. For example, increasing the flow-rate of an inert sweep gas (e.g., nitrogen) leads to the production of higher molecular-weight products during polystyrene pyrolysis, since the nitrogen removes these compounds as soon as they are sufficiently volatile, preventing them from over-cracking. The promising results suggest that this technology can be utilized to produce useful liquid fuels with tunable product distributions. It can also be easily modified for Fischer-Tröpsch wax cracking during Fischer-Tröpsch synthesis to improve its overall conversion (Refs. 7 and 12).

### Employment of Catalysts in Reactors: Engineering Issues

Engineering of catalytic reactors will be required for any process. The chemical process industries have substantial experience designing catalytic reactors (Ref. 68) and much of this experience can be leveraged for ISRU applications (Refs. 1 to 6). Although many catalytic reactor variations are conceivable, they typically fall broadly into one of 3 types, summarized in Table 7 as packed bed, fluidized bed, and slurry reactor. Of these, the packed bed is the simplest and often preferred as its plug-flow residence time distribution leads to the most efficient use of the reactor volume to obtain a desired conversion level.

The primary challenge with packed bed reactors is the high pressure drop, a problem that is more challenging for small catalyst particles and can be especially troublesome in ISRU applications where parasitic losses must be minimized. Because pressure drop scales inversely with the square of the catalyst particle diameter, a common strategy for minimizing pressure drop is to support the catalyst particles on an inert support. Examples of common support materials are  $Al_2O_3$ ,  $SiO_2$ , and C, though ceria ( $CeO_2$ ),

zirconia ( $ZrO_2$ ), and  $TiO_2$  have also been used. Support materials can influence catalytic activity, so selection of supports should balance both economic and technical issues. Further disadvantages of the packed bed reactor are that heat and mass transport rates are often slow and catalyst recovery requires reactor shut down. Slow heat transport rates can be especially problematic for design of reactors for highly exothermic reactions, as removing the heat of reaction can become challenging. For example, removing heat from FT reactors is a primary design consideration.

To surmount the pressure drop, heat/mass transport, and catalyst recovery problems, fluidized bed and slurry reactors can be used. In a fluidized bed, the incoming feed (typically a gas) fluidizes the catalyst particles so that they are in constant circulation. In this configuration, heat and mass transport rates are fast and the pressure drop is negligible. Moreover, the fluidized bed reactor can be designed for continuous recirculation of the catalyst, allowing reaction and catalyst regeneration to be carried out continuously. Continuous catalyst regeneration is a key advantage for systems in which the catalyst deactivates rapidly. For example, coking reactions, which accompany catalytic cracking rapidly, de-activate the zeolite catalysts used for this commercial process. The solution has been to perform catalytic cracking in a fluidized bed reactor, hence “fluidized catalytic cracking.” On the downside, catalyst attrition can be high in a fluidized bed reactor and the well-mixed flow pattern means that it is a less efficient use of reactor volume than the packed bed. In practice, most fluidized bed reactors are used for processing gaseous streams at elevated temperatures ( $>200\text{ }^\circ\text{C}$ ) at residence times less than about 10 sec. Flash pyrolysis of biomass is typically performed in a fluidized bed operating at 350 to 500  $^\circ\text{C}$  and at residence times on the order of 1 sec (Ref. 68). For processing solid feeds, an inert carrier gas (typically nitrogen) and inert heat transfer agent (typically silica sand) is needed for the fluidized bed reactor.

The final common reactor type is the slurry reactor. Here, the catalyst particles are disbursed in liquid phase as a slurry. Typically, the slurry would then be mixed using an impeller. Relative to the packed bed reactor, slurry reactors have negligible pressure drop and much greater heat and mass transport rates. Relative to a fluidized bed reactor, the residence times in a slurry reactor can easily be on the order of minutes or hours. Moreover, catalyst attrition is generally less than in a fluidized bed reactor. For these reasons, slurry bed reactors are useful for catalytic reactions that occur in the liquid phase at temperatures less than about 250  $^\circ\text{C}$ . The most familiar example of a commercial process that has been developed for a slurry reactor is the low-temperature FT process. For the low-temperature FT process, the FT-wax product constitutes the continuous liquid phase and the slurry configuration is preferred over a packed-bed because of superior heat transfer rates that allow the heat of reaction to be removed more easily (Refs. 12 to 14).

In any practical system, especially one that would necessarily involve minimal human intervention, catalyst poisoning and/or deactivation is a significant concern. A review of the recent CWAO literature enables a listing of the following findings that can provide lessons learned for other, related catalytic reactions: (Refs. 69 to 72)

- The main concerns for deactivation of noble metal catalysts are leaching of metal from supports by ligating species and formation of carbonaceous layers; (Ref. 69)
- Under conditions of CWAO, limited oxygen seems to be a significant issue; re-oxygenating a system can actually re-activate catalysts by degrading carbonaceous deposits; (Ref. 70)
- It is possible to mitigate concerns related to carbonaceous deposits by inclusion of strong oxidizing co-catalysts such as ceria ( $Pt-CeO_2/Al_2O_3$  or  $Pt/CeO_2$ ); (Ref. 71)
- It is also possible to pre-treat catalysts with  $SO_2$ , for example, to increase resistance to S poisoning, there is also likely an equivalent  $N_2O$  treatment (Ref. 72)

A significant issue for systems involving oxidation processes for production of carbon oxides is to avoid oxygen starvation to push reactions to the right and possibly re-activate catalysts after C-build up (Ref. 70). It is prudent to be concerned about deactivation/poisoning of catalysts but noble metals (Pt, Pd, Rh, Ru, Ir, Au) generally have superior performance relative to conventional metal and oxide catalysts

(Cu, Fe, Ni, V, MoO<sub>3</sub>, WO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, NiO, CuO, etc.). Also, as discussed above sulfide materials themselves have been demonstrated to have wide ranging activity for catalysis (Refs. 49, 52 to 59). A facile method to enhance activity is to tailor the oxide supports (add CeO<sub>2</sub>, MgO, etc.) to enhance resistance to carbonaceous deactivation (Ref. 71). Finally, pre-treatment may be effected to increase resistance to deactivation by leaching or poisoning of catalyst surfaces by Lewis base species (carbonates, sulfates, hydrogen sulfides, ammonia, alkyl ammonias, nitrates, etc.) (Ref. 72).

## **Selection of Processing Technology Based Upon Anticipated Mission or Application(s)**

As mankind ventures farther from Earth and for greater periods of time, it becomes imperative to develop technologies and mission architectures that utilize local resources such as Lunar regolith or Martian atmosphere, referred to ISRU (Refs. 1 and 2). Lighter elements such as O, N, and particularly C and H are either not readily available or strongly bonded to metal or metalloid atoms in rocks and minerals (especially O) requiring significant energy for extraction (Refs. 2 and 3). In-flight utilization of waste and trash to produce essential materials such as H<sub>2</sub>O, fuel(s), and oxygen is a further example of ISRU or LRR for space exploration. For prudent and efficient utilization of terrestrial raw materials and energy for transportation fuel production, re-use or recovery of hydrocarbons (or syn-gas) from waste materials or gas flares is increasingly integrated into process design(s) (Refs. 5, 11, and 62).

Organic waste materials can be recycled or further utilized via a range of “primary” to “quaternary” methods, respectively, as physical and/or chemical breakdown increases. These include recycling (primary) and mechanical recovery (secondary) that are not discussed further, chemical recycling (tertiary), and energy recovery (quaternary) (Ref. 11). Commercial processes including incineration (for direct production of electricity) (Ref. 74) and biologically-assisted digestion (Ref. 69) are outside of the scope of this discussion and will also not be addressed.

There have been numerous excellent reviews that summarize and analyze in detail the various technologies, products, energy balance, and economics of several mainstream waste-to-energy (WTE) technologies. Several example tertiary or quaternary processes include: chemical recycling via pyrolysis (thermal or catalytic cracking) to produce mostly higher hydrocarbons; gasification (thermal cracking in air and/or steam) to produce CO<sub>2</sub> and syn-(thesis) gas (CO and H<sub>2</sub>) and small amounts of oxygen, H<sub>2</sub>O, and CH<sub>4</sub>, sometimes called producer gas; (Ref. 69) and plasma-assisted gasification (also a quaternary process) (Ref. 11) that relies on a very high temperature plasma torch to produce primarily syn-gas (Ref. 74). A comparison of relevant technical details as well as energy utilization and the potential suitability for potential use in mobile platforms or space missions is detailed in Table 8.

The list of processes considered includes primary processes such as thermal cracking, steam reforming, flash cracking, and plasma assisted gasification technologies; for comparison, auxiliary processes - photocatalysis and catalytic wet air oxidation are included. The first two processes previously discussed in detail (Ref. 5) are typical of technologies that use heat in a variety of gaseous environments to break down polymers into a product soup, that is either mostly hydrocarbon or C1-based, respectively. As discussed below, the steam reforming process includes an integrated Sabatier process to produce CH<sub>4</sub> but requires a H<sub>2</sub> source. Flash pyrolysis is a quite flexible method that can be run under a variety of conditions to produce different target products and hence is somewhat similar to FTS, the most flexible of the secondary processes of syn-gas or producer gas conversion.

The rather complex plasma-assisted gasification process relies on a significant balance-of-system and high temperatures to recover thermal energies; it is included for the sake of comparison, it is being considered for larger-scale (municipal) use. While it is difficult to make direct comparisons regarding scale of infrastructure required, a typical plasma system requires significant balance-of-system hardware in order to enable self-sustaining electrical power (Ref. 9). An energy-efficient system will include reusing otherwise wasted thermal energy from stage-one products (i.e., syn-gas at > 1000 °C) to drive

TABLE 8.—COMPARISON OF RELEVANT METRICS FOR TERTIARY AND QUATERNARY WTE PROCESSES

| Process (Type) <sup>a</sup>      | Temperature; pressure (MPa) range(s) | Product output   | Technical complexity | Energy efficiency or utilization                         | Appropriate application(s)            |
|----------------------------------|--------------------------------------|--|----------------------|--|---------------------------------------|
| Thermal cracking (T)             | 400 to 450 °C<br>4 to 6.9            | C1-C5<br>Mostly > C6<br>Hydrocarbons                             | Low                  | Burning C1-C5 fraction supplies 80% energy               | Chemical recycling plant              |
| Flash cracking (T or Q)          | 400 to 600 °C<br>0.1 to 1.0          | Flexible: C1-C10 depending upon T, P, catalyst                   | Medium               | Designed to be low energy; potential solar energy use    | Recycling or Mobile/ISRU              |
| Photocatalysis (Q)               | 25 °C<br>0.1                         | Oxygenated C1-C5 depends upon time, light energy & photocatalyst | Low <sup>b</sup>     | Low energy; relies on solar energy use                   | Municipal water or Auxiliary for ISRU |
| Catalytic wet air oxidation (Q)  | 200 to 350 °C<br>2.0 to 20           | Syn-Gas (CO +H <sub>2</sub> ), CO <sub>2</sub> , CH <sub>4</sub> | Medium <sup>b</sup>  | Designed to be low energy; potential solar energy use    | Auxiliary process for ISRU            |
| Steam reforming (Q)              | ~850 °C<br>0.3 to 0.7                | Syn-Gas (CO +H <sub>2</sub> ), CO <sub>2</sub> , CH <sub>4</sub> | Medium <sup>b</sup>  | Balancing endothermic and exothermic reactions           | Mobile/ISRU                           |
| Plasma assisted gasification (Q) | ~5,000 °C<br>0.1                     | <i>Primarily</i> Syn-Gas   | High <sup>b</sup>    | Recovery of thermal energy from > 1000 °C Syn-Gas stream | Municipal power                       |

<sup>a</sup>Chemical recycling (T/Tertiary) or energy recovery (Q/Quaternary)

<sup>b</sup>Needs to be combined with a secondary process to produce fuels

turbines to generate electricity. This would then be followed by a FT operation to convert syn-gas into a product soup of saturated and unsaturated hydrocarbons as well as some oxygenated products such as alcohols of C5 to C20 or so with some waxy materials. The balance-of-system technology requirements drive up the complexity (and cost) (Ref. 74) and minimize suitability for space applications; in fact, these issues eliminate PAG technology from further consideration for use in space exploration.

The remaining primary technologies to be considered include a pyrolysis chemical recycling technology being developed by (among others) an Akron, Ohio-based start-up company (RES Polyflow), (Ref. 5) flash cracking (simple or catalytic), (Ref. 75) and an SBIR-funded steam reforming process (Ref. 5). The RES Polyflow pyrolytic process is quite simple but scalability may be an issue (Ref. 5). As discussed above, a flash cracking reactor is quite flexible from a process perspective; the final product mix can be tailored depending upon the temperature and pressure as well as the presence of a catalyst (Ref. 75). The lower energy demand for this process can be met by solar thermal and photovoltaic sources, as discussed below. Pioneer Astronautics has combined two unit operations that work in tandem to produce CH<sub>4</sub> and oxygen. The process is quite scalable and was delivered to NASA GRC in Summer 2013 as a prototype unit from a Phase II program. One issue is the need for an external H<sub>2</sub> source for a Sabatier reactor: this would most likely come from splitting H<sub>2</sub>O (Ref. 4).

Solar energy as well as efficient thermal energy utilization will be required if either of these technologies is to be considered as a serious flight candidate. Electric power derived from photovoltaics is the most likely source of process energy, including the energy needed for running pumps and splitting H<sub>2</sub>O. There may be merit in considering solar thermal to augment the process energy, particularly for the endothermic (primary and gas shift) reactions ((1) to (3)). Numerous studies have been completed on the various types of solar thermal concepts available for possible use, ranging from rigid structures having facets with high quality optical surfaces and concentration ratios of the order of 8000:1, to concepts that utilize light weight inflatable structures, light pipes, and trough systems with lower efficiency and concentration ratios (Refs. 3 to 6). Small diameter thick-walled tubing coated with a highly light-absorbing coating, located at the focus of the trough, would enable high-pressure high-temperature operation.

## Conclusions

A deeper understanding of the electronic environments associated with methane (CH<sub>4</sub>) selectivity is useful in order to facilitate the design of more effective fuel-production catalysts. Our preliminary work and literature review provide a glimpse into the wide array of catalysis opportunities available from utilizing sulfide catalyst materials. From the perspective of ISRU and re-cycling, it is important to note that sulfur is often considered a by-product waste; the ability to synthesize catalytic sulfides from materials that would otherwise be discarded could potentially be a mission enabling capability or contributing in operational success or economic viability. It is prudent to be concerned about deactivation/poisoning of catalysts but noble metals generally have superior performance (although higher costs) relative to conventional metal and oxide catalysts. Many catalysts explored have potential for multi-functional utilization. Photocatalysis for the decomposition of organics in order to mitigate potential health and environmental problems in the controlled environment of a spacecraft or space station, particularly for long-term manned missions, provides an impetus to further develop and deploy technologies that exploit plentiful and cost-effective resources such as (ultraviolet) solar radiation. A significant issue for systems involving oxidation processes for production of carbon oxides is to avoid oxygen starvation to push reactions to the right and possibly re-activate catalysts after C-build up.

There are still balance-of-system issues remaining. Energy efficiency is a critical consideration at the system level; heat must be added to the system for driving the endothermic reactions while heat should be harvested from the exothermic reactions for improving overall system efficiency. Overall heat rejection must also be considered. The need for utilization and storage of hydrogen (H<sub>2</sub>) to drive the hydrocarbon production processes, raises one of several safety concerns. Finally, integration of the candidate technology into the mission architecture is essential for prudent for introducing flexibility and ruggedness into the overall system design.

In summary, we have considered a number of waste handling and fuel production processes to assess their suitability for ISRU. Because of the moderate cost, scalability for space applications, energy utilization and technology heritage, flash cracking and steam reforming processes are superior options to competing technologies. The flexible flash cracking process that can be integrated with a number of secondary methods and a combined steam reformation/Sabatier technology appear to have potential for further development. Auxiliary processes such as photocatalysis and CWAO are available to upgrade gas streams and assist in by-product re-processing.

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