Creating Methane from Plastic: Recycling at a Lunar Outpost

Edgardo Santiago-Maldonado and Janine Captain.
NASA KSC, Kennedy Space Center, FL, 32899

Robert Devor
ASRC Aerospace, Kennedy Space Center, FL, 32899

and

Jeremy Gleaton
University of South Carolina, Columbia, SC, 29802

The high cost of re-supply from Earth demands resources to be utilized to the fullest extent for exploration missions. The ability to refuel on the lunar surface would reduce the vehicle mass during launch and provide excess payload capability. Recycling is a key technology that maximizes the available resources by converting waste products into useful commodities. One example of this is to convert crew member waste such as plastic packaging, food scraps, and human waste into fuel. This process thermally degrades plastic in the presence of oxygen producing CO₂ and CO. The CO₂ and CO are then reacted with hydrogen over catalyst (Sabatier reaction) producing methane. An end-to-end laboratory-scale system has been designed and built to produce methane from plastic, in this case polyethylene. This first generation system yields 12-16% CH₄ by weight of plastic used.

Nomenclature

Å = Angstrom
C = Carbon
ECLSS = Environmental Control and Life Support System
GC = Gas Chromatography
GC-MS = Gas Chromatography-Mass Spectroscopy
g = grams
kg = kilograms
sccm = standard cubic centimeter per minute

I. Introduction

The mass of propellant required for space exploration is significant, and may be a major driver when designing the overall exploration architecture. For example, the propellant required for a round trip from Earth to Mars may require the return propellant to be produced in-situ on the surface of Mars. This type of architecture reduces the mass of the Earth departure stage, allowing for more cargo capability or reducing the cost of launch. Mars offers the reagents required to produce in-situ propellants: carbon dioxide (CO₂) to produce methane-oxygen (CH₄-O₂) with hydrogen (H₂) brought from Earth or hydrogen-oxygen (with recent finding of water ice on the surface of Mars). On the case of the Moon, production of propellant is limited to the production of oxygen due to the lack of an in-situ source of carbon or hydrogen required to produce fuel. However, recent NASA missions have indicated the presence of water throughout the surface of the Moon, and the water could be used to produce H₂-O₂. It must be emphasized that the findings of water on the Moon are very young at this time and water is found at low

---

1 Chemical Engineer, Surface Systems Office, Mail Code: NE-S2, AIAA Member.
2 Chemist, Engineering Directorate, Mail Code: NE-L5
3 Chemist, Applied Technology, Mail Code: ASRC-434
4 Chemist (summer intern), Department of Chemistry and Biochemistry University of South Carolina

American Institute of Aeronautics and Astronautics
concentrations (10 − 1,000 ppm²) on the surface of the Moon. NASA’s In-Situ Resource Utilization (ISRU) project has been developing various oxygen production processes² to extract oxygen found in lunar soil, which is nearly 50% oxygen. In order to produce fuel on the Moon, it is required to use other resources that are available due to the presence of humans. For example: trash (leftover food, food wrappers, paper, etc) and human waste (fecal matter, and metabolic CO₂) are a good source of carbon from which methane can be produced. The ESAS report⁴ estimates the propellant required for the ascent stage is approximately 4,000 kg of propellant (at a 3.4 O₂:CH₄ ratio: 3,090 kg of O₂ and 910 kg of CH₄). If all this propellant is produced on the surface of the Moon, it would make available 4,000 kg for payload usage, a total of 40,000 kg over a 10-year life of the lunar outpost.

Table I shows an estimate of the typical dried waste stream generated each day for a crew of four and the elemental composition of each type of waste. Packaging waste accounts for nearly 86% of the dry waste stream and is a significant source of carbon on the lunar surface. The conversion of carbon in the waste shown in Table I will produce 360 kg of methane per year. The use of outpost waste to produce methane produces about a third of the CH₄ required to fuel an ascent stage, and also minimizes the waste accumulation at the outpost. The latter is important since once on the Moon, bringing trash back to Earth, as it’s done on the International Space Station, takes mass allocation away from other payloads and sample returns. The remainder two-thirds of the fuel requirement is produced by the Environmental Control Life Support System (ECLSS) from the oxygen recovery system, where metabolic CO₂ (0.998 kg/CM-d⁵) is reduced to CH₄ and H₂O⁶.

<table>
<thead>
<tr>
<th>Waste Type</th>
<th>Total Wt.</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>S</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Packaging waste</td>
<td>1049</td>
<td>650</td>
<td>93</td>
<td>64</td>
<td>16</td>
<td>0</td>
<td>225</td>
</tr>
<tr>
<td>Human dry solid waste</td>
<td>112</td>
<td>63</td>
<td>9</td>
<td>35</td>
<td>3</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Dry food attached to plastic</td>
<td>60</td>
<td>29</td>
<td>4</td>
<td>26</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Total waste for crew of 4</td>
<td>1221</td>
<td>741</td>
<td>106</td>
<td>125</td>
<td>20</td>
<td>3</td>
<td>225</td>
</tr>
</tbody>
</table>

The three main approaches examined for the degradation of the plastics were pyrolysis, gasification, and biological methods. Pyrolysis and gasification processes use high temperatures to degrade the plastics. While pyrolysis is performed under an inert atmosphere, and gasification involves adding a controlled amount of oxygen during degradation. The products of both processes vary with temperature and the amount of oxygen added during gasification. The CO and CO₂ produced during the degradation can be converted to methane using the Sabatier process⁶.

The three main approaches for the characterization of the plastics were pyrolysis, gasification, and biological methods. Pyrolysis involves heating the plastic in the absence of oxygen, allowing the organic material to decompose into a mixture of gases, liquids, and solids. Gasification involves heating the plastic in the presence of a controlled amount of oxygen, allowing the organic material to be partially combusted into a gas mixture. Biological methods involve using microorganisms to break down the plastic into smaller organic compounds.

The overall methane production process by gasification will require initial oxygen from ISRU to begin the thermal degradation of plastic producing CO₂ and CO as intermediate products. The CO₂ and CO are then reduced over a catalyst on the presence of H₂ producing CH₄ and H₂O. The CH₄ can easily be liquefied and stored, while H₂O is electrolyzed into H₂ and O₂. The only consumable during this process will be the hydrogen lost in CH₄. However, the hydrogen can be replenished from residual H₂ on the Lander descent stage⁸ after its mission is over.

II. Experimental

The experimental approach for the PROduction of Methane from Plastic (PROMP) began with separate subsystems, which then are integrated for the end-to-end system. The testing was done in four separate phases:

1. Characterization of plastic degradation products
2. Gas separation to capture and release of CO₂ (to separate O₂ from CO₂)
3. Conversion of CO and CO₂ into CH₄
4. Integrated system test
A. Characterization of plastic degradation products.

Experimental work was performed to investigate the distribution of products at varying temperature and gas compositions. Two experimental approaches were taken to examine the degradation products using a tube furnace as the heated chamber. A flow through system was set up to deliver the degradation products from the furnace to gas sampling valves on a Gas Chromatography-Mass Spectrometry (GC-MS) instrument. Samples were taken approximately every 35 seconds and the degradation products were monitored over a 30 minute period. The carrier gas fed into the furnace to deliver the products to the gas sampling valves had a total flow of 30 sccm of gas, consisting of either helium or helium and a varying percentage of oxygen depending on the experiment being run (pyrolysis or gasification). Three sampling temperatures were chosen to evaluate, 400°C, 600°C and 800°C. This range was chosen based on a data obtained using a Simultaneous Thermal Analyzer data, showing degradation starting at 400°C. 600°C was chosen as the next temperature because it was below the melting point of aluminum, a component in some of the material used for food packaging (Table I) currently used for ISS and Shuttle missions. Avoiding the melting of aluminum maximizes the oxygen conversion to CO and CO₂. Melting the aluminum would expose un-oxidized aluminum, which would react with the oxygen in the reaction chamber. These side reactions of oxygen need to be minimized because the oxygen is a limited resource on the lunar surface. 800°C was chosen as the highest temperature because it was comparable to temperatures used in other high temperature lunar technologies (hydrogen reduction).

The samples at 400°C had limited products, mainly methane/ethane and CO/CO₂ for pyrolysis and gasification, respectively. Higher temperatures in pyrolysis showed new products being produced, these being higher molecular weight hydrocarbons. 800°C showed the largest amount of hydrocarbon production with several cyclic molecules being produced. Although, these samples showed differences between the samples at different temperatures and different gas compositions, it was unclear how we could clearly identify the temperature effects during the ramp up phase of the experiment. The problem was that there was gas swept into the detector while the polymer/furnace was heating, so some of the gas being analyzed was produced when the sample was at a lower temperature during ramping.

A static system was then developed to increase the residence time of the products in the heated zone at the desired temperature equipped with a pressure transducer to monitor the pressure. The samples were heated for 30-35 minutes in a static (no flow) system. The system pressure was monitored during the heating to measure the gas evolved during the degradation of the polymer. An inert purge gas was used to deliver the sample to the GC-MS. The products were again analyzed by the GC-MS; however, this time only 1-2 samples were taken and chromatography was performed for separation of CO₂ from the inert gasses. The GC program ramped the temperature from 25°C to 300°C with a total run time of 13 minutes. Figure 1A shows the spectra of two samples comparing pyrolysis and gasification at 800°C. During gasification, there are two peaks, one from the inert gases and a second from CO₂. The products of pyrolysis are much more complicated starting from methane and continuing up to benzene and other complex hydrocarbons.
Figure 1B shows the CO-CO$_2$ relative peak areas during the flow through experiments at 600°C with varying concentrations of oxygen. As it was expected, the trend in Figure 1B suggests that the production of CO-CO$_2$ is proportional with the oxygen concentration in the gas phase, with CO:CO$_2$ ratios of 0.38, 0.48, and 0.44 for O$_2$ concentrations of 22%, 44%, and 67%, respectively.

Up to this point, all the plastic degradation tests have been done with milligram sample size. The results from the small scale test were promising allowing for scaled up of the system in order to run larger samples. Even though the results suggested that higher O$_2$ concentration yielded higher amounts of CO-CO$_2$, it was decided to use air for safety reasons regarding systems for enriched O$_2$ gas mixtures. Also, a flow-through technique was used in order to continuously introduce un-reacted O$_2$ to the system.

The balanced combustion chemical equations of importance here are shown below:

$$\text{(C}_2\text{H}_4)_n + 2\text{O}_2 \rightarrow 2\text{CO} + 2\text{H}_2\text{O}$$

$$\text{(C}_2\text{H}_4)_n + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$$

Ideally, the gasification products would be essentially a “clean” process with only the production of CO/CO$_2$ and water. However, other byproducts are possible if the degradation process is incomplete. This is most commonly seen if there is not enough oxygen present to allow for complete reaction.

The experiments consisted of loading the reactor with 10.0g of polyethylene, then air was run through the apparatus prior to heating the reactor to obtain a sample baseline at a pre-determined flow rate, after which the reactor was heated to 800°C at a rate of 10°C/min. A molecular sieve 3Å (Angstrom) absorption bed was used to capture water produced during the reaction in order to protect the GC columns. GC (without MS) samples were taken continuously to allow for monitoring of the reaction process. A drop in the O$_2$ levels and a simultaneous increase in the CO$_2$ and CO levels indicated the beginning of the degradation process, as shown in Figure 2. CO$_2$ generation occurred from four to six hours whereas CO generation was shorter. The CO$_2$ and CO levels declined and the amount of O$_2$ present in the chromatograms increased back to baseline levels.

Two different flow rates were tested: 75 sccm (standard cubic centimeter per minute) and 150 sccm of air. The data showed that CO and CO$_2$ were generated from the degradation of the polyethylene proportionally to the flow rate of air (or oxygen). These results were expected since the faster the flow rate of air the more oxygen is available to react. However, it is expected to reach a limit, since there must be a balance between O$_2$ availability and residence time of oxygen in the reactor. This relationship has not been studied, yet. Table II shows the carbon balance on the tests for the flow rates investigated.

![Figure 2. GC results from plastic degradation. Run with 150 sccm of air.](image-url)

Table II. Carbon mass balance from the large scale polyethylene degradation by gasification.

<table>
<thead>
<tr>
<th>ID</th>
<th>Flow Rate (sccm)</th>
<th>C from CO (g)</th>
<th>C from CO$_2$ (g)</th>
<th>Maximum C (g)</th>
<th>C to CO-CO$_2$ Conversion Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>75</td>
<td>0.29</td>
<td>0.96</td>
<td>8.54</td>
<td>14.6</td>
</tr>
<tr>
<td>Test 2</td>
<td>150</td>
<td>0.51</td>
<td>1.25</td>
<td>8.56</td>
<td>20.6</td>
</tr>
</tbody>
</table>

These results were calculated by analyzing the chromatograms generated from the experiment. Previously generated calibration curves allowed for the determination of the composition of the generated vapor stream at a given time during the experiment, which could then be converted to a mass of CO$_2$. Plotting this data allowed for the generation of a function which could be integrated to determine the total mass of CO$_2$ and CO generated during the gasification process. The calculated CO:CO$_2$ ratio for these tests are 0.3 for the 75 sccm case and 0.4 for the 150 sccm case. These values are similar to those CO:CO$_2$ ratios observed in the initial characterization tests. As can be seen from the data, greater than 14% conversion efficiency was obtained using the aforementioned parameters and techniques. The other 80%-86% carbon was lost due to the formation of polycyclic aromatic hydrocarbons (PAH) that were collected by condensation in the molecular sieve 3 Å. Higher efficiency and reduction of PAHs may be
possible upon optimization of the gasification process (flow rates, temperatures, etc); however, the data shows the feasibility of producing CO₂ from polyethylene.

B. Gas separation

The goal of this testing was to develop a method of selectively capturing CO₂ from a CO₂-Air mixture, and releasing it in a controlled manner. This is necessary due to the exothermic nature of the reaction which will occur if the Sabatier catalyst is exposed to oxygen once it has been activated. The production of the CO₂ is performed in the presence of oxygen and cannot be directly run through the rest of the integrated system.

Molecular sieves were investigated as a possible method for the separation of CO₂ from a gas stream. These molecular sieves are designed to have different pore sizes which are the basis for how they can separate different molecules (based upon atomic radii). The atomic radii are calculated using ab initio methods resulting in a CO₂ atomic radius of ~5.57Å. Based upon this and a background literature search on various gas separation techniques it was decided to test the effectiveness of molecular sieve 5Å for the separation of CO₂ from a gas stream containing air.

For this experiment, 8.18g of molecular sieve 5Å was loaded into the test bed. Prior to the introduction of any CO₂, the molecular sieve was regenerated by heating to a temperature of 250°C for ~2.5 hours. Following the regeneration, the bed was cooled to room temperature under vacuum.

Testing of the loading capacity of the molecular sieve 5Å was conducted using a 20:80 CO₂:Air mixture. A total flow rate of 50 sccm was used in these experiments. Baseline chromatograms were collected prior to testing with the molecular sieves. Once the CO₂:Air flow began, GC chromatograms were collected to verify that the CO₂ was being adsorbed and to determine the exact time of breakthrough (~45 minutes at these flow rates). After breakthrough is detected, the test system is flushed with inert gas until only negligible amounts of CO₂, N₂, and O₂ were detected in the chromatograms (~90 minutes). Static desorption was employed to determine the amount of adsorbed CO₂ within the molecular sieve bed. The molecular sieve was heated to 250°C while the pressure within the bed was monitored. When a temperature of 250°C or a pressure of 55 psia was reached (whichever occurred first) the isolation valve for the bed was opened to flush desorbed CO₂ into the GC. This procedure was repeated until no additional CO₂ was seen or a pressure increase was not detected within the molecular sieve bed. Calculations based upon a derivation of the ideal gas law and the observed pressure changes from the desorption step of the test indicate that an average of 0.0167 moles of CO₂ (~0.7348g CO₂) was desorbed from the molecular sieve 5Å. A graphical summary of this experiment is shown in Figure 3.

This work has shown that molecular sieve 5Å is capable of absorbing CO₂ at room temperature from a mixture of gases, and desorbs the captured CO₂ at temperatures in excess of 150°C. Testing has shown an uptake capacity of 0.09g of CO₂ per gram of molecular sieve 5Å. This methodology can successfully be used to selectively separate CO₂ from other incineration products for further use as a feed stock for the Sabatier reaction (for the production of methane). However, an off-the-shelf oxygen scavenger was installed (shown on Figure 4 and 5) as a final safety protection.

C. Conversion of CO and CO₂ to CH₄

The goal of this testing phase was to demonstrate the capability of converting CO and CO₂ into methane by the Sabatier process. A Ni/Mg catalyst on an Al₂O₃ substrate was used, which is capable of converting CO-CO₂/H₂ into CH₄/H₂O at elevated temperatures. The relevant balanced equation is shown here:

\[ \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} + \text{Heat} \]

This reaction is known as Sabatier reaction. This reaction requires a 4:1 ratio of H₂:CO₂ and a 3:1 ratio for H₂:CO for complete conversion to CH₄. There are safety concerns associated with the use of this Sabatier catalyst. The
Sabatier reaction is only carried out at temperatures above 300°C to avoid the formation of a toxic nickel carbonyl compound. The catalyst is received in an inert form (nickel oxide) and must be activated in the testing apparatus prior to use. This is accomplished by exposing the inert catalyst to pure H₂ at temperatures between 200°C – 400°C. Once activated, the catalyst can react exothermically with O₂ and moisture which requires the system be pressurized with inert gas when not in use. This is also the reason molecular sieves are used to capture generated CO₂ and H₂O (to prevent introduction of air/water into the Sabatier reactor).

Active cooling was used to collect/condense water produced from the reaction. Initial testing used both CO and CO₂ as reactants for the Sabatier reaction. However, since only CO₂ is absorbed in the molecular sieve 5Å from the gasification of the polyethylene, only the CO₂ data will be reported. Different reactor temperatures were tested to see how this would affect CH₄ production. Different flow rates of H₂:CO₂ were tested as well, although the 4:1 minimum ratio of the reactants was maintained for these experiments.

The experiment tested the conversion of CO₂ into methane at 300°C and at 375°C to study the affect of temperature on the catalyst efficiency. Two different sets of flow rates were tested at these temperatures: 1) 100 sccm CO₂ and 400 sccm H₂ and 2) 140 sccm CO₂ and 560 sccm H₂. The gas streams were quantified to determine the percentage CO₂ within the mixture and compared to the starting concentration of 20%. These values were normalized to only account for the presence of CO₂ and CH₄ (analytes of interest). There was no detectable H₂ in the outlet gas streams of any of these tests. Multiple samples were analyzed and the average % concentrations of CO₂ and CH₄ in the outlet gas streams are given in Table III.

### Table III. Summary of data from Sabatier reactor test.

<table>
<thead>
<tr>
<th>Test #</th>
<th>Reactor Temp (°C)</th>
<th>CO₂ flow (sccm)</th>
<th>H₂ flow (sccm)</th>
<th>%CO₂ (norm.)</th>
<th>%CH₄ (norm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>300</td>
<td>100</td>
<td>400</td>
<td>6.86</td>
<td>93.14</td>
</tr>
<tr>
<td>2</td>
<td>300</td>
<td>140</td>
<td>560</td>
<td>8.27</td>
<td>91.73</td>
</tr>
<tr>
<td>3</td>
<td>375</td>
<td>100</td>
<td>400</td>
<td>10.88</td>
<td>89.12</td>
</tr>
<tr>
<td>4</td>
<td>375</td>
<td>140</td>
<td>560</td>
<td>11.02</td>
<td>88.98</td>
</tr>
</tbody>
</table>

As can be seen from Table III, the majority of the outlet gas stream was composed of CH₄ (~90%) confirming the capability of converting CO₂ into CH₄ in this test setup. While all of the H₂ appeared to be consumed, significant amounts of CO₂ were left in the gas stream (post-Sabatier reaction), which could be related to the inaccuracy of the flow controllers used. From these initial results, it appears that the lower temperature Sabatier reaction was more efficient in the conversion process. Additionally, it doesn’t appear that increased amounts of reactants (at this test ratio) increase the amount of conversion seen. This may indicate that the conversion process may require additional time in the Sabatier reactor than was given in these experiments. Further optimization of temperature and the ratio of reactants will be necessary in order to produce the maximum amount of CH₄ possible from a given amount of CO₂. This will be vitally important because the CO₂ must be produced as feed stock from the gasification reactor (discussed previously) and any unused portion of the CO₂ will be have to be recycled from the Sabatier reactor.

### D. Integrated methane production test.

The final phase of testing integrated all three tested subsystems (CO₂ adsorption/desorption, CO₂ production from plastic degradation, and conversion of CO₂ into CH₄ using Sabatier catalyst) into a single unit. The individual subsystems have been shown to work independently of each other, now the entire process will be tested in a single experiment.
Figure 4. Schematics of the integrated PROMP system.

The integrated testing apparatus is shown in Figure 4. LABVIEW 2009 was used to control the entire system, controlling all the valves, heaters, and flow controllers found in this system. For this initial integrated test, 2.983 g of polyethylene was loaded into the plastic degradation reactor. The catalyst was activated (as done previously) and kept under an inert nitrogen blanket until it was used in the experiment. GC samples were taken continuously throughout the experiment to monitor the \( \text{O}_2 \) levels. With the testing apparatus in Sabatier reactor-bypass configuration, 150 sccm of air was run through the plastic degradation reactor. The plastic degradation reactor was heated to a temperature of 800°C at 10°C/min to degrade the polyethylene. This temperature was maintained for ~4 hours and then allowed to cool to room temperature, at which point the air flow was replaced with helium flowing at 200 sccm. The \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) produced during the degradation reaction were captured on the 3Å and 5Å molecular sieves, respectively. Following the degradation of the polyethylene, the water was desorbed from the 3Å molecular sieve bed by heating it to 200°C at 2°C/min and holding for ~30 minutes. Next, the Sabatier reactor was heated to 300°C at 3°C/min and the nitrogen flow was replaced with \( \text{H}_2 \) flowing at 300 sccm. The chiller and pump unit was turned on to condense any water produced from the Sabatier reaction. Once the Sabatier reactor bed was at temperature the 5Å molecular sieve bed was heated to 200°C at 2°C/min to release the generated \( \text{CO}_2 \). This \( \text{CO}_2 \) was directed through the Sabatier reactor and the resulting output flow was sampled by the GC.

The GC analysis of the gas stream from the Sabatier reactor confirmed that \( \text{CH}_4 \) was produced during this experiment. This demonstrates the capability of degrading waste plastics and converting the by-products to a useful fuel. The data from the integrated test confirmed the methane percent yield predicted from the subsystem tests of 15% \( \text{CH}_4 \).
III. Conclusion

The production of methane from plastic offers a feasible process to recycle the lunar outpost trash, that otherwise would be stored somewhere in or near the outpost, to make fuel for the ascent stage. The methane produced from the outpost’s trash and methane produced by ECLSS during the oxygen regeneration process would be enough to fuel the ascent stage once per year. If fully implemented, methane production and ISRU $O_2$ production for propellant would reduce Earth launch mass by 40,000 kg over a 10 year life of the lunar outpost. The first generation end-to-end system was successfully designed, built, and tested, as shown in Figure 5. Even though this system has not been optimized to maximize the production of methane, the PROMP system has a 16% methane yield.

References