

# Use of Pyrolysis Processing for Trash to Supply Gas (TtSG)

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Technologies that reduce logistical needs will be a key component of long term space missions. For this reason, NASA has recently begun a Logistic Reduction and Repurposing (LRR) project. This project involves four hardware oriented tasks: 1) conversion of logistical items to useable products using Heat Melt Compactor (HMC) processing; 2) conversion of trash to supply gas (TtSG) in order to make propellants (e.g., CH<sub>4</sub>, H<sub>2</sub>) from solid waste products; 3) use of an Advanced Clothing System (ACS) to reduce mass, volume, and flammability; 4) use of Logistics-to-Living (L2L) technologies to repurpose launch packaging containers. The current paper addresses TtSG technologies, in general, and pyrolysis processing in particular. The overall goal of TtSG is to develop methods to convert trash and other solid waste materials to valuable products (e.g., propellants) plus materials that can benefit the life support system (e.g., oxygen, water). The production of propellants could be especially important, as it would reduce the need to launch fuel to locations beyond earth orbit. In addition, since over 5 kg per day of trash is produced for a crew of 4, there is significant logistical leverage to be gained by this conversion process. Recently, several TtSG processes were evaluated by NASA in laboratory testing using simulated waste streams, including a High Fidelity Waste Simulant (HFWS). In the project that is the subject of the current paper, two-stage pyrolysis processing of the HFWS was studied over a range of conditions, in order to examine the effects of cracking temperature, residence time, gas atmosphere, sample size, etc. For all of these experiments, relatively high yields (0.5 to 10 wt. %) of individual gas products (CO<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and H<sub>2</sub>) were observed, with the total gas yields ranging from ~30 to 45 wt. %. The largest yield was generally a liquid product (~40 to 50 wt. %) that was assumed to be mainly water (based on condensates produced from similar two-stage pyrolysis experiments), while modest amounts of a char product (~10 to 15 wt. %) were formed.

## Nomenclature

ACS = Advanced Clothing System  
DAF = Dry, Ash-Free  
DAQ = Data Acquisition Card  
FTIR = Fourier Transform Infrared  
HFWS = High Fidelity Waste Simulant  
HMC = Heat Melt Compactor  
ISRU = In-Situ Resource Utilization  
KPP = Key Process Parameters  
L2L = Logistics-to-Living  
LPM = Liters per Minute  
LRR = Logistics Reduction and Repurposing (LRR)  
MFC = Mass Flow Controller

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MFM = Mass Flow Meter  
MS = Mass Spectrometry  
TtSG = Trash to Supply Gas  
WMS = Waste Management System

## I. Introduction

### A. Background

Technologies that reduce logistical needs will be a key component of long term space missions. For this reason, NASA has recently begun a Logistic Reduction and Repurposing (LRR) project [1]. The LRR project involves four hardware oriented tasks: 1) conversion of logistical items to useable products using Heat Melt Compactor (HMC) processing; 2) conversion of trash to supply gas (TtSG) in order to make propellants (e.g., CH<sub>4</sub>, H<sub>2</sub>) from solid waste products; 3) use of an Advanced Clothing System (ACS) to reduce mass, volume, and flammability; 4) use of Logistics-to-Living (L2L) technologies to repurpose launch packaging containers. One of the main opportunities to accomplish this objective is to develop useful products from the solid wastes that are generated by the crew during these missions, which is the focus of Tasks 1 and 2.

The work on Task 1 has mainly been done by the NASA Ames Research Center (NARC) [2-6]. The HMC process meets some important logistical requirements, including volume reduction, sterilization, and water recovery and also provides the potential benefit of radiation shielding from the plastic disk products. The trash to supply gas (TtSG) technologies produce some of the same logistical benefits (volume reduction, sterilization, and water recovery), but also some benefits that are quite different (e.g., propellant production) [7]. Clearly, both technologies may be useful for a long term space mission and only a systems engineering analysis can determine how much of the waste stream should be diverted to each process.

The purpose of the current paper is to address TtSG technologies, in general, and pyrolysis processing in particular. The overall goal of TtSG is to develop technologies to convert trash and other solid waste materials to valuable products (e.g., propellants) plus materials that can benefit the life support system (e.g., oxygen, water) [7-10]. The production of propellants could be especially important, as it would reduce the need to launch fuel to locations beyond earth orbit. In addition, since over 5 kg per day of trash is produced for a crew of 4, there is significant logistical leverage to be gained by this conversion process [7-10].

Several processes have been considered for TtSG, including pyrolysis, thermal oxidation, catalytic decomposition, gasification, and incineration [7,8,10]. Recently, many of these processes were evaluated in laboratory testing using simulated waste streams.

### B. Solid Waste Management Technologies for Advanced Life Support

There are many constraints on the life support systems that can be used for both short and long duration flights and space outposts. Such systems should be of low volume, low weight, low power and oxygen consumption, have the ability to handle a variety of wastes, require low maintenance, and be able to reduce volume and increase stability of the wastes [11-14]. This is a complex optimization problem, which is why it still remains an area of active R&D. An additional layer of complexity results from the uncertainty of the NASA near term mission objective, as going to the moon will place different demands on the Waste Management System (WMS) than going to Mars or Asteroids/Phobos [1,7,9]. In addition, the final system will require relatively sophisticated control schemes to ensure that it operates properly and is integrated with the rest of the life support system [15].

Solid wastes will include inedible plant biomass (IPB), paper, plastic, cardboard, waste water concentrates, urine concentrates, feces, etc. It would be desirable to recover usable constituents such as H<sub>2</sub>O, CO<sub>2</sub>, nitrogen, nitrogen compounds, and solid inorganics. Any unusable byproducts should be chemically and biologically stable and require minimal amounts of storage volume. Many different processes have been considered for dealing with these wastes: incineration, aerobic and anaerobic digestion, wet oxidation, supercritical oxidation, steam reforming, electrochemical oxidation, catalytic oxidation and heat melt compaction [1-8,10-25]. All the above approaches have their advantages, but also disadvantages which have prevented adoption of any single method. For example, incineration (oxidation) utilizes a valuable resource, oxygen, and produces undesirable byproducts such as oxides of sulfur and nitrogen. In addition, incineration will immediately convert all of the waste carbon to CO<sub>2</sub>, which will require venting excess CO<sub>2</sub>. Finally, incineration is not well suited to handling mixed waste streams that consist of large unground pieces present in different phases and having different heating values. Pyrolysis can be used in combination with oxidation to introduce a degree of homogeneity to the incinerator feedstock, e.g., through the so-called wet carbonization process from EnerTech Environmental, Inc. and Energy and Environmental Research

Corporation [20]. TDA recently developed a low temperature waste oxidation system [21]. A Heat Melt Compactor for stabilizing plastics and related wastes has been under active development by NASA with promising results [2-6].

Gasification can be thought of as an intermediate case between pyrolysis (no oxygen present) and incineration (complete oxidation). Typically, gasification would utilize an oxidizing gas like  $\text{CO}_2$  or  $\text{H}_2\text{O}$  (steam). Similar to pyrolysis, gasification can result in char production, some methane, along with tar. The tar production can complicate the gas cleanup process, although it can also be destroyed in a separate cracking bed. Both gasification and pyrolysis can be advantageous relative to incineration or other types of complete oxidation because the production of significant amounts of  $\text{CH}_4$  and  $\text{H}_2$  can reduce the power and mass requirements for the electrolyzer (to generate  $\text{H}_2$  from  $\text{H}_2\text{O}$ ) and the Sabatier Reactor (to generate  $\text{CH}_4$  from  $\text{CO}_2/\text{CO}$ ).

One of the main advantages of pyrolysis for near term life support is that it can provide the baseline functions of a Waste Management System, i.e., reduce volume, stabilize, and recover water, along with several enhancements. These include thermochemical water and oxygen recovery, production of fuels, and multi-purpose carbon, and In-Situ Resource Utilization (ISRU). In addition, when compared to incineration or gasification, pyrolysis has some advantages due to lower amounts of feedstock preparation, lower oxygen requirements, lower total gas volume, larger production of  $\text{CH}_4$  and  $\text{H}_2$  and lower tar production when compared to gasification and no  $\text{NO}_x$  and  $\text{SO}_2$  (production when compared to incineration).

Besides the benefits cited above, pyrolytic waste treatment has some other potential advantages when compared to other possible solid waste processing methods: 1) it can be used for all types of solid products and can be more easily adapted to changes in feedstock composition; 2) the technology is relatively simple and can be made compact and lightweight and thus is amenable to spacecraft operations; 3) it can be conducted as a batch, low pressure process, with minimal requirements for feedstock preprocessing; 4) it can produce several usable products from solid waste streams (e.g.,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ , etc.); 5) the technology can be designed to produce minimal amounts of unusable byproducts; 6) it can produce potentially valuable chemicals, chemical feedstocks, and materials (e.g., activated carbon); 7) pyrolysis will reduce the storage volume of the waste materials, while important elements such as carbon and nitrogen can be efficiently stored in the form of pyrolysis char and later recovered by gasification or combustion when needed. In addition to being used as a primary waste treatment method, pyrolysis can also be used as a pretreatment for more conventional techniques, such as combustion or gasification.

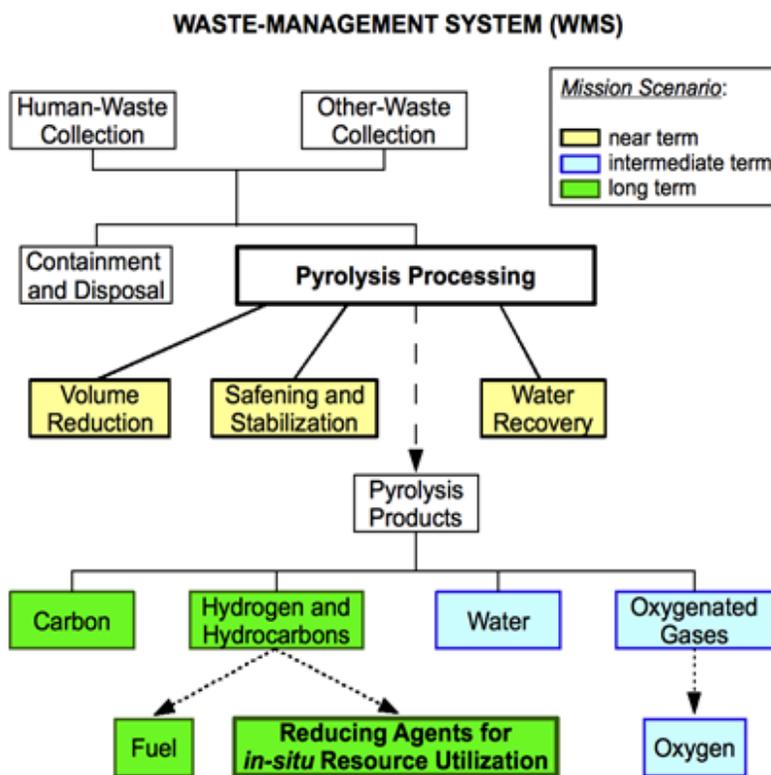
The main disadvantages of pyrolysis processing are: (1) the product stream is more complex than for many of the alternative treatments; (2) the product gases cannot be vented directly in the cabin without further treatment because of the high  $\text{CO}$  concentrations. The latter issue can be addressed by utilization of a water-gas shift reactor, by introducing the product gases into a catalytic oxidizer or a high-temperature fuel cell, or by a reduction step using a methanation catalyst.

### C. Pyrolysis Processing of Solid Waste Materials

Pyrolysis is a process of thermal decomposition to produce gases, liquids (tar) and char (solid residue). Pyrolysis is usually understood to be thermal decomposition which occurs in an oxygen-free atmosphere, but oxidative pyrolysis is nearly always an inherent part of combustion processes. Gaseous, liquid and solid pyrolysis products can all be used as fuels, with or without prior upgrading, or they can be utilized as feedstocks for chemical or material industries. The types of materials which are candidates for pyrolysis processes include plant biomass, human wastes, food scraps, paper, cardboard, plastics, rubber [26,27]. These products are primarily polymeric in nature and pyrolysis represents a method of processing all of these materials into useful products. In the case of plant biomass, human wastes, food scraps, paper and cardboard, pyrolysis can be used to produce fuels or chemicals in gaseous and/or liquid form. In the case of plastics and rubber, pyrolysis can sometimes be used for “recycling” previously manufactured materials back to monomers.

As discussed above, one of the biggest advantages of pyrolysis for near term life support is that it can provide the baseline functions of a Waste Management System, i.e., reduce volume, stabilize, and recover water, along with several enhancements. These include thermochemical water and oxygen recovery, production of fuels, and multi-purpose carbon, and ISRU, as shown in Figure 1. Consequently, pyrolysis processing can provide a bridge technology between near term and long term mission scenarios.

An understanding of the key features of pyrolysis processing can be gained by looking at the results from primary pyrolysis of some representative waste materials, shown in Figure 2. These are results from a standard pyrolysis experiment at 30 K/min using a thermogravimetric analyzer with FTIR analysis of evolved gases (TG-FTIR). The samples include rice powder and spinach powder. For these samples, the pyrolysis yields are dominated by tar produced during the pyrolysis process which ranged from 20-30% on a dry, ash-free (daf) basis. The next important products were pyrolytic  $\text{H}_2\text{O}$ , followed by  $\text{CO}_2$  and  $\text{CO}$ .



**Figure 1. Schematic of Waste Management System (WMS) indicating how a pyrolysis pyrolysis-centric approach impact near term, intermediate term and long term mission scenarios, including in-situ resource utilization.**

In Figure 3, we can see results for a set of 46 biomass samples for tar (bio-oil), which include the samples in Figure 2. Additional details and more extensive pyrolysis results on these samples have been described in a previous publication [28]. It can be seen that the tar yields average close to 40% in a primary pyrolysis experiment, i.e., in an experiment which is not designed to crack or oxidize the tar. The tar component would primarily be useful to NASA for long term mission scenarios as a fuel or reactant for ISRU. Alternatively, it could be used as a binder for construction materials made from char residues and/or regolith. Under the current project, the tar resulting from primary pyrolysis of biomass, plastic, and other components of the simulated space trash will be cracked in a second pyrolysis stage to produce additional supply gas ( $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ).

Figure 4 shows the oxygen concentrations for some 46 biomass samples, which indicates that the average oxygen concentration is about 40% on a daf basis. This also makes these materials a rich source of additional  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CO}$ , as shown in Figure 5. The nearly 20% by weight of water that can be produced by primary pyrolysis of common biomass materials is indeed one of the main advantages of pyrolysis processing of solid wastes, especially for intermediate term missions scenarios. Recent NASA-sponsored work at Advanced Fuel Research, Inc. (AFR) indicates that, for a fecal simulant material, most of this additional water can be released under relatively mild pyrolysis conditions ( $\leq 300^\circ\text{C}$ ), a process also known as torrefaction [29].

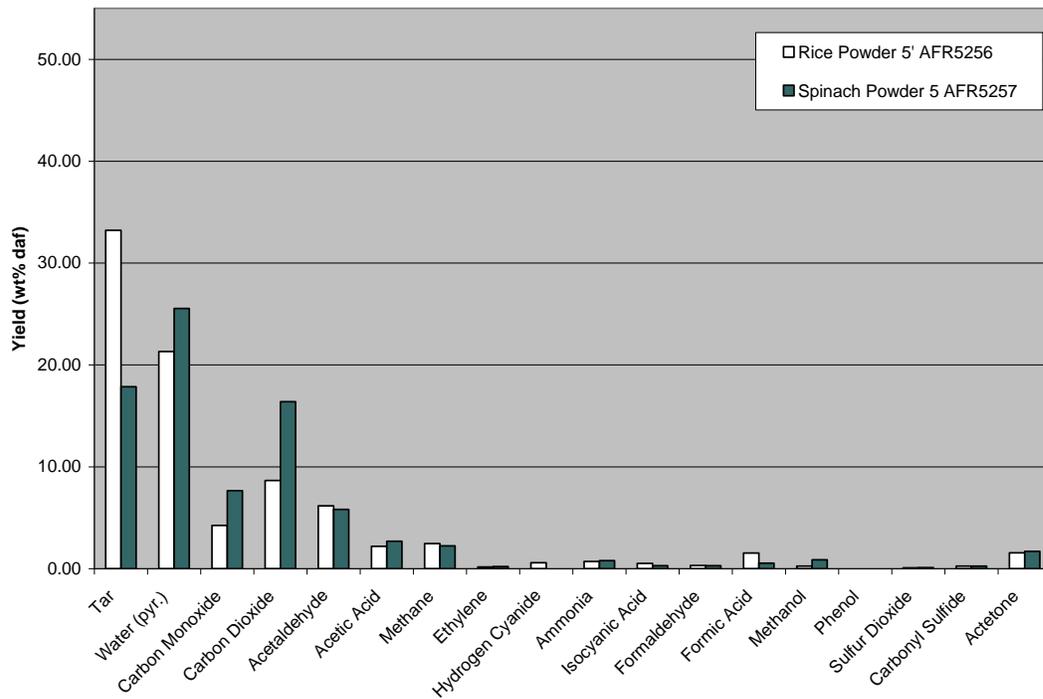


Figure 2. TG-FTIR pyrolyzer yields from rice and spinach (wt. % daf).

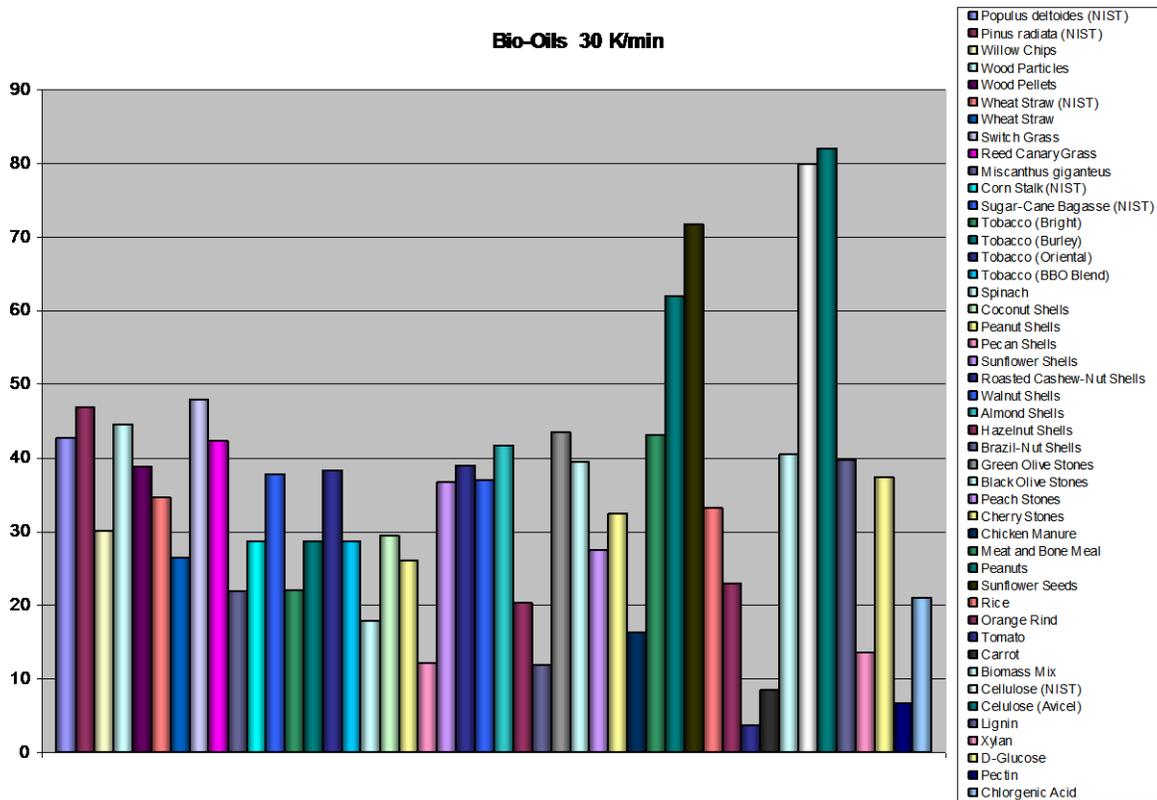


Figure 3. Yields of bio-oil (tar) for diverse biomass feedstocks used in this study.

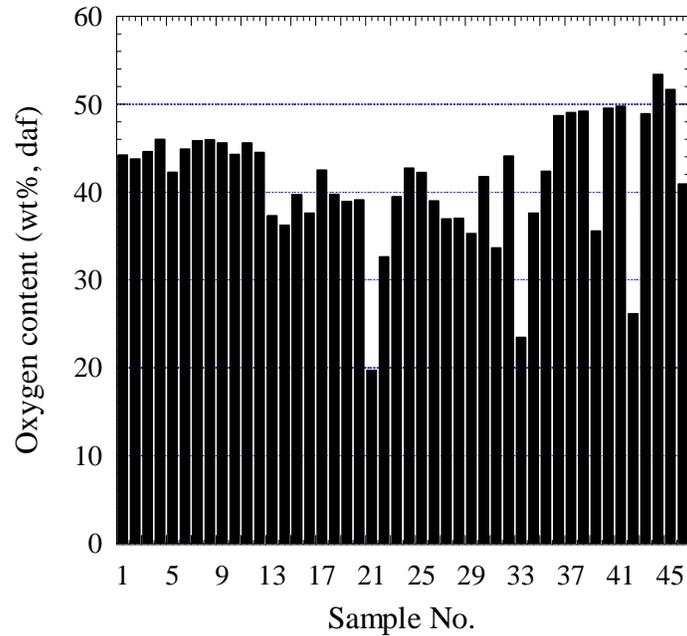


Figure 4. Oxygen content, on a dry, ash-free basis, for 46 diverse biomass feedstocks. See Figure 3 for sample identification.

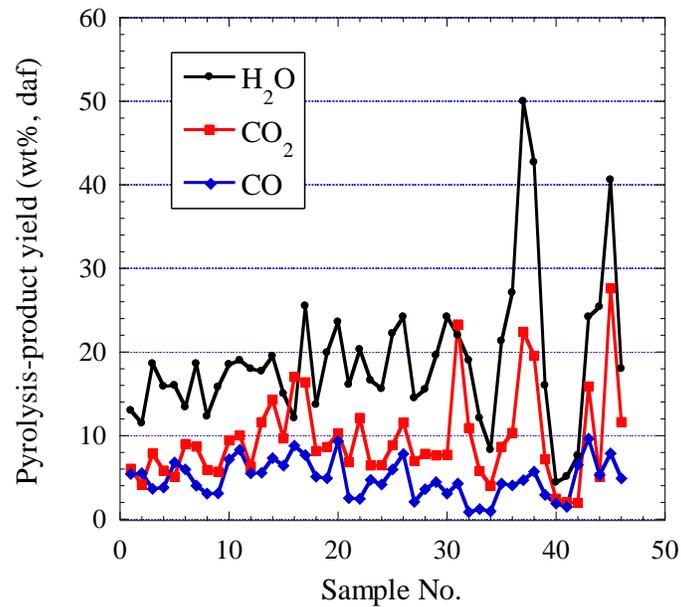


Figure 5. Yields of selected oxygen containing pyrolysis products (water, carbon dioxide, and carbon monoxide) for 46 diverse biomass feedstocks; TG-FTIR data collected at a heating rate of 30 K/min. See Figure 3 for sample identification.

## II. Experimental

### A. Introduction

Under the current study, several experiments were done to fill in the Key Process Parameters (KPPs) for pyrolysis relative to other TtSG technologies (e.g., gasification, incineration, low-temperature oxidation), so that a more detailed comparison could be done on a standardized feedstock. These included a set of 16 experiments to examine the following parameters: 1) effect of secondary cracking bed temperature on gas composition; 2) effect of flow rate and residence time on gas composition; and 3) effect of hydrogen or water addition on gas composition and cracking bed regeneration. The analysis of gas composition included determination of major gas products ( $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$ ) and impurities ( $\text{NH}_3$ ,  $\text{HCN}$ ,  $\text{H}_2\text{S}$ ) using a combination of FTIR and MS technologies.

### B. Experimental Design and Apparatus

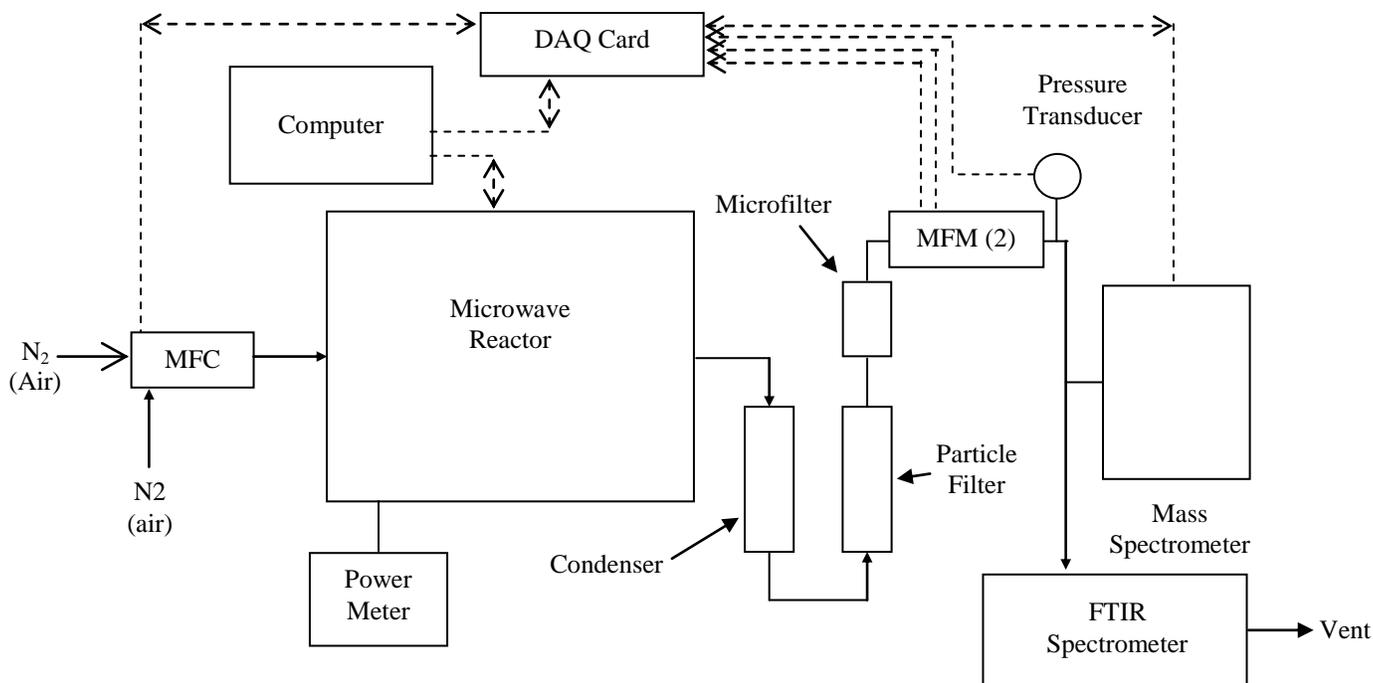
A set of High Fidelity Waste Simulant (HFWS) samples was obtained from the Kennedy Space Center (KSC), which were made according to the specifications developed by Hintze [10,30]. In mass %, the HFWS included urine brine (21.3), polyethylene (16.2), tee-shirts (12.6), fecal simulant (11.2), food (8.9), hand/face wipes (5.5), tissues (4.9), towels (4.8), and nylon (4.6) as major components, along with shampoo (2.4), aluminum foil (2.3), nitrile gloves (2.1), toothpaste (1.2), paper (0.6), garments (0.5), disinfecting wipes (0.4), and duct tape (0.4), as minor components.

A schematic of the microwave reactor system that was employed for pyrolysis of the HFWS samples is shown in Figure 6. The primary components are the reactor (described below) and the gas analysis instrumentation. A two-stage condenser (room temperature and  $5^\circ\text{C}$ ) is employed for collecting condensable products (water, oil) and a wool filter and microfilter are used to prevent residual particulate species from contaminating the instrumentation. A mass spectrometer (MS) and a Fourier transform infrared (FTIR) spectrometer were employed to measure the non-condensable product gas composition. The MS is a quadrupole type with a detection range of 1 – 100 atomic mass units (amu) and an ultimate resolution of less than 0.5 amu and is calibrated for quantitative measurements of  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{C}_2\text{H}_2$ . It is designed for atmospheric sampling and includes a hybrid turbomolecular/drag pump backed by a diaphragm pump and a fast response, two-stage pressure reduction system for atmospheric sampling. The FTIR gas analyzer has a frequency range of  $700 - 6500 \text{ cm}^{-1}$  with a resolution of  $0.5 \text{ cm}^{-1}$  and is calibrated for  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$  and  $\text{H}_2\text{O}$  (which is not completely condensed). The heated ( $125^\circ\text{C}$ ), single pass gas sampling cell (~ 50 cc volume, pathlength = 4 inches) has an exchange rate of 4-5 seconds. For all experiments performed in this study, the MS data and FTIR data were continuously collected at 13 and 10 second intervals, respectively.

The carrier gas is controlled by a mass flow controller (MFC) and two mass flow meters (MFM) measure the total gas volume, as shown in Figure 6. The volumetric flow is recorded continuously throughout the experiment, along with the gas analyzer measurements. Since the MFMs are calibrated for nitrogen, a correction factor (conversion factor) is applied based on the volume fraction of the measured gases, the manufacturer supplied conversion factors for the individual gases being quantified and the total flow of nitrogen, which is held constant during each experiment. The flow rates for each individual gas are calculated based on the corrected total flow measured at the MFMs and the gas concentration measured by the spectrometers.

Two reactor configurations were explored for pyrolyzing the HFWS samples. Most of the work was performed with the two-stage pyrolysis geometry shown schematically in Figure 7. The main reactor component is a custom-modified industrial microwave oven from Microwave Research & Applications, Inc. (MRA, [www.microwaveresearch.com/](http://www.microwaveresearch.com/)) that was developed under a previous NASA-sponsored project [31,32]. The oven (model BP-211) provides 3.2 kW of power using four air-cooled 800 W magnetrons (2450 MHz) and also incorporates four mode stirrers for enhanced power uniformity in the oven cavity. The oven has been modified to safely enable sample insertion into the cavity and extraction of product gases. The reaction vessel is an approximately 34 inch long quartz tube (2.24 inch i.d. x 2.4 inch o.d.). Quartz is employed because it is essentially transparent to the microwave radiation. The vessel includes a “shelf”, formed into the quartz, which supports a secondary pyrolysis (tar-cracking) zone with a length of up to about nine inches. Top and bottom flanges with piston type (radial) seals form the gas-tight connections with the quartz vessel. The top flange also supports a 0.125 inch diameter thermoprobe that is inserted into the cracking layer for temperature monitoring and control via a programmable temperature controller. The thermoprobe is a shielded thermocouple with a metal sheath that is grounded to the oven cavity.

Primary pyrolysis occurs in the sample crucible, which can be inserted or retracted from the oven cavity during operation of the oven. The crucible includes a special feature for support of a central microwave susceptor (absorber) material to enhance the heating of materials that are poor absorbers of microwave radiation. During the



**Figure 6. Schematic of the prototype microwave reactor system used for trash pyrolysis experiments. (MFC = mass flow controller, MFM = mass flow meter.)**

previous project [31], AFR developed this unique susceptor approach whereby a core of an efficient absorber material, such as activated carbon or silicon carbide (SiC), is located at the center of the reaction vessel. Upon exposure to the microwave energy, the absorber core quickly heats up and begins to pyrolyze the surrounding biomass material in close proximity. Initially, the heating efficiency is relatively poor, since only a fraction of the microwave energy is absorbed by the rod. As heated biomass is converted to char, the effective microwave absorbing surface area core grows at a linear rate. However, in this case, the reaction continues to accelerate until all of the biomass is converted to char. This “inside-out” heating approach offers some important potential advantages. First, the growing surface of the central absorbing rod/char is always the hottest area and close to the raw biomass. Second, radiative losses are reduced – the outer raw biomass transmits microwave radiation to the inner core, but thermal radiation from the center core itself is absorbed until the biomass is completely pyrolyzed. For the earliest HFWS sample runs, an existing crucible that could hold 50 g of simulant was used. Later on, a new crucible was fabricated that could hold 100 g samples.

Figure 8 displays a photograph (top left) of the interior microwave cavity and quartz reaction vessel. A sample crucible (smaller version) is shown partially inserted into the microwave cavity (inside the quartz reaction vessel) at the bottom of the photo. The photo also shows the secondary pyrolysis section of the reaction vessel. The material used for tar-cracking in this region is a stack of predominantly (80 %) silicon carbide foam (TaoFil FCF-2) discs (2 inch dia. x 0.875 inch thick). These foam discs have good microwave absorption properties and can be regenerated in air to burn off carbon residue accumulated from the pyrolysis experiments. As shown in the bottom left photo in Figure 8, the foam is a porous, open-celled structure of interconnected ceramic ligaments. The pore size of the foam used for these HFWS pyrolysis experiments using a secondary reaction zone was 20 pores per inch (ppi).

Figure 8 also depicts (top right) a photograph of the reactor geometry that was utilized for primary pyrolysis-only tests. In this case, the sample crucible is a closed-end quartz tube that is attached directly to the top flange of the microwave reactor in Figure 7. An alumina tube provides additional support for the crucible. In keeping with the inside-out heating approach described above, a SiC susceptor tube is located at the center of the quartz vessel. A thermocouple is shown inserted into the susceptor and is used for controlling the sample temperature.

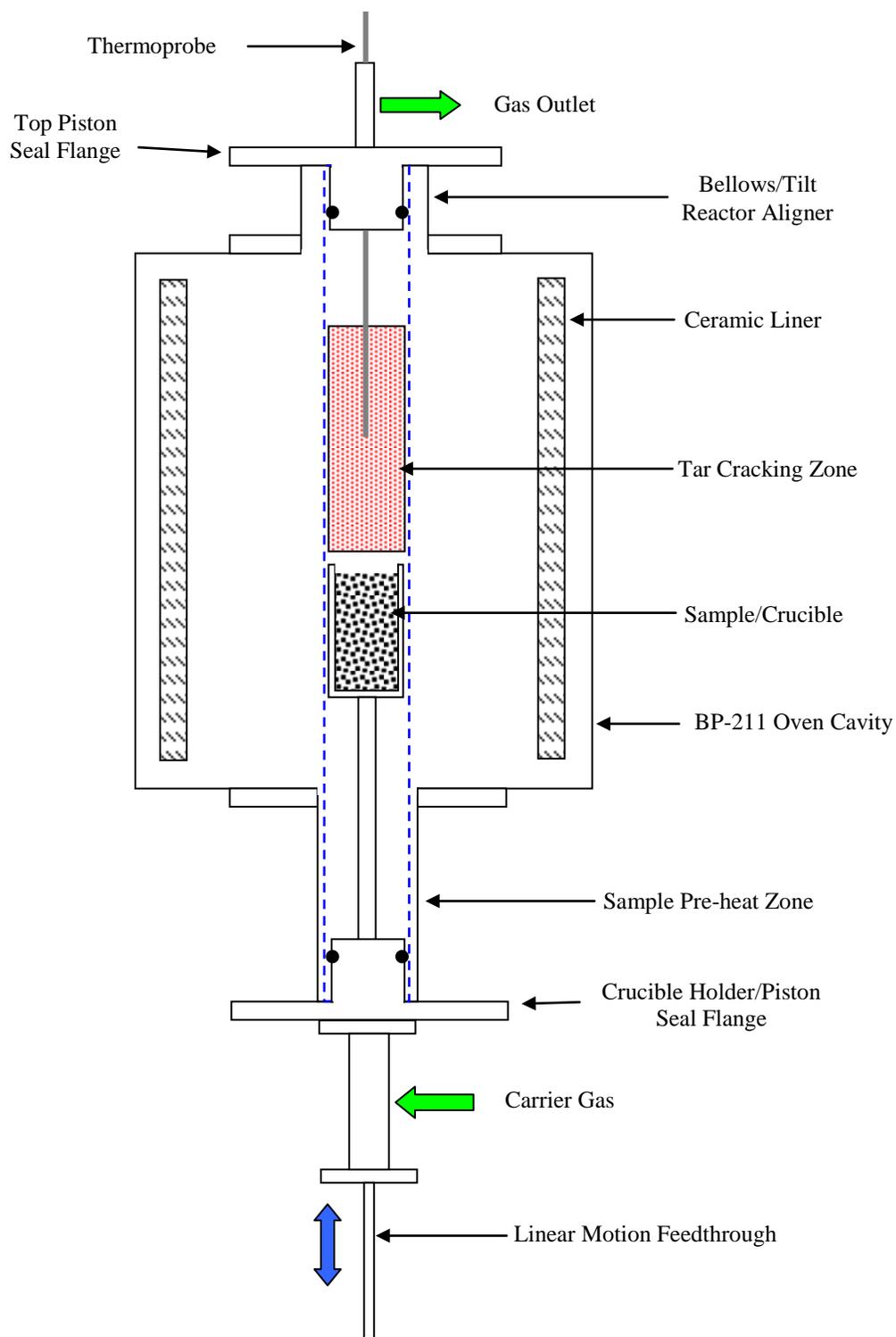


Figure 7. Schematic of the microwave reactor employed for two-stage pyrolysis of HFWS samples.

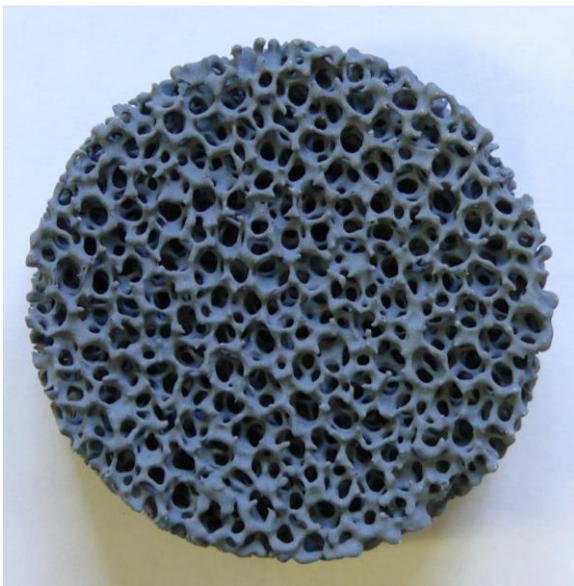
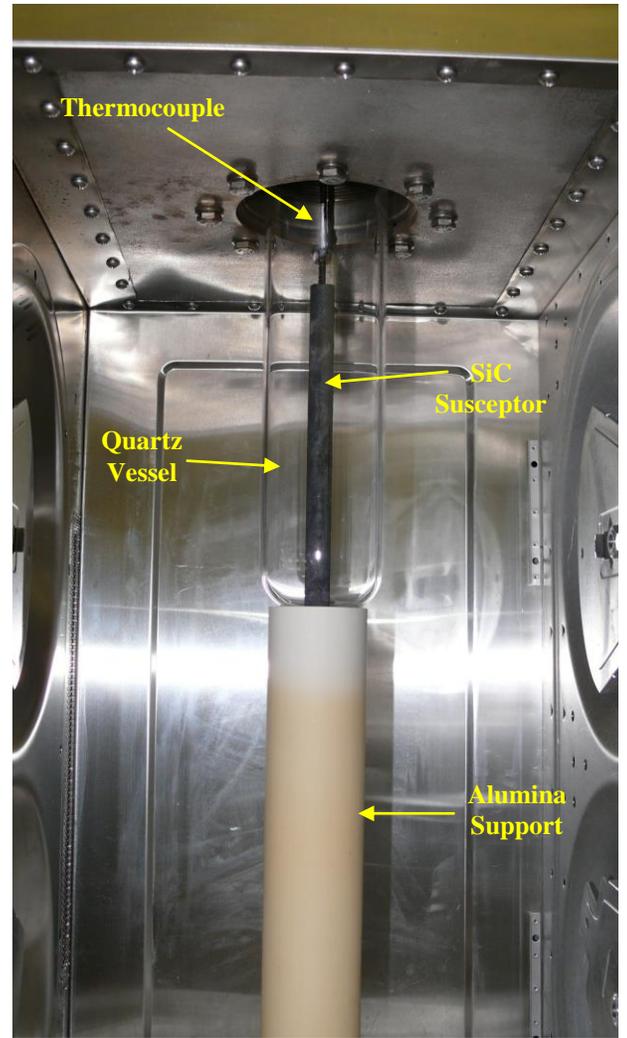
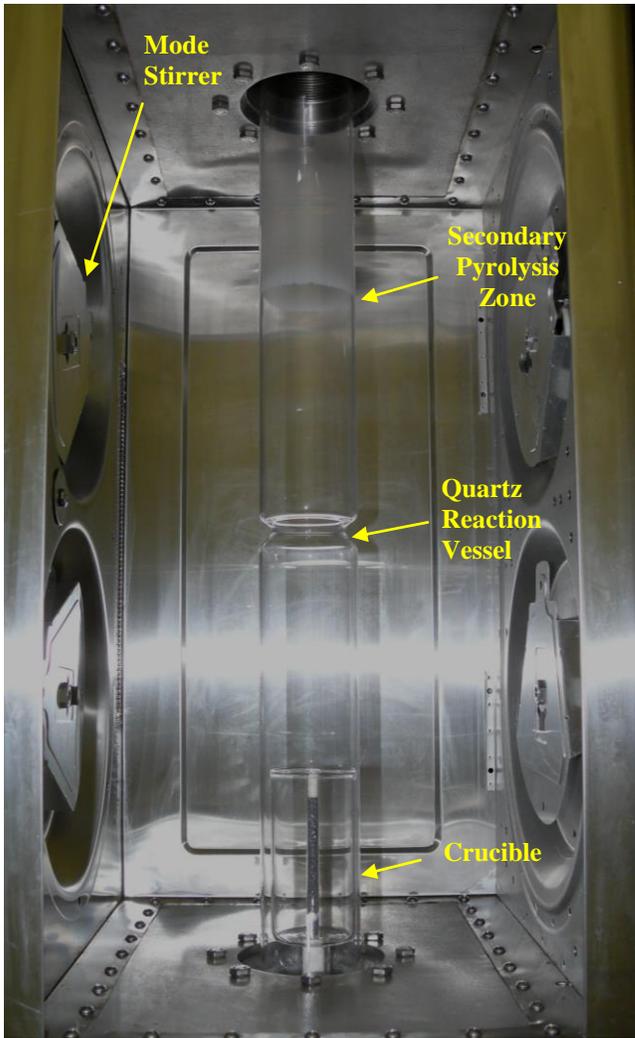


Figure 8. Photographs of the microwave reactor configurations used for HFWS pyrolysis testing. Top left) interior view of the BP-211 oven cavity with the quartz reaction vessel and crucible. Bottom left) 2 inch diameter TaoFil FCF-2 SiC foam filter used for tar-cracking zone. Top right) closed-end quartz vessel geometry used for primary pyrolysis-only experiments.

### III. Results and Discussion

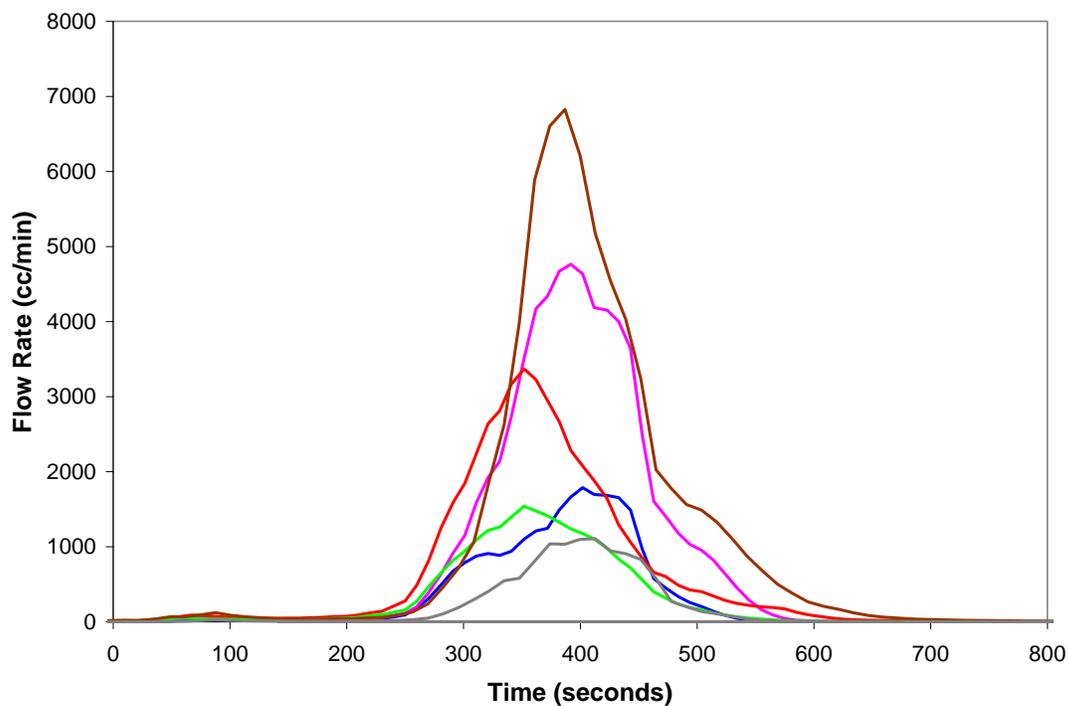
HFWS samples were provided by the KSC in nominally 100 g quantities. The samples were contained in zip-locked plastic bags. The actual samples retrieved from each bag ranged from about 95 – 104 g in size. There was concern that, in some cases, the samples had been contaminated with condensed moisture during shipping or while being stored in a laboratory refrigerator. As mentioned above, the first experiments were performed with ~ 50 g quantities, which was the limit of the sample crucible that was available at that time. In this case, efforts were made to split the samples evenly, in terms of their composition (plastic, foil, cotton, etc.). Eventually, a new crucible was fabricated that could hold entire 100 g samples.

For all experiments, the sample was loaded into the reaction vessel and purged with at least 1 LPM carrier gas for a minimum of 30 minutes prior to heating. For experiments involving two-stage pyrolysis, the secondary pyrolysis zone was preheated to the setpoint temperature (~8–10 minutes), prior to inserting the sample crucible into the oven cavity. After cooldown, the reaction vessel was weighed to determine the remaining char (carbon plus ash). The condenser, filters, and gas transfer lines were also weighed to determine the amount of condensate produced during each run. Finally, a “regeneration” step was employed for the secondary pyrolysis zone after each run. In this case, the SiC foam cracking layer was heated to 500 – 800°C in a flow of dry air (~1 LPM) to burn off any carbon residue accumulated during the HFWS pyrolysis. It should be noted that this step was performed to round out the mass balance for each run and is normally not necessary. It is also worth noting that the regeneration was found to be largely self-sustaining at temperatures  $\geq 500^\circ\text{C}$ , with sufficient air flow.

As described above, MS and FTIR data were collected and analyzed continuously throughout each pyrolysis run. Figure 9 displays the gas evolution profiles for  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CO}_2$ , and  $\text{C}_2\text{H}_2$  for a run where the secondary pyrolysis zone was heated to ~950°C and the sample size was ~96 g. (The sample crucible was inserted into the oven at time = 0 seconds.) After an initial delay of only a few minutes, the bulk of the pyrolysis gases are observed. The entire reaction is complete in less than 14 minutes from when the sample was first inserted. It should be noted that absorption features associated with other gases (e.g.,  $\text{NH}_3$ ) were also observed in the FTIR data. Although the instrument was not calibrated for this gas, the amount of  $\text{NH}_3$  that passed through the condenser was roughly estimated to be on the order of 0.25 g for each given run (for a 100 g HFWS sample). Figure 10 displays a photograph of the remaining char (plus ash) after this particular pyrolysis run, along with an untreated HFWS sample. In addition to the nearly 90% weight reduction, a significant reduction in volume, compared to the untreated sample, is evident.

A total of 16 samples were processed with the microwave pyrolysis system, although the first two were split into two separate runs because of the size of the crucible at that time. The other difference between the 50 g and 100 g sample runs was that the length of the secondary cracking zone was increased ~ 37 % for the larger samples. In addition to the sample size, the main pyrolysis process parameters that were varied were the temperature of the secondary pyrolysis zone (650 – 950°C) and the flow rate (1 – 2 LPM) and composition ( $\text{N}_2$ ,  $\text{CO}_2$ , 2%  $\text{H}_2$ , 2%  $\text{H}_2\text{O}$ ) of the carrier gas. In addition, three samples were processed without the secondary pyrolysis zone. Table 1 summarizes the data for all of the HFWS samples that were studied, with the exception of run #3. This was the first pyrolysis run involving a 100 g sample, but it was aborted midway through the run because of a clog in the first stage of the condenser. This event did lead to improvements in the condenser system that ultimately provided better mass balance results for later runs (#4 – #16, typically 93 – 97%). The table provides the key process parameters, the gas, liquid, and solid yields, and the electrical energy usage (for the microwave reactor) for each run. Note that two temperatures are provided in the temperature column. The first temperature is the setpoint temperature of the microwave controller and the second temperature is the average of the actual measured temperature during pyrolysis.

In general, the *total* gas, liquid and solid yields were relatively independent of the secondary pyrolysis zone temperature for all of the 100 g sample runs (#4 – #13), over the range of temperatures that were studied (650 – 950°C). For the liquid yields, run # 6 is a special case, however. It was suspected that the HFWS sample used in this run was contaminated with a significant amount of moisture, possibly several grams, during storage in a laboratory refrigerator. As can be seen in Table 1, the starting mass of this sample was several grams higher than normal, and the accompanying liquid yield after processing was similarly different. While the total gas yield was fairly insensitive to the cracking zone temperature, the gas composition was strongly influenced. In general, higher temperatures result in higher yields of both  $\text{CH}_4$  and  $\text{H}_2$ . Conversely, the maximum levels of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  are observed at an intermediate temperature of 750°C, presumably because these gases are both produced and consumed by cracking reactions. Both  $\text{CO}_2$  and  $\text{CO}$  yields were relatively insensitive to the temperature of the secondary zone.



**Figure 9.** Gas evolution profiles for H<sub>2</sub> (brown), CH<sub>4</sub> (pink), CO (red), C<sub>2</sub>H<sub>4</sub> (blue), CO<sub>2</sub> (green), and C<sub>2</sub>H<sub>2</sub> (gray) for microwave pyrolysis of HFWS where the secondary pyrolysis zone was heated to ~ 950°C.



**Figure 10.** Photograph of a typical HFWS sample before and after microwave pyrolysis.

**Table 1. Summary of product yields for microwave pyrolysis studies of HFWS samples. Experiments listed with yellow shading used a two-stage pyrolysis geometry. For the experiments listed with green shading, the secondary pyrolysis zone was not employed.**

Run #	Sample Mass (g)	Carrier Gas	Carrier Flow (LPM)	Temp. <sup>1,2</sup> (°C)	Gas Yields (g)						Char Yield <sup>3</sup> (g)	Liquid Yield <sup>4</sup> (g)	Carbon Burn-off <sup>5</sup> (g)	Energy Usage (kWh)
					C <sub>2</sub> H <sub>4</sub>	CH <sub>4</sub>	CO	CO <sub>2</sub>	H <sub>2</sub>	C <sub>2</sub> H <sub>2</sub>				
1a	50.42	N <sub>2</sub>	2	950, 952	2.11	3.00	4.63	3.82	0.62	1.00	5.31	8.68	1.58	1.53
1b	45.47	N <sub>2</sub>	2	950, 950	2.55	3.77	3.25	2.65	0.70	1.16	5.19	11.96	2.55	1.47
2a	49.76	N <sub>2</sub>	2	500-950, 927	2.35	2.54	3.65	3.54	0.49	0.90	5.28	17.65	1.55	1.12
2b	47.37	N <sub>2</sub>	2	500-950, 932	3.29	3.61	4.59	3.74	0.69	1.47	5.53	8.04	1.82	1.05
4	96.06	N <sub>2</sub>	2	950, 931	4.78	7.30	9.23	7.28	1.24	2.67	10.31	43.37	3.11	1.56
5	95.68	N <sub>2</sub>	2	850, 851	6.30	6.46	6.61	7.05	0.74	2.23	11.11	43.26	2.38	1.6
6	104.25	N <sub>2</sub>	2	750, 750	6.96	6.39	8.12	8.11	0.57	2.80	11.47	51.31	1.74	1.41
7	96.08	N <sub>2</sub>	2	650, 650	5.95	4.12	6.73	8.02	0.44	2.08	12.71	45.56	0.92	1.41
8	96.53	N <sub>2</sub>	2	750, 750	6.27	5.93	6.29	6.92	0.50	2.40	11.69	48.42	1.75	1.62
9	97.7	N <sub>2</sub>	1	950, 945	3.62	7.47	8.22	7.64	1.51	1.84	10.94	47.05	4.82	1.77
10	98.85	2% H <sub>2</sub>	1	950, 949	3.13	7.56	9.94	8.90	1.73	1.51	11.48	42.21	6.36	1.9
11	97.33	N <sub>2</sub>	1	950, 930	4.29	7.69	9.79	7.84	1.42	2.44	10.36	45.46	4.50	1.77
12	95.69	CO <sub>2</sub>	1	950, 940	4.65	8.43	NA	NA	1.28	2.16	10.10	45.57	5.05	1.54
13	98.15	3% H <sub>2</sub> O	1	950, 930	5.09	7.71	9.27	7.52	1.13	2.42	10.52	49.28	3.24	1.7
14	99.53	N <sub>2</sub>	1	600, 495	3.64	2.72	8.11	9.66	0.50	1.52	11.06	56.44	NA	0.46
15	101.98	N <sub>2</sub>	1	600, 367	NA	1.90	NA	8.66	0.31	1.02	14.83	64.51	NA	0.47
16	94.79	N <sub>2</sub>	1	500, 330	NA	1.87	NA	8.06	0.29	1.06	10.95	59.09	NA	0.36

Notes

1. The temperature for experiments listed with yellow shading is the temperature of the secondary cracking zone. The temperature for the experiments listed with green shading is the temperature of the SiC absorber rod in the center of the sample crucible.
2. The first temperature listed is the setpoint temperature of the controller. The second temperature is the average of the actual temperature measured during pyrolysis.
3. Carbon and ash residue in crucible.
4. Includes water measured in gas phase and liquids and solids captured in the condenser and traps.
5. Measured during regeneration of secondary cracking zone (in air)

These trends can be seen more clearly in Table 2, where the data are shown for runs that were done under the same nominal conditions and the yields for the split run (1a, 1b) are combined. When compared to run #14 with no cracking zone, CO<sub>2</sub> appears to be in decline, while CO is still trendless. Both gases can be produced by gasification reactions and consumed by water-gas shift reactions. However, if the secondary pyrolysis temperature was increased even further beyond 950°C, it would be expected that CO would increase significantly since the effects of chemical equilibrium would begin to dominate the gas composition (also leading to a further increase in H<sub>2</sub>) [33].

For the three runs that were performed without a secondary pyrolysis zone, the individual gas data are a bit sparse because the FTIR gas analyzer was not operating during the final two experiments, thus C<sub>2</sub>H<sub>4</sub> and CO measurements were not available for these two runs. Nevertheless, it can be seen in Table 1 that the other gas species generally show higher yields at the higher primary pyrolysis *sample* temperatures. Based on the complete set of gas data in run #14, it can be seen that the total gas yields, as well as the individual gas yields, without the secondary pyrolysis zone are generally lower than those runs involving this second stage of pyrolysis, except for CO and CO<sub>2</sub>. Conversely, the liquid yields are somewhat higher in the absence of the secondary zone, as would be expected. It should be noted that the current microwave-based reactor system did not allow for completely independent heating of the primary and secondary pyrolysis zones. Otherwise, these trends would likely have been even more pronounced.

The yields of CO<sub>2</sub> are much lower than for processing of the HFWS samples using incineration [10], although the yields of fuel gases (CH<sub>4</sub>, H<sub>2</sub>) are significantly higher. The yields of CO and H<sub>2</sub>O appear to be comparable, under the conditions that have been studied to date.

For most of the sample runs, the carrier gas was nitrogen and no strong effects on the gas yields are seen from changing the carrier gas flow rate. The gas yields also appear to have no strong dependence on the carrier gas composition, particularly in the cases where 2 % hydrogen (#10) and 3% water (#13), both in nitrogen balances, are used. It is notable, however, that the highest yield of CH<sub>4</sub> is observed where the carrier gas is pure CO<sub>2</sub>. In summary, for the experiments that included secondary pyrolysis, relatively high yields (0.5 to 10 wt. %) of individual gas products (CO<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and H<sub>2</sub>) were observed, with the total gas yields ranging from ~30 to 45 wt. %. The largest yield was generally a liquid product (~40 to 50 wt. %) that was assumed to be mainly water (based on condensates produced from similar two-stage pyrolysis experiments [34]), while modest amounts of a char product (~10 to 15 wt. %) were formed.

From the standpoint of electrical energy usage, it can be seen that much less energy is required to pyrolyze the HFWS in the single-stage reactor geometry. However, as stated earlier, for the runs that used the two-stage configuration, the secondary pyrolysis zone was always heated from room temperature up to the desired setpoint before inserting the waste sample into the reactor. This step consumed as much as half the energy used to complete the process. In a more energy-efficient batch design, the secondary zone temperature would be maintained, while processing successive batches, thus minimizing the energy required for ramp-up.

**Table 2. Effect of Temperature of Secondary Cracking Zone on Gas Yields.**

Run #	Sample Mass (g)	Temp (°C)	Gas Yields (g)					
			C <sub>2</sub> H <sub>4</sub>	CH <sub>4</sub>	CO	CO <sub>2</sub>	H <sub>2</sub>	C <sub>2</sub> H <sub>2</sub>
1	95.89	951	4.66	6.77	7.88	6.47	1.32*	2.16
4	96.06	931	4.78	7.30*	9.23*	7.28	1.24	2.67
5	95.68	851	6.30	6.46	6.61	7.05	0.74	2.23
6	104.25	750	6.96*	6.39	8.12	8.11	0.57	2.80*
8	96.53	750	6.27	5.93	6.29	6.92	0.50	2.40
7	96.08	650	5.95	4.12	6.73	8.02	0.44	2.08
14	99.53	----	3.64	2.72	8.11	9.66*	0.50	1.52

Notes: a – combination of two runs, 1a and 1b

\* – maximum yield

#### IV. Summary and Conclusions

In general, the *total* gas, liquid and solid yields were relatively independent of the secondary pyrolysis zone temperature for all of the 100 g sample runs, over the range of temperatures that were studied (650 – 950°C). However, the gas composition was strongly influenced by the secondary zone temperature. Higher temperatures result in higher yields of both CH<sub>4</sub> and H<sub>2</sub>. The results of this study confirmed that two-stage pyrolysis is a viable way to produce significant amounts of CH<sub>4</sub> and H<sub>2</sub> from mixed solid waste samples. Carbon monoxide also was

expected to appear in higher levels at the higher secondary pyrolysis zone temperatures, but no strong trend was observed for CO (or CO<sub>2</sub>). Conversely, higher levels of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> are observed at intermediate temperatures, both showing maximum levels around 750°C.

For the three runs that were performed without a secondary pyrolysis zone, it was found that the gas species generally show higher yields at the higher primary pyrolysis *sample* temperatures. It can also be seen that the total and individual gas yields without the secondary pyrolysis zone are generally lower than those runs involving this second stage of pyrolysis. Conversely, the liquid yields are generally higher in the absence of the secondary zone, as would be expected. For most of the sample runs, the carrier gas was nitrogen and no strong effects on the gas yields are seen from changing the carrier gas flow rate or composition. Pyrolysis processing of the HFWS produces much smaller yields of CO<sub>2</sub> when compared to incineration, although yields of fuel gases (CH<sub>4</sub>, H<sub>2</sub>) are significantly higher.

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