Pyrolysis Yields from Microwave-Assisted Heating of Solid Wastes

Michael A. Serio[1], Joseph E. Cosgrove[2], and Marek A. Wójtowicz[3]
Advanced Fuel Research, Inc., 87 Church Street, East Hartford, CT 06108-3728 USA

Kanapathipillai Wignarajah[4] and John Fisher[5]
NASA Ames Research Center, Moffett Field, CA 94035-1000 USA

This paper continues previous work on pyrolysis processing of solid wastes for spacecraft and planetary surface applications. A domestic microwave oven was modified for use in this work for scoping studies in which the effects of sample composition, use of central microwave absorbers, and secondary pyrolysis of liquids were studied. Experiments were done with wheat straw and various formulations of a feces simulant. The microwave absorbers examined included activated carbon and char produced from previous experiments. The addition of a separate microwave-heated secondary pyrolysis zone was also examined as a means of reducing the liquid product yields. In general, the feces simulants had similar pyrolysis yields when compared to wheat straw for the char and total gas yields, but individual gas yields were different. For example, the feces simulants produced significantly more ethylene, larger amounts of methane, and smaller amounts of carbon oxides ($CO + CO_2$). This can be largely explained by the differences in elemental compositions. A comparison was also made of the microwave-assisted pyrolysis of feces simulants of variable moisture contents (0-60 wt. %). The higher moisture contents (40-60 wt. %) result in a delay for the onset of pyrolysis and a higher energy demand per gram of sample, as might be expected. However, at lower moisture contents, such as the 20 wt. % water for the baseline sample, it was found that the overall energy demand appeared to be lower than for the dried sample, perhaps due to the more efficient absorption of microwave energy.

Nomenclature

CELSS = Controlled Ecological Life Support System (CELSS)
DAF = Dry, Ash-Free
ESM = Equivalent System Mass
FC = Fixed Carbon
FTIR = Fourier Transform Infrared
HHV = Higher Heating Value
ISRU = In-Situ Resource Utilization
MAP = Microwave-Assisted Pyrolysis (MAP)
MFM = Mass Flow Meter
VM = Volatile Matter

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[1] President, Advanced Fuel Research, Inc. (AFR), 87 Church Street, East Hartford, CT 06108.
[2] Laboratory Manager, AFR, 87 Church Street, East Hartford, CT 06108.
[3] Vice President, Clean Energy & Carbon Materials, AFR, 87 Church Street, East Hartford, CT 06108.
[4] Senior Scientist, SCB Branch, MS 239-8, NASA-Ames Research Center, Moffett Field, CA 94035.
[5] Lead Engineer, Exploration Life Support, NASA-Ames Research Center, Moffett Field, CA 94035.

I. Introduction

Pyrolysis is a commonly utilized method for destruction of waste products [1-3]. It is often considered as an alternative to incineration, wet oxidation and other treatment processes. The products of pyrolysis are typically gases, liquids and a solid char, although the process can be designed to avoid the formation of hydrocarbon liquids by having a secondary pyrolysis (cracking) stage. From the perspective of management of waste streams in a space environment, pyrolysis offers certain advantages as a means of solid waste disposal [4]. One significant advantage is the partial decoupling of issues of CO_2 management from the waste stream disposal problem, since some of the carbon will end up in the char residue and some will end up as CH_4 and other hydrocarbons (as well as CO and CO_2). Besides reducing the O_2 demand for complete combustion, there are clear incentives for tying up carbon in its elemental form in the char residue. One is the compactness of storage, another is that it may be combusted on demand to provide CO_2 for plant growth (or it may be gasified with H_2 to provide methane). A third option would be to activate the char residue and use it for purification of gas or liquid streams. Solid waste pyrolysis also functions as a method for biological stabilization and sterilization of waste.

The initial pyrolysis products are primarily hydrocarbon liquids, but these liquids can be cracked to gases (and small amounts of carbon) as the temperature is raised from 600-1000 °C. The major gas products are H_2, CO, H_2O, CO_2, and CH_4. Other gas products, present in much smaller amounts, will include NH_3 and H_2S, if nitrogen and sulfur compounds are present in the solid waste stream. The liquids initially include a large yield of a complex mixture of chemicals. This characteristic of the pyrolysis of waste streams allows for the possibility of staging the pyrolysis process. The initial step converts the solids to liquids and reduces the volume of the waste. In the second step, the liquids are cracked almost completely to gases, which can occur simultaneously with the first step by using a two-stage pyrolysis reactor, where the second stage includes a cracking zone [5-10]. In an optional third step, the char residue can be subsequently converted into activated carbon. The char residue is typically less than 25-30% of the initial mass of the solid waste, unless there is a high inorganic content of one of the waste components, in which case it could be as high as 35-55%.

One of the features of the pyrolysis of solid waste materials that contain large amounts of oxygen (along with some hydrogen), such as plant biomass or paper, is the production of water as a product. Consequently, pyrolysis processing not only leads to recovery of the moisture in the solid waste, it also generates additional amounts of water for life support. If the hydrogen and hydrocarbon gas products from pyrolysis are subsequently oxidized, then even more water will be produced. A significant advantage of the pyrolysis processing scheme is that the individual stages of the process can be separated in time by minutes, days, or weeks, depending on the demand for the products that are being recovered from the waste. For example, adjusting the pyrolysis conditions to primarily produce liquids will reduce the waste storage volume without increasing the volume of gases that must be used, stored, or discarded.

In general, pyrolysis processing could be useful to NASA in at least eight respects: 1) volume reduction; 2) as a pretreatment for a combustion process; 3) a more efficient means of utilizing oxygen and recycling carbon and nitrogen; 4) to supply fuel gases to fuel cells for power generation; 5) production of chemicals and materials (such as activated carbon) in space; 6) recovery of moisture and generation of additional amounts of water from solid waste; and 7) rendering the solid waste biologically stable and/or sterile; 8) the hydrocarbon products (e.g. H_2, CH_4) can be used as reducing agents for metal oxides in lunar or Martian soil for ISRU. 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 CO concentrations. The latter issue can be addressed by utilization of a water gas shift reactor, or by introducing the product gases into an oxidizer or a high-temperature fuel cell.

Advanced Fuel Research, Inc. (AFR) previously developed a two-stage solid waste pyrolyzer prototype under a NASA-funded project [5,6]. That work was extended to add an optional oxidation stage in a subsequent project [10-12]. The overall objective of the current study was to demonstrate the feasibility of using Microwave-Assisted Pyrolysis (MAP) as the basis for development of a more compact and efficient pyrolyzer, i.e., lower Equivalent System Mass (ESM), for mixed solid waste streams in space applications [13]. A previous paper presented the initial results of pyrolysis experiments done in a modified domestic microwave oven using wheat straw samples blended either with activated carbon or pyrolysis char as the microwave absorber [14]. The addition of a separate microwave-heated secondary pyrolysis zone was also examined as a way of reducing the liquid product yields. A comparison was made of the energy consumed (per gram) for microwave heating with a previous experiment using conventional heating. A related objective was to demonstrate that a MAP approach can meet the short term, intermediate term, and long term objectives of NASA for closed-loop life support. This thesis is summarized in Figure 1, which indicates how MAP can perform the near term objectives of volume reduction, stabilization, and water recovery, the intermediate term objectives of recovering additional amounts of water and oxygen from waste

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materials, and the long term objective of a Controlled Ecological Life Support System (CELSS) and In-Situ Resource Utilization (ISRU).

A follow-up paper presented additional data in which the effects of sample size, sample rotation, and the use of distributed versus central microwave absorbers were studied. The central microwave absorbers included a ferrite rod, a quartz tube filled with activated carbon, and silicon carbide [15]. In addition, a further examination was made of the energy demands of microwave versus conventional heating.

This paper continues the previous work on microwave-assisted pyrolysis processing of solid wastes from spacecraft and planetary surface applications, with a greater focus on various formulations of a feces simulant, in addition to wheat straw. The effect of moisture content was also examined in more detail.
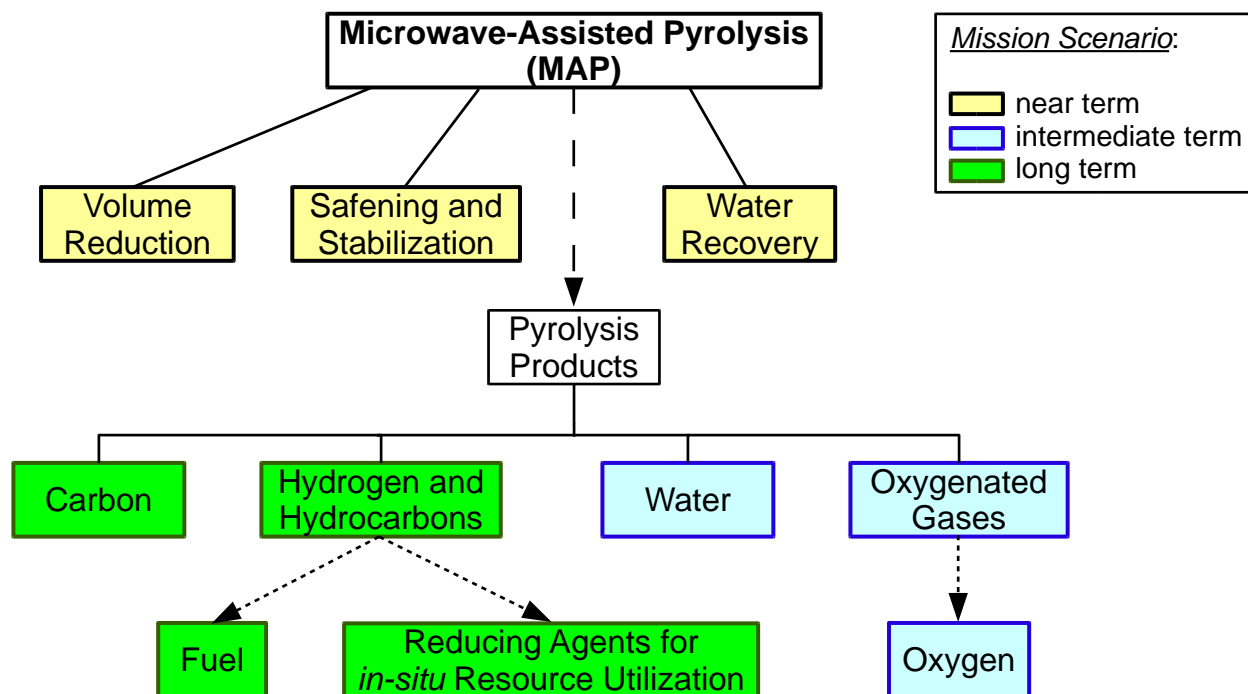

Figure 1. Schematic indicating how a Microwave-Assisted Pyrolysis (MAP) process would impact near term, intermediate term and long term mission scenarios.

II. Experimental

A. Background

Microwave pyrolysis can offer several advantages including lower capital cost, lower power consumption, faster heat-up times, greater control over the heating process, higher gas yields, lower oil yields, lower production of aromatic hydrocarbons, and higher char porosity [16,17]. However, since the raw solid waste feedstocks are not always good absorbers of microwave energy, blending with microwave absorbers, such as the pyrolysis char residue, will sometimes be required [16,17]. In this regard, the addition of activated carbon particles was also explored for simultaneous microwave absorption and tar cracking. The use of microwave energy has been previously employed with good success in drying and stabilization of solid waste in NASA funded R&D [4] and also in pyrolysis of methane for hydrogen recovery [18].

B. Experimental Apparatus

As discussed above, the experimental apparatus was based on microwave heating of the waste samples. A Fourier transform infrared (FTIR) gas analyzer was used for quantifying the major gaseous species evolved during pyrolysis and/or oxidation. A schematic of the laboratory reactor system is shown in Figure 2. The system incorporated a domestic microwave oven (Panasonic model # NN-T664SF) as the microwave source for the proof-of-concept-testing. Using inverter technology, it provides ten different power levels, and all but the two lowest levels are supplied at a continuous intensity. The oven was modified to include an open access port or "choke

tunnel" that enables a 25 mm o.d. closed-end quartz tube reaction vessel to be inserted into the oven cavity without excessive leakage of microwave radiation during operation of the oven. A cold trap (-30 °C) and condenser (5 °C) were employed for collecting condensable products (water, tar) and a dry glass wool filter was used to prevent residual tar from contaminating the sampling cell of the FTIR instrument. Visually, some tar was always observed at the inlet of the glass wool filter for each run, but this amount was not quantified. Additional details of the various traps are provided below. The FTIR gas analyzer has a frequency range of $800 – 6500$ cm^{-1} with a resolution of 0.5 cm^{-1}. The instrument was calibrated for CO_2, CO, CH_4, C_2H_4 and H_2O (which is not completely condensed). The heated (125 °C) gas sampling cell (~ 50 cc volume) has an exchange rate of 4-5 seconds and is ideal for observing transients in the various gas evolutions during the pyrolysis experiments. For all experiments performed in this study, the FTIR data were continuously collected at 10 second intervals.

Gas flows were controlled and measured using precision rotameters and mass flow meters. Nitrogen carrier gas (~0.5 ℓ/min.), controlled by a precision rotameter, is introduced at the bottom of the quartz tube reaction vessel (i.d. = 22 mm) during each run. The sample was purged with nitrogen for ~1 hour prior to each run to ensure that no oxygen was present. An electronic mass flow meter (MFM) measures the total gas volume entering the FTIR analyzer including ~1.5 ℓ/min. nitrogen dilution gas, as shown in Figure 2. The volumetric flow is recorded continuously throughout the experiment, along with the FTIR measurements. Since the MFM is calibrated for nitrogen, we apply a correction factor (conversion factor) to the data based on the volume fraction of the measured gases, the manufacturer supplied conversion factors for the pure gases and the total flow of nitrogen, which is held constant during each experiment. Note that additional nitrogen is introduced into the sample plus carrier gas stream prior (using a mass flow controller) to the MFM so that the gas monitored is predominantly nitrogen. This minimizes errors in calculating the MFM conversion factor for the mixed gas stream. The flow rates for each gas are calculated based on the corrected total flow measured at the MFM and the gas concentration measured by the FTIR. The flow rate of hydrogen plus any other gases not currently measured by the FTIR is then determined by the difference of the corrected total gas flow and the nitrogen and FTIR-measured gases.
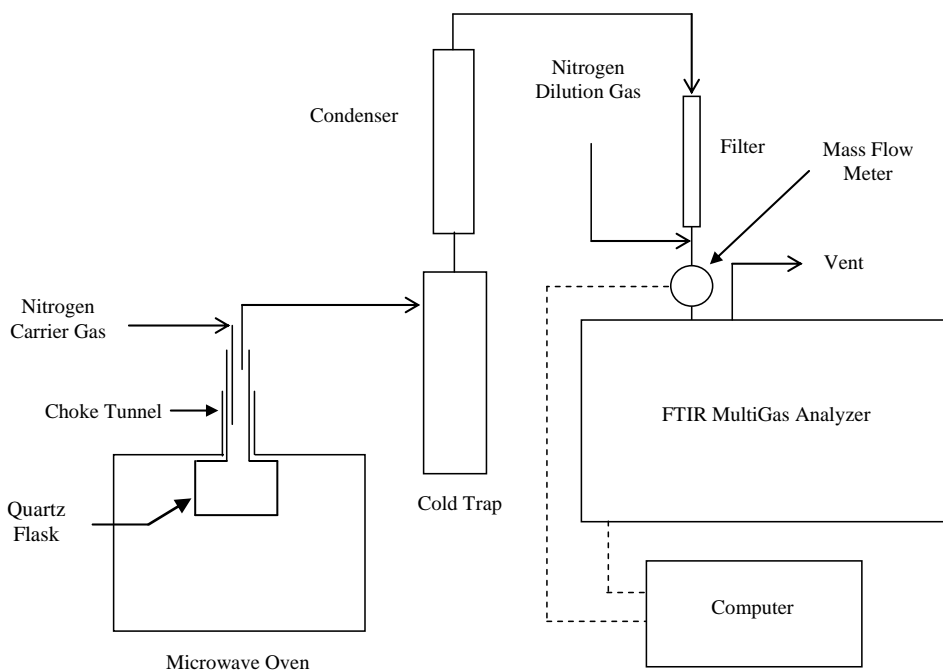

Figure 2. Schematic of current laboratory apparatus for microwave-assisted pyrolysis experiments.

Tar removal and collection from the evolved product stream is provided in three stages. The first stage is a modified version of the previous apparatus [13,15] and consists of a pair of two-piece traps: a room temperature (RT) trap (submerged in a room temperature water bath) followed by a cold trap (submerged in a 50/50 mixture of water/ethylene glycol at -30°C). The room temperature trap was added to prevent ice plugging that was occurring in the cold trap because of the high water content in the synthetic feces samples. The second stage is a coiled condenser tube connected to a water chiller (5°C). The final stage is a ceramic wool filter. The room and cold traps are the

primary vessel for oil and tar collection. The condenser and wool filter ensure that no tar or oil reaches the FTIR gas cell.

The initial feasibility study was performed on small quantity (1.5 g) wheat straw samples that were pyrolyzed in a modified domestic microwave oven operating at 2.45 GHz [13]. By itself, the wheat straw was determined to be a poor absorber of microwave energy and thus could not be efficiently pyrolyzed in the oven. The situation was dramatically improved by mixing in good microwave absorber materials such as activated carbon and wheat straw char. Here, the activated carbon or char quickly heats up and pyrolyzes the wheat straw in close proximity. A potential problem with this approach, however, is that shielding by char formed at the outside edges of the reaction vessel could slow down the heating of sample in the center of the reaction vessel. This could be particularly problematic for larger samples to the extent that the sample heating rate becomes conduction-limited, similar to electric heating. In recent work [15], an alternative approach was explored whereby a rod of an efficient absorber material is inserted into the sample at the center of the reaction vessel. Upon exposure to the microwave energy, the absorber rod will quickly heat up and begin 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 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. In addition, the outer raw biomass acts as an insulation layer, thereby reducing convective losses. Another potential advantage is that the pyrolysis reaction zone is always exposed to the microwave radiation and may benefit from "non-thermal" microwave effects, leading to less tar formation, for example. Finally, any restrictions on the diameter or width of the reaction vessel are relaxed, provided the raw biomass has sufficient penetration depth and that uniform microwave irradiation is maintained throughout the process. The use of a central microwave absorber has been continued in the current study.

C. Materials

Selected samples of feces simulant and wheat straw samples were sent out for proximate, ultimate, and heating-value analyses to Huffman Laboratories of Golden, Colorado. The description of these samples is given in Table 1, below. The results of the analyses are given in Tables 2. For all samples, the ash content was determined at 750 °C in air, and VM, FC, HHV and daf stand for volatile matter (VM), fixed carbon (FC), higher heating value (HHV) and dry, ash-free basis (DAF), respectively. Hydrogen and oxygen contents reported on an as-received sample basis include contributions from contained moisture.

The feces simulant sample used for most of the microwave pyrolysis experiments is the one identified as Simulant #3 in Part III of this paper. The component composition consists of cellulose, polyethylene glycol, peanut oil, miso, potassium chloride, and calcium chloride in the amounts indicated in Table 1. The miso is also associated with water content which amounts to about 20 wt. % upon drying. The Simulant #3 sample was similar to that described by Wignarajah et al. [19] in a recent paper and is also close to our Simulant #2, except for the source of miso. We were able to confirm that the moisture content of our Feces Simulant #3 sample was about 20 weight percent (as-received basis), as indicated in Table 2.

Table 3 shows results on a daf basis for elemental composition for historical wheat straw samples used by AFR [20], a human feces sample used by NASA [21], and a poultry litter sample used by AFR [20]. When compared to the dried feces simulant data shown in Table 2, the actual human feces sample has less carbon and less hydrogen and presumably more oxygen. The elemental composition has a large effect on the pyrolysis gas composition; especially under more severe conditions where equilibrium is approached [22]. In many respects, the wheat straw samples are probably closer to human feces with regard to pyrolysis behavior, as indicated by the similar elemental compositions in Table 3. The wheat straw samples typically produce far less ethylene (~1% by volume) when compared to the feces simulant samples and larger amount of CO and CO_2. The latter result is likely due to the higher oxygen content and lower hydrogen content of the wheat straw when compared to the feces simulants.

The char yields of the Simulant #3 samples (see Part III, below) are in the range of 20-25 wt% on a dry basis which compare well to those obtained for wheat straw [15] under similar microwave pyrolysis conditions. With a few exceptions, the total volume of pyrolysis gas produced (per gram of dry starting material) also appears to be comparable for Simulant #3 and wheat straw (see Part III, below). Consequently, it appears that Simulant #3 may be a good analog for human feces in pyrolysis experiments in terms of the char and total gas yields, but not in the individual gas yields.

Table 1. Samples used in this project that have been characterized by Huffman Laboratories.

Sample Designation	Description
Feces Simulant[a]	14.3 wt% cellulose, 7.1 wt% polyethylene glycol, 28.6 wt% peanut oil, 42.9 wt% miso, 5.7 wt% KCl, 1.4 wt% CaCl$_2$
Miso[b]	Hikari miso, Kodawattemasu Kome-Koshi type
Peanut Oil[c]	LORIVA roasted peanut expeller pressed oil
Wheat Straw[d]	obtained on March 7, 2008 from Mark Prater, 1878 Francis Ferry Rd., McMinnville, TN 37110, tel. 931-808-8095

Table 2. Proximate and ultimate analyses of samples used in this study.

Sample	Basis	Moisture (wt%)	Ash (wt%)	VM (wt%)	FC (wt%)	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O (wt%)	HHV (BTU/lb)
Feces Simulant (Undried)	as received	NR	10.50	61.81	8.26	41.45	8.17	0.65	0.04	39.19	8,097
Feces Simulant (Dried)	as received	19.43	10.76	60.91	8.90	40.04	8.43	0.78	0.05	39.94	NR
	dry		13.35	75.60	11.05	49.70	7.77	0.97	0.06	28.15	NR
	daf					57.36	8.97	1.12	0.07	32.49	NR
Miso (Undried)	as received	NR	11.63	55.46	9.27	22.09	7.91	1.79	0.12	56.46	NR
Miso (Dried)	as received	23.64	11.81	55.44	9.11	22.57	7.91	1.79	0.09	55.82	NR
	dry		15.46	72.61	11.93	29.56	6.90	2.35	0.12	45.61	NR
	daf					34.97	8.16	2.78	0.14	53.95	NR
Peanut Oil	as received	NR	< 0.01	NR	NR	77.37	12.06	0.02	< 0.01	10.55	NR
Wheat Straw	as received	4.64	4.42	72.09	18.84	43.71	6.32	1.31	0.11	44.12	7,477
	dry		4.64	75.60	19.76	45.84	6.08	1.37	0.12	41.95	7,841
	daf					48.07	6.38	1.44	0.13	43.99	8,223

Table 3. Comparison of elemental compositions of previous waste samples studied at AFR [20] and NASA Ames [21].

Sample	Basis	Moisture wt%	Ash wt%*	VM wt%	FC wt%	C wt%	H wt%	N wt%	S wt%	O wt%	HHV BTU/lb
NIST Wheat Straw	daf	NR	9.9	NR	NR	48.0	6.2	0.7	0.2	44.9	NR
Danish Wheat Straw	daf	NR	7.9	NR	NR	50.4	6.0	0.9	0.2	42.5	NR
Local Wheat Straw	daf	NR	6.0	NR	NR	49.0	6.1	1.8	0.2	42.9	NR
Human Feces	daf	NR	12.5	NR	NR	49.1	7.2	2.7	NR	NR	NR
Poultry Litter	daf	NR	22.5	NR	NR	47.4	6.5	5.6	1.0	1.0	NR

Notes: NR = not reported

* = dry basis

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A wheat straw was used also as a representative type of solid waste in the current project. The sample was originally obtained for a different project from Mark Prater, 1878 Francis Ferry Rd., McMinnville, TN 37110 (tel. 931-808-8095), and the elemental analysis and the heating value of this material are presented in Table 2.

The activated carbon used in this study was Filtrasorb 400 (F-400), CAS #: 7440-44-0, obtained from Calgon Carbon Corporation, Pittsburgh, Pennsylvania. The physical properties of F-400, determined by nitrogen gas adsorption at 77 K using an automatic adsorption instrument ASAP 2000, are as follows: BET surface area of 1026 m^2/g, total pore volume of 0.61 cm^3/g, and average pore diameter of 17.65 Å [23]. The average true density, analyzed by AccuPyc 1330VI.01, was found to be 2.18 g/cm^3 [23].

III. Results and Discussion

A. Secondary Pyrolysis Experiments

The addition of a secondary pyrolysis zone in our microwave system, in order to reduce the oil and tar yields, was investigated. Our initial series of experiments involved the simplest approach, where a bed of activated carbon was located immediately downstream of the primary pyrolysis zone, in the same oven cavity, and heated simultaneously with the wheat straw sample. By varying the carbon bed size, and to some degree the bed temperature, we are able to observe significant changes in the tar and oil yields.

A total of four experimental configurations, illustrated in Figure 3, have been studied thus far. Case 1 (Figure 3a) is a control experiment, employing no tar-cracking layer, similar to the majority of experiments that have been performed to date. In Case 2 (Figure 3b), 5.67g of activated carbon is loaded immediately above (downstream) the wheat straw sample. In Case 3 (Figure 3c), a larger carbon bed is used (11.08 g) and in Case 4 (Figure 3d), the larger carbon bed is insulated with ceramic wool in an attempt to increase the carbon bed temperature without changing the incident microwave power on the wheat straw sample. Note that the microwave irradiation of the wheat straw in each case was similar (~ 300 W) but not exactly the same, due to the slight differences in the sample position in the oven as well as the size of the carbon bed. For all cases, the central (core) absorber material is a quartz tube filled with activated carbon.

Figure 4 compares the gas evolution profiles for CO, CO_2, CH_4 and C_2H_4 measured for Case 1 (Figure 4a) and Case 4 (Figure 4b). Overall, the data are not significantly dissimilar. The onset of pyrolysis, as indicated by the point where gases are first observed, occurs 40-50 seconds into the run in each case. The shapes of the gas profiles are clearly different, but this is typical of what has been observed in previous experiments. Table 4 summarizes the gas and char yields for all four cases. As expected, it appears that more gas is produced as the size of the secondary pyrolysis zone is increased. It should be noted that he normal range of variation of individual gas, total gas, and char yields for experiments with the same samples done under the same nominal conditions is about 10 %.

The gas analyses for the tar-cracking case study do not provide much insight regarding the effectiveness of the activated carbon layer. On the other hand, visual examination of the cold trap after each experiment, along with subsequent analyses of their tar extracts shows much more dramatic results [13]. As the activated carbon cracking layer is increased from 0 g to 5.67 g to 11.08 g, there is a clear reduction in the tar collected on the trap walls and in the glass bead layer. For Case 4, where the activated carbon layer region of the quartz flask reactor was wrapped in ceramic insulation, there is a further decrease in the tar and oil deposits.

Table 4. Comparison of gas and char yields for microwave pyrolysis of wheat straw, with and without an activated carbon secondary pyrolysis zone.

Case	Mass of Act. C Cracking Layer (g)	Incident Mic. Power (W)	Total Gas Volume (dry) (cc)	Char Recovered[1] (%)
1	0	285	5897	24
2	5.67	285	6595	27
3	11.08	300	7996	27
4	11.08	300	8205	27

1. *Calculated as 100 x (mass of char/mass of initial sample).*
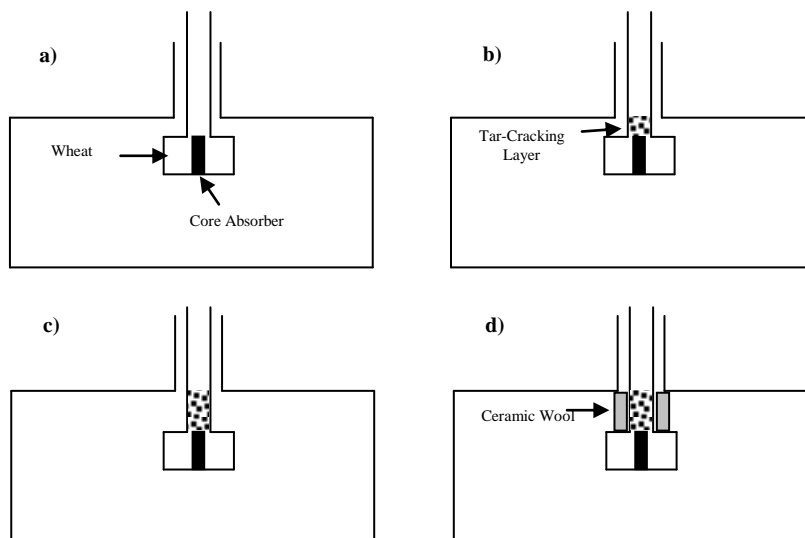
Figure 3. Experimental configurations employed for tar-cracking study with a central core absorber: a) no tar-cracking layer (Case 1), b) 5.67 g activated carbon tar-cracking layer (Case 2), c) 11.08 g activated carbon tar-cracking layer (Case 3) and d) 11.08 g activated carbon tar-cracking layer with ceramic wool insulation (Case 4).
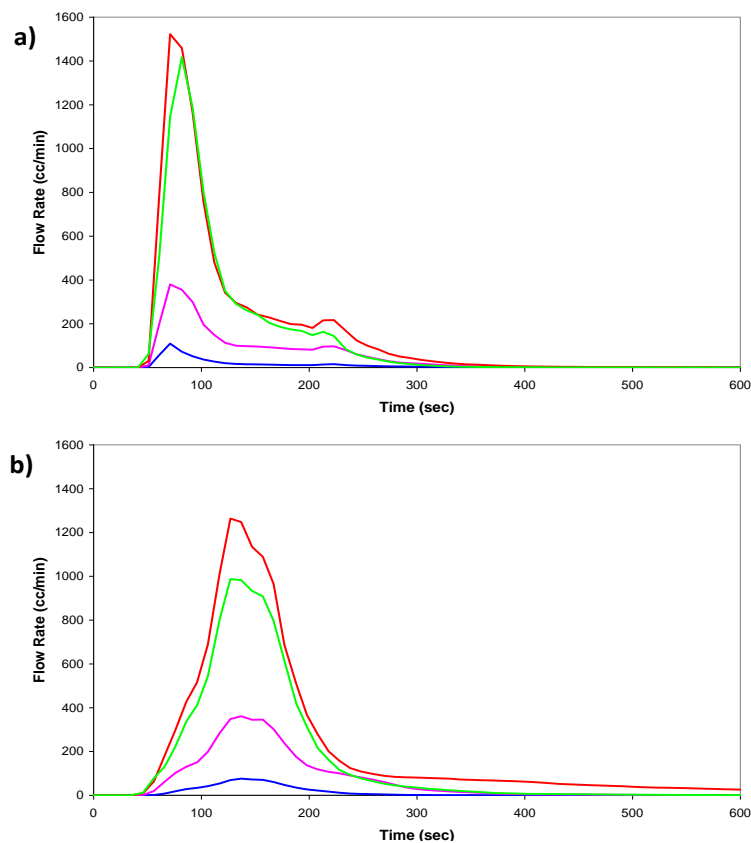

Figure 4. Comparison of gas evolution rates during microwave-assisted pyrolysis of 20 grams of wheat straw for two cases: a) pyrolysis with no tar-cracking bed (Case 1) and b) pyrolysis with an insulated tar-cracking layer consisting of 11.08 g of activated carbon (Case 4). Both cases used activated carbon as the central core absorber. The evolution rates for CO, CO_2, CH_4 and C_2H_4, determined by FTIR, are shown in red, green, pink and blue, respectively. The estimated incident microwave power was ~300 W for each case.

For each experiment performed in the tar-cracking case study, the tar (and other liquids) were recovered from the cold trap by washing with 25 ml of acetone, and then stored in polypropylene containers. The extracts were then analyzed by visual comparison and infrared spectroscopy. For visual comparison, one drop of extract was applied to a glass microscope slide, which was pre-heated to 100°C on a temperature-controlled hotplate. After a period of about 5-10 seconds, where the acetone and water (and other low boiling point liquids) were evaporated, a tar residue stain of about 1 cm in diameter was formed on the slide. We found that this technique resulted in a stain of consistent size, with careful control of the slide temperature and the evaporation period. Figure 5 compares the microscope slide tar samples that were prepared for each experiment in the tar-cracking study. Similar to the cold trap images discussed above (not shown), a steady decrease in the tar residue for each successive experimental case in the study is clearly observed and there is a corresponding change in the functional group compositions, as measured by FT-IR spectroscopy [13].
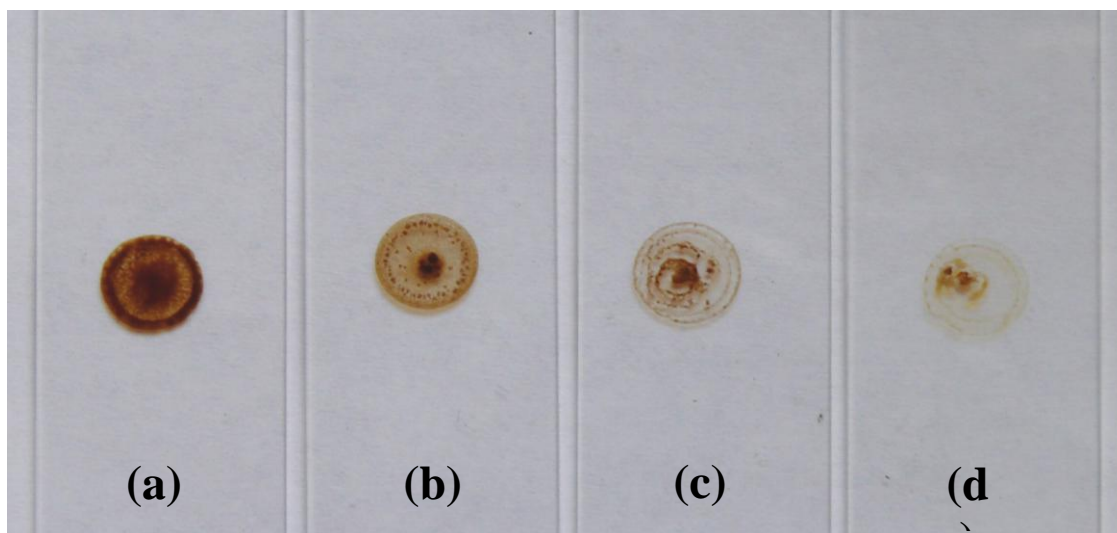

Figure 5. Digital images of tar stains prepared on glass slides after microwave-assisted pyrolysis of wheat straw: a) no activated carbon cracking layer (Case 1), b) 5.67 g activated carbon cracking layer (Case 2), c) 11.08 g activated carbon cracking layer (Case 3) and d) 11.08 g activated carbon cracking layer with insulation (Case 4).

B. Experiments with Feces Simulant Samples

The synthetic feces samples, which represent human feces, provide us with much higher density biomass materials than the wheat straw samples we have studied thus far. Pyrolysis experiments were initially performed on two different compositions of simulated feces, shown in Table 5. The first simulant studied (Simulant # 1) was prepared using components readily available from local grocery/pharmacy stores. It is similar to the Combination 1 synthetic feces described in Ref. 24, except it lacks the addition of E. coli (for safety reasons), inorganics and a minor amount of dried vegetable matter. The miso that was used is a regional brand (South River), with listed ingredients of water, brown rice, soybeans, sea salt, sea vegetables and koji culture. The second simulant is nearly identical to the composition described in Ref. 25. The table also displays the water content for each simulant. These values were determined by oven drying samples of each composition at 80°C for a period of 24 hours. The value of 22.2% is in reasonable agreement with the inherent water content measured for the synthetic feces prepared in Ref. 25 (18.75%) and results that were determined by an independent test laboratory for a slightly different formulation, Simulant #3 (see Tables 1 and 2), discussed above.

The pyrolysis experiments with the synthetic feces samples involved sample sizes of 20 g, similar to the wheat straw experiments. However, as discussed above, these materials are much denser than the wheat straw and thus occupy a much smaller volume (~ 20 cc lightly packed). For this reason, the samples are pyrolyzed in a 22 mm i.d. closed end quartz tube, rather than the 180 cc quartz flask used for wheat straw samples of the same mass. Because the fill factor of the synthetic feces sample relative to the microwave oven cavity is so small, we also employed a 900 cc water dummy load to minimize the risk of damage to the oven magnetron source. This water dummy load is in a separate flask from the sealed and nitrogen-purged sample flask, no there is no possibility of the sample

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contracting water or steam. The downside of this geometry is that sample heating uniformity is degraded, presumably due to poorer field uniformity in the oven cavity.

Table 5.   Chemical composition of two synthetic feces samples.

Component	Weight Percent Simulant # 1	Weight Percent Simulant # 2
Cellulose	-	14.3
Polyethylene Glycol	31	7.1
Psyllium	31	-
Peanut Oil	31	28.6
Miso	7	42.9
KCl	-	5.7
CaCl$_2$	-	1.4
Water Content	5.1	22.2

A single attempt was made to pyrolyze a sample of undried synthetic feces (Simulant #1) without the addition of an absorber material, such as activated carbon or silicon carbide, but was not successful. As a result, all experiments described below used a central core absorber rod of packed activated carbon, unless otherwise noted. Note also that most of the pyrolysis experiments performed on simulated feces samples for this paper were on samples that had not been dried.

Figure 6 depicts digital images of Simulant # 1 untreated (Figure 6a) and after microwave heating at an incident power level of ~ 75 W for ~ 35 minutes (Figure 6b). The untreated sample has the consistency of moist sand. After heating, the simulant is fully charred and reduced to a mass of ~ 2 g or about 10 wt.% on an as-received basis. Figure 7 compares the gas evolution profiles for CO, CO$_2$, CH$_4$ and C$_2$H$_4$ measured for Simulant # 1 at incident power levels of 75 W and 115 W. Not surprisingly, pyrolysis occurs much faster in the higher power level case and higher gas flow rates are observed.

A summary of the pyrolysis gas yields for the two different feces simulants is provided in Table 6 for individual experiments. As discussed above, there is generally about a 10% variation in gas and char yields for experiments done under the same nominal conditions with the same sample (see Table 8, below). For comparison, the gas yields for pyrolysis of wheat straw at a similar power level are also included. In this limited study, we do not observe a strong dependence on the gas yield or composition as a function of microwave power for simulant # 1. As indicated in Table 6, we do observe a much higher concentration of ethylene for the feces simulants compared to the wheat straw, along with much lower concentrations of CO$_2$ and, to some degree, CO.

Table 6.   Summary of microwave pyrolysis gas yields from simulated feces and wheat straw samples (dry basis).

Sample	Incident Microwave Power (W)	Total Volume (cc)	CO Vol. %	CO$_2$ Vol. %	CH$_4$ Vol. %	C$_2$H$_4$ Vol. %	H$_2$[1] Vol. %
Simulant # 1	75	7248	16.1	8.2	10.7	11.8	53.3
Simulant # 1	115	6984	18.2	8.7	12.6	9.6	50.9
Simulant # 2	115	3373	12.5	14.2	11.2	5.0	57.1
Wheat Straw	132	4367	22.1	29.2	8.7	0.7	39.3

1. *H$_2$ plus other gases, determined by difference*
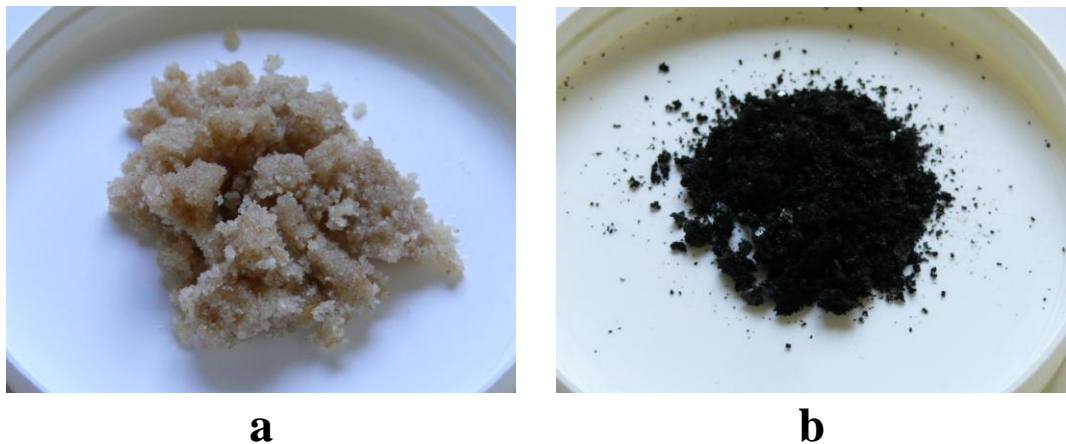
a **b**

Figure 6. (a) Digital image of 20 g of feces simulant # 1 (undried). (b) Digital image of 20 g of feces simulant # 1 after microwave pyrolysis at an incident power level of 75 W.
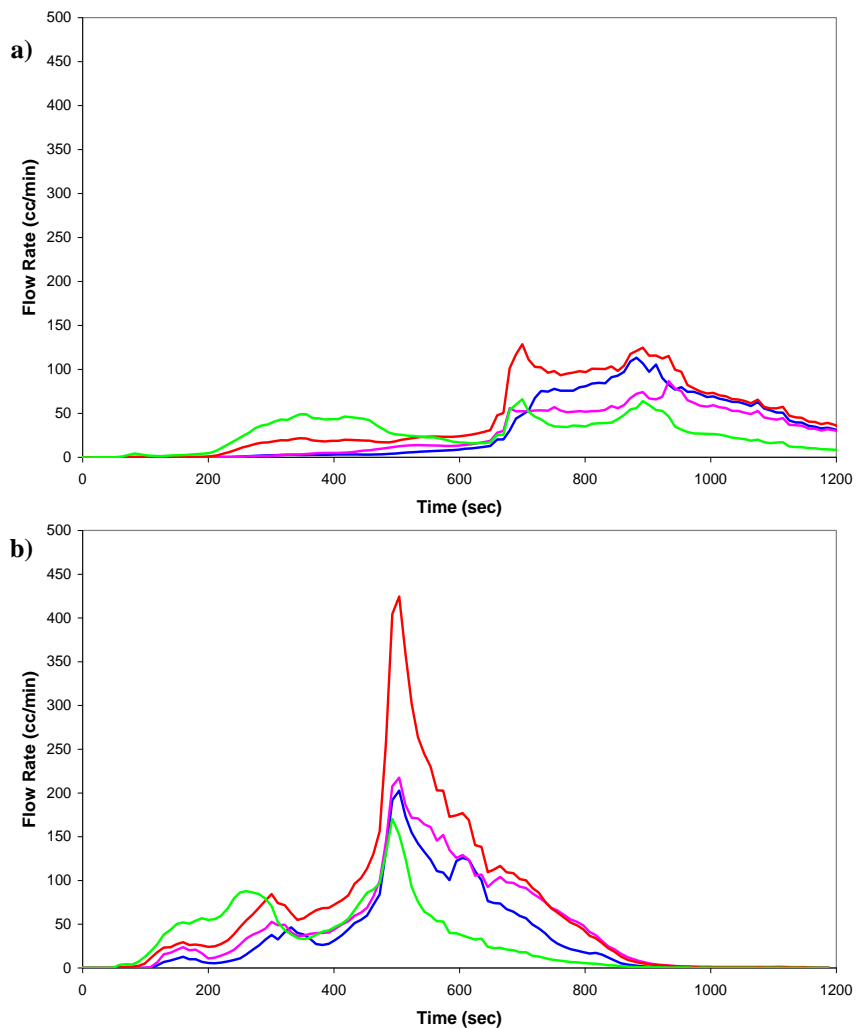

Figure 7. Gas evolution rates measured during microwave-assisted pyrolysis of feces simulant #1 at two incident microwave power levels: a) 75 W and b) 115 W. The evolution rates for CO, CO_2, CH_4 and C_2H_4, determined by FTIR, are shown in red, green, pink and blue, respectively.

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Additional pyrolysis experiments were done on synthetic feces prepared with the composition shown in Table 1 (Simulant #3). This was also the formulation that was subjected to detailed characterization, discussed above (see Table 2). This preparation is identical to one of the simulants studied previously (Simulant #2 in Table 5) except that we are using a different miso source (Hikari Miso Co.). The newer miso has a more consistent texture and thus allows for more even mixing with the other components.

Pyrolysis experiments were conducted on synthetic feces samples with four different water concentrations: 0% (dry), 20% (as received), 40% and 60%. For all samples, the volume in the quartz reactor was ~ 23 cc and the incident microwave power was estimated to be ~ 200 W. For the samples with water content ranging from 0-40%, the sample mass on a dry basis was ~ 16 g. For the 60% moisture samples, the dry sample mass was reduced to ~ 10g to maintain the 23 cc sample volume in the reactor. Two absorber configurations were also compared: use of a core absorber (activated carbon packaged in a thin-wall quartz tube) versus the use of either activated carbon or char (from previous pyrolyzed simulant) directly mixed with the sample. In both configurations, the mass of the absorber was 1.5 g.

Figure 8 compares the CO evolution profiles measured for the four different water concentration samples, using the core absorber configuration. Not surprisingly, we observe that the pyrolysis "kick-off" period, the time where we first observe CO, increases with increasing water content. In fact, for the estimated incident power level of 200 W, the average difference in the delay period between successive experiments, ~ 40 seconds, seems reasonable based on the water difference (~ 4-6 g) between each sample. Figure 9 compares the evolution profiles for CO, CO_2, CH_4, and C_2H_4 obtained using either the core absorber or mixed (activated carbon) absorber pyrolysis configurations at a water content of 40%. For this and other sample moisture contents, similar kick-off points are measured, although steeper evolution profiles are usually observed after each kick-off point using the core absorber geometry. In general, it appeared that the activated carbon core and the activated carbon mixture led to similar pyrolysis gas evolution profiles.
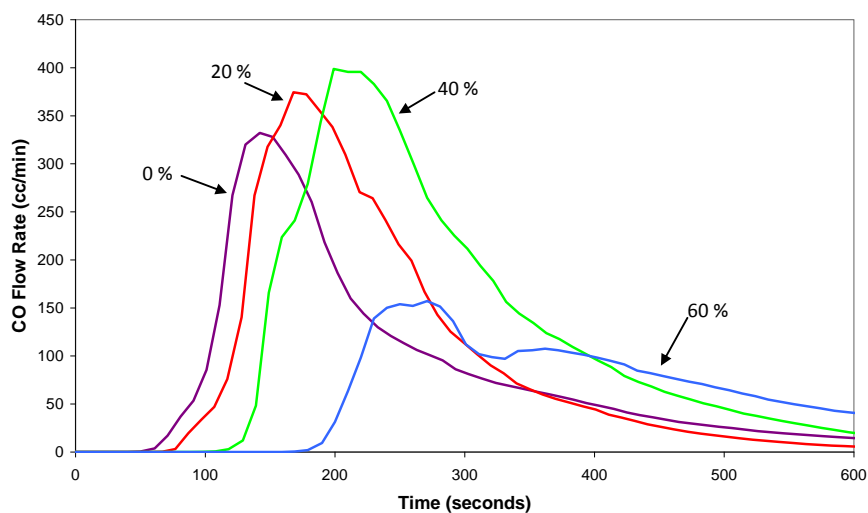

Figure 8. CO evolution profiles measured during pyrolysis of synthetic feces at four different moisture levels, employing an activated carbon core absorber configuration. The estimated incident microwave power was 200 W for each case.

A summary of the pyrolysis gas yields for several experiments is provided in Table 7. This table compares the results for the various moisture loadings and also compares results using the two different absorber configurations. The table also lists the calculated energy consumed per gram of waste (synthetic feces + water) for each run. This value is estimated from the incident microwave power and the time required to reach 99% completion (based on the CO evolution) and assumes 65% conversion efficiency for the microwave oven. In general, the gas composition does not appear to be greatly influenced by the sample water content or the absorber geometry or material. In terms of the absorber geometry, there does not appear to be a preferred method, based on the energy consumed during each run. An encouraging result is that the char from a previous pyrolysis run also acts as an effective microwave absorber material. The most surprising result is that the dry sample requires nearly twice the energy to reach completion, compared to the wet samples. Recall that the mass of synthetic feces in the samples is the same (on a

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dry basis) when the water content varies from 0-40%. The excess water actually seems to improve the efficiency of the process. These are important results because they suggest that a waste pre-drying step, particularly one involving a separate drying system, may be unnecessary and may also decrease the efficiency of the pyrolyzer. This result is likely related to the fact that water is a very efficient absorber of microwave energy.
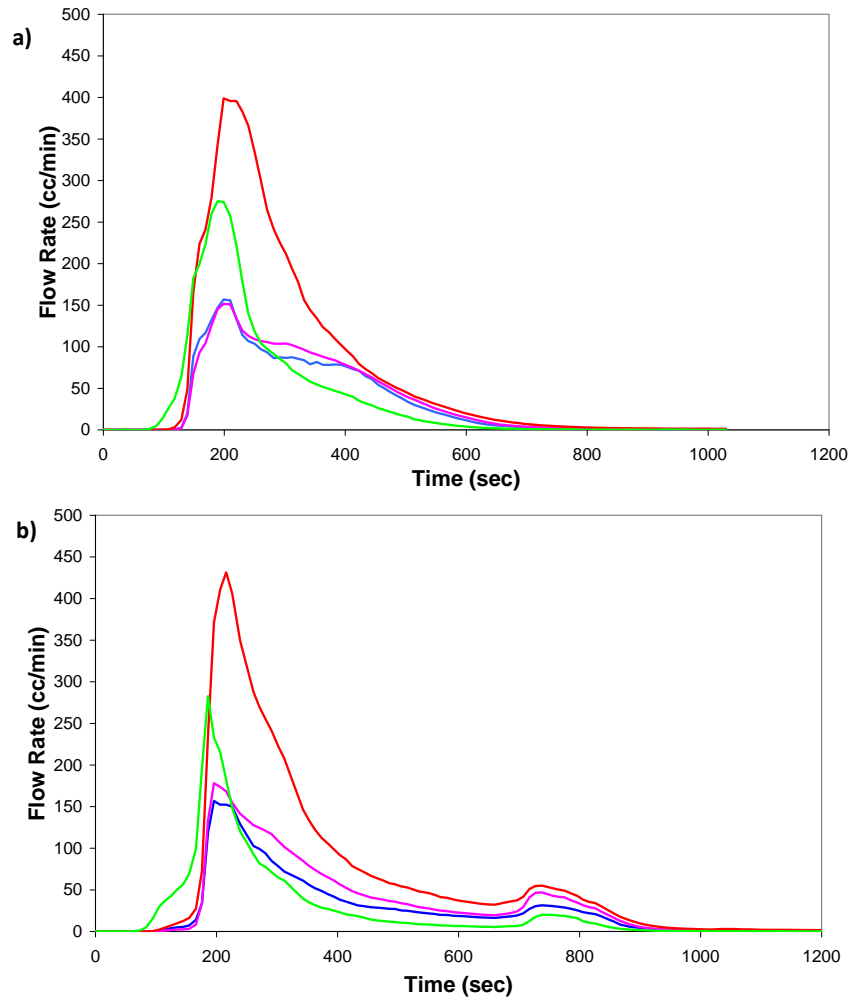

Figure 9. Comparison of gas evolution rates during microwave-assisted pyrolysis of synthetic feces (Simulant #3) with a water content of 40%, for two different absorber geometries: a) activated carbon core and b) activated carbon mixture. For both cases the estimated microwave irradiation level was 200 W. The evolution rates for CO, CO$_2$, CH$_4$ and C$_2$H$_4$, determined by FTIR, are shown in red, green, pink and blue, respectively.

Table 7.   Summary of microwave pyrolysis gas yields from simulated feces samples (dry basis).

Sample Water Content (%)	Absorber Type	Total Volume (cc) (dry)	CO Vol. %	CO$_2$ Vol. %	CH$_4$ Vol. %	C$_2$H$_4$ Vol. %	H$_2$[1] Vol. %	Energy Required (Whr/g)
0	A.C. core	6074	15	10	11.7	11	52.3	5.6
20	A.C. core	5599	17.4	10.1	10.1	9	53.4	2.9
40	A.C. core	6614	18.5	10.1	9.3	8.8	53.3	2.6
40	A.C. mix	6894	18.7	7.9	9.9	7.8	55.7	3.2
60	A.C. core	5334	13.8	9.9	9.1	10.0	57.1	3.1
60	A.C. mix	4894	16.4	8.8	11.9	10.8	52.1	2.6
60	Char mix	5662	15.1	11.1	8.8	8.1	56.9	3.8

1.   *H$_2$ plus other gases*

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Results for several experiments with Simulant #3 at 40-60% water concentration, including some duplicates, are summarized in Table 8 and seem to confirm that the additional water (above ~40%) usually leads to a higher energy demand, as expected.

Table 8. Comparison of microwave heating using a central core absorber geometry (activated carbon-filled quartz tube) versus a mixed absorber geometry. For all runs the sample was Feces Simulant #3, the microwave irradiation level was 200 W, and the mass of the absorber material (activated carbon or char) was 1.5 g).

Run #	Absorber Type	Water Content (%)	Total Gas Volume (dry) (cc)	Energy Required (Whr/g)	Char Recovered[1] (%)
79	Act. C Core	40	5941	2.34	24
80	Act. C Core	40	6614	2.57	23
81	Act. C Core	60	5334	3.06	22
83	Act. C Mix	40	6927	3.37	28
84	Act. C Mix	40	6894	3.15	30
85	Act. C Mix	60	3938	3.53	25
86	Act. C Mix	60	4894	2.60	26
87	Char Mix	60	5662	3.84	19

 1. *Calculated as 100 x (mass of char/mass of dry initial sample).*

IV. Conclusions

This paper continues previous work on pyrolysis processing of solid wastes for spacecraft and planetary surface applications. A domestic microwave oven was modified for use in this work for scoping studies in which the effects of sample composition, use of microwave absorbers, and secondary pyrolysis of liquids were studied. Experiments were done with wheat straw and various formulations of a feces simulant. The microwave absorbers examined included activated carbon and char produced from previous experiments. The addition of a separate microwave-heated secondary pyrolysis zone was also examined as a means of reducing the liquid product yields. In general, the feces simulants had similar pyrolysis yields when compared to wheat straw for the char and total gas yields, but individual gas yields were different. For example, the feces simulants produced significantly more ethylene, larger amounts of methane, and smaller amounts of carbon oxides ($CO + CO_2$). This can be largely explained by the differences in elemental compositions. A comparison was also made of the microwave-assisted pyrolysis of feces simulants of variable moisture contents (0-60 wt. %). The higher moisture contents (40-60 wt. %) result in a delay for the onset of pyrolysis and a higher energy demand per gram of sample, as might be expected. However, at lower moisture contents, such as the 20 wt. % water for the baseline sample, it was found that the overall energy demand appeared to be lower than for the dried sample, perhaps due to the more efficient absorption of microwave energy.

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