A Prototype Pyrolyzer for Solid Waste Resource Recovery in Space

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ABSTRACT

Pyrolysis processing is one of several options for solid waste resource recovery in space. It has the advantage of being relatively simple and adaptable to a wide variety of feedstocks and it can produce several usable products from typical waste streams. The objective of this study is to produce a prototype mixed solid waste pyrolyzer for spacecraft applications. A two-stage reactor system was developed which can process about 1 kg of waste per cycle. The reactor includes a pyrolysis chamber where the waste is heated to temperatures above 600°C for primary pyrolysis. The volatile products (liquids, gases) are transported by a N_2 purge gas to a second chamber which contains a catalyst bed for cracking the tars at temperatures of about 1000 °C – 1100 °C. The tars are cracked into carbon and additional gases. Most of the carbon is subsequently gasified by oxygenated volatiles (CO_2, H_2O) from the first stage. In a final step, the temperature of the first stage can be raised and the purge gas switched from N_2 to CO_2 in order to gasify the remaining char in the first stage and the remaining carbon deposits in the second stage. Alternatively, the char can be removed from the first stage and saved as a future source of CO_2 or used to make activated carbon. The product gases from the pyrolyzer will be rich in CO and cannot be vented directly into the cabin. However, they can be processed in a shift reactor or sent to a high temperature fuel cell. A control system based on artificial neural networks (ANNs) is being developed for the reactor system. ANN models are well suited to describing the complicated relationships between the composition of the starting materials, the process conditions and the desired product yields.

INTRODUCTION

A key element of a Controlled Ecological Life Support System (CELSS) is a means for solid waste resource recovery. 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 carbon, CO_2, H_2O, hydrogen, 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 biodigestion, wet oxidation, supercritical water oxidation, steam reforming, electrochemical oxidation and catalytic oxidation [1-13]. However, some of these approaches have disadvantages which have prevented their adoption. For example, incineration utilizes a valuable resource, oxygen, and produces undesirable byproducts such as oxides of sulfur and nitrogen. Incineration also will immediately convert all of the waste carbon to CO_2, which may require storing excess CO_2. Supercritical water oxidation requires the use of high pressure equipment which is expensive to fabricate and transport into space.

"Pyrolysis," in the context of this paper, is defined as thermal decomposition in an oxygen-free environment. Primary pyrolysis reactions are those which occur in the initial stages of thermal decomposition, while secondary pyrolysis reactions are those which occur upon further heat treatment. A pyrolysis based process has several advantages when compared to other possible approaches for solid waste resource recovery: 1) it can be used for all types of solid products and can be more easily adapted to changes in feedstock composition than alternative approaches; 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., CO_2, CO, H_2O, H_2, NH_3, CH_4, etc.); 5) the

technology can be designed to produce minimal amounts of unusable byproducts; 6) it can produce potentially valuable chemicals and chemical feedstocks; e.g., nitrogen-rich compounds for fertilizers, monomers, hydrocarbons); 7) pyrolysis will significantly 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 incineration when needed. In addition to being used as the primary waste treatment method, pyrolysis can also be used as a pretreatment for more conventional techniques, such as incineration or gasification. A summary of the proposed processing scheme is shown in Figure 1 for a model waste feedstock.

The primary 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 former issue is a feature of pyrolysis processing (and also a potential benefit, as discussed above). The latter issue can be addressed by utilization of a water gas shift reactor or by introducing the product gases into an incinerator or high temperature fuel cell.

EXPERIMENTAL METHODS

SAMPLE SELECTION

In previous work at Advanced Fuel Research, Inc. (AFR) [14] and Hamilton Sundstrand Space Systems International (HSSSI) [11], a model waste feedstock was used, the so-called "Referee Mix." This composite mixture consisted of 10 wt. % polyethylene, 15% urea, 25% cellulose, 25% wheat straw, 10% Gerepon TC-42 (space soap) and 5% methionine. The materials that were obtained and the elemental compositions of each are given in Reference 14. For the development of the current reactor system, the initial focus is on wheat straw as the test waste stream, since it is available at a relatively low cost and its elemental composition is similar to the average elemental composition of the composite mixture used previously. Two different samples of wheat straw have been used to date. The elemental composition of each is provided in Table 1.

The outer closure of the first generation reactor is a stainless steel tube with flanges on both sides. It was manufactured by welding commercially available 8 inch half nipples and flanges (Huntington Lab. Inc.) onto both ends of an 8 inch stainless steel tube. The copper gasket seals between the reactor body and flanges allows for a 450 °C maximum shell temperature. The thermal insulation and electric heaters are placed inside the tube. This allows for operating the reactor at high (up to 1100-1200 °C) temperatures without the necessity to excessively increase the size and mass. The other advantage of the design is that a more reliable seal can be established.

The inner volume is divided into two chambers, and the temperature of each is regulated independently. The right chamber is partially filled with silica xerogel and functions to completely break down the tar produced in the pyrolysis chamber to elemental carbon and light gases. In a previous project on diesel fuel pyrolysis, xerogel was found to be an exceptionally good catalyst for cracking carbonaceous materials to carbon as well as catalyzing high temperature gasification of the carbon deposited on the xerogel surface [15]. The xerogel is prepared from silica gel (Aldrich Co.) by a slow stepwise dehydration and stabilization process. The cracking chamber containing the xerogel bed is isolated at both the inlet and outlet sides by two perforated Zircar or Alumina disks.

The inner ceramic tube is a medium density machineable ceramic fiber reinforced refractory alumina cylinder (Zircar Products, Inc., Type RS-101). The left edge of this cylinder is sealed against a flexible silicone O-ring. The thermal insulation of the hot section of the inner cylinder is facilitated through the alumina-silica (Zircar Products, Inc Type AXL) outer cylinder and inserts.

The tar formed in the pyrolysis chamber is carried downstream with an inert (nitrogen) or reactant (steam, CO_2) gas. It has been previously observed that waste can swell significantly during pyrolysis. Therefore the pyrolysis chamber must be oversized relative to the volume of waste (about 2.5 liters versus 1.0 liters).

The volume of the second chamber for tar

Table 1. Composition of the Wheat Straw Samples (wt. %, Dry Ash Free Basis)

Species	C	H	O	N	S	Ash
Danish wheat straw	50.4	6.0	42.5	0.86	0.25	7.9
NIST wheat straw	48.0	6.2	44.9	0.68	0.21	9.9

The moisture content of each is about 5-7 wt.% (as-received basis).

REACTOR SYSTEM

The schematic of the two-stage reactor system is shown in Figure 2. The system was designed in order to incorporate the pyrolysis, tar cracking, and gasification steps into a single reactor unit with two chambers.

cracking/gasification is determined by two factors: the amount of carbon which accumulates from one charge (1 liter) of waste and the maximum allowable amount of
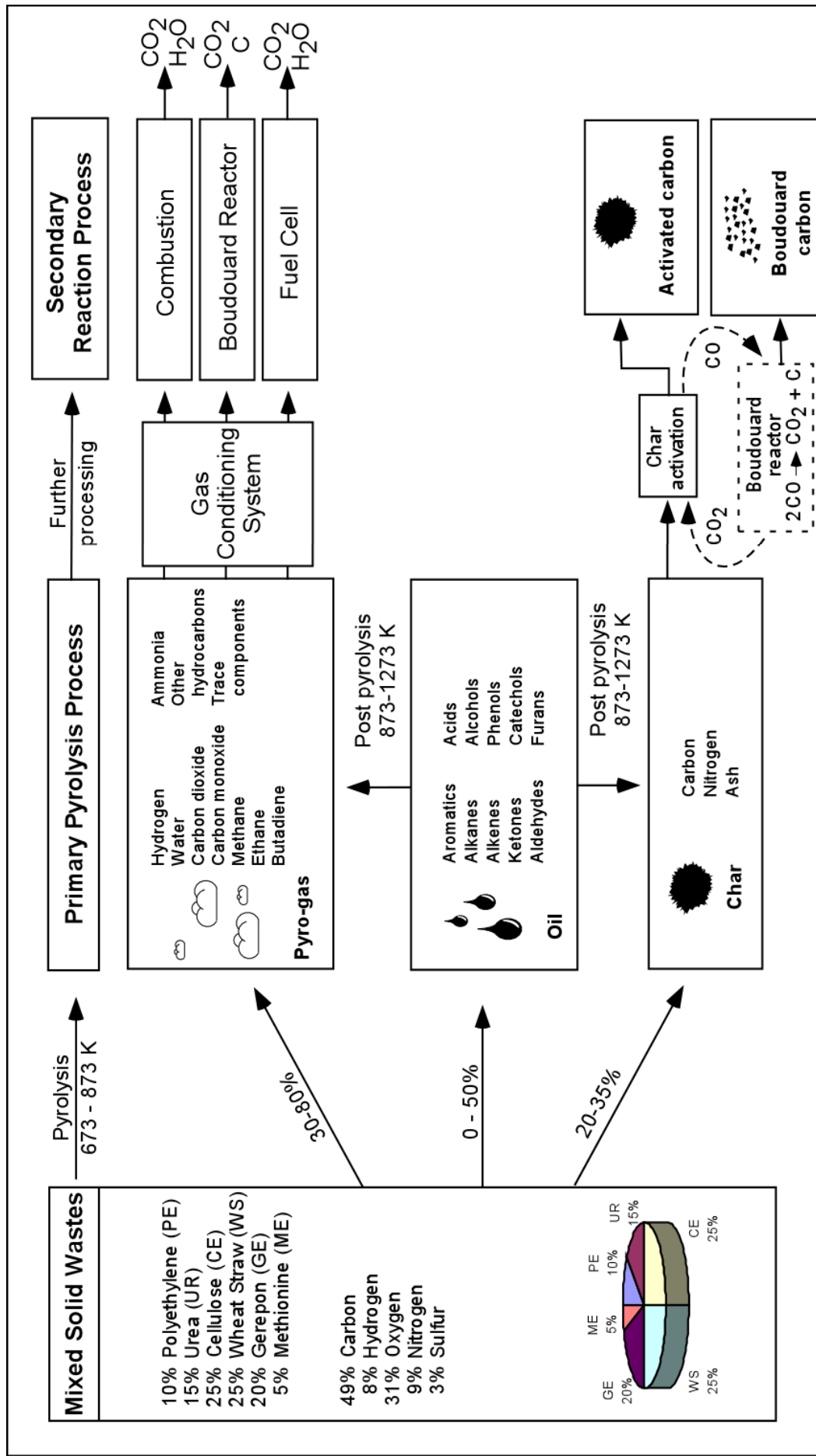
Secondary Reaction Process

Combustion → CO_2, H_2O

Boudouard Reactor → CO_2, C

Fuel Cell → CO_2, H_2O

Primary Pyrolysis Process

Further processing

Gas Conditioning System

Pyrolysis 673 - 873 K

Pyro-gas

Hydrogen
Water
Carbon dioxide
Carbon monoxide
Methane
Ethane
Butadiene

Ammonia
Other hydrocarbons
Trace components

30-80%

Post pyrolysis 873-1273 K

Oil

Aromatics
Alkanes
Alkenes
Ketones
Aldehydes

Acids
Alcohols
Phenols
Catechols
Furans

0 – 50%

Post pyrolysis 873-1273 K

Char

Carbon
Nitrogen
Ash

20-35%

Char activation

Activated carbon

Boudouard reactor
$2CO \rightarrow CO_2 + C$

CO
CO_2

Boudouard carbon

Mixed Solid Wastes

10% Polyethylene (PE)
15% Urea (UR)
25% Cellulose (CE)
25% Wheat Straw (WS)
20% Gerepon (GE)
5% Methionine (ME)

49% Carbon
8% Hydrogen
31% Oxygen
9% Nitrogen
3% Sulfur

UR 15%
PE 10%
ME 5%
GE 20%
CE 25%
WS 25%

Figure 1. The pyrolysis processing scheme for solid waste proposed by AFR.
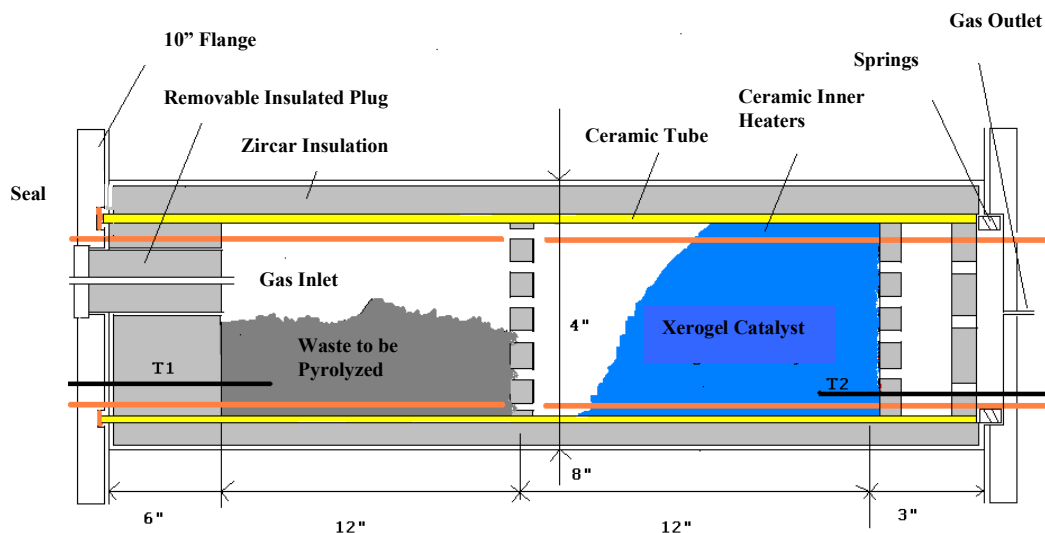
Figure 2. Schematic of two-stage pyrolysis reactor system.

carbon to deposit before the reactor gets plugged (capacity of carbon capture ΔC). The maximum amount of carbon formation is approximately equal to the amount of tar formed, or $w_{tar} \approx 0.2\ w_{waste} \approx 90$ g. ΔC was found in earlier experiments to be 28 cm^3/1g carbon with 2/3 of the reactor volume filled with xerogel [15]. This translates to 90x28 = 2520 cm^3. Based on these calculations, the volumes of the two chambers are approximately equal.

During the initial processing step, the first stage is the primary pyrolysis zone, while the second stage is the secondary pyrolysis zone. During the second processing step, the purge gas is switched from N_2 to CO_2 and gasification of the char can occur in the first stage (if the temperature is raised sufficiently) while gasification of

the carbon deposits will occur in the second stage.

The main features of the reactor are:

- The electric heaters of both chambers are placed inside the ceramic reactor tube.
- The first reactor chamber is supplied with a large removable insulated plug containing the gas inlet. This allows the reactor to be loaded without removing the flange.
- The outlet side of the ceramic reactor tube is spring loaded in order to compensate for thermal expansion-contraction.

The flow chart of the entire reactor system is shown in Figure 3. A slip stream of the exhaust gas is created with
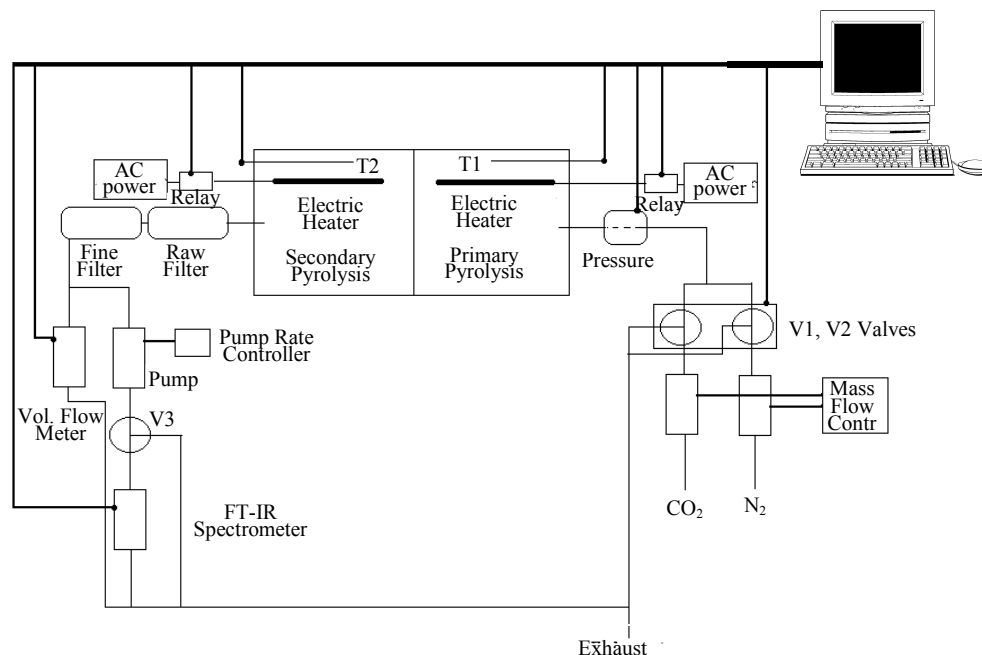

Figure 3. Schematic of reactor with associated control and monitoring system.

a teflon piston/cylinder pump. The flow rate of this stream is regulated with a Hewlett-Packard DC power supply and directed through an infrared (FT-IR) spectrometer for analysis. The FT-IR spectrometer is an Online Technologies, Inc. Model 2010 mid-IR spectrometer equipped with a multi-pass cell allowing continuous monitoring of a variety of gases.

The volumetric flow meter is a Bios International DC-Lite flowmeter (0-15 liter/min) which is connected to the PC through an RS-232 serial communication protocol. The CO_2 and N_2 flows are regulated with Brooks Instruments mass flow controllers and Valco Instruments solenoid valves (V1,V2). The pressure transducer is an Omega strain bridge excited with 8V DC. The temperature of the two reactor chambers is controlled independently from the PC (thermocouples T1,T2, solid state relays and two AC regulated 3 kW power supplies). The steady state power consumption is about 600 watts, which increases 15%-20% during the active pyrolysis period.

The entire control and data collection operation is facilitated through one PC running a LabView program written for this particular experiment. The data collection (except for the FT-IR data) and control functions are interfaced to a National Instruments 6023 board and the serial port of the PC.

The major problem of the original reactor design was the extremely short lifetime of the inside electric heaters. The advantage of cartridge type (inside) electric heaters is that it allows for significantly smaller reactor size, while the obvious disadvantage is the higher watt density and accompanying increased exposure to corrosion by the pyrolysis gases. Since small size is one of the most important aspects of a viable technology in space applications, development of long lasting specific cartridge type heaters for this application is important.

In each type of the several heaters that were tested in the reactor, the following two areas of increased stress were observed: the leads connecting to the electric feedthroughs on the flanges and the two ends of the cartridge heaters.

In addition, with commercially available Incoloy sheathed cartridge heaters, serious corrosion of the metal sheath was observed. The heaters are operated in a reducing environment containing carbonaceous materials as precursors of carbon. At elevated temperatures, carbon dissolved in the metal heating element wire and sheath materials results in fast deterioration of the metals. Local overheat of the opposite ends of cartridge heaters are caused by Lorentz currents induced in the wire crossing the collapsing electromagnetic fields, in the case where AC power is used.

Commercially available cartridge heaters broke down after only one or two cycles where the major problem was corrosion of the outer sheath material. Therefore, it was concluded that metal sheathed cartridge heaters are not suitable for this application. Since corrosion

problems might also be expected for SiC and $MoSi_2$ ("Kanthal") heating elements, no attempts were made to use these types of heating elements.

The logical choice would be high temperature alumina sheathed cartridge heaters. However, no suitable ceramic heaters were found to be available. Therefore, it was necessary to develop an appropriate long service life ceramic heater. Several types of cartridge heaters were tested in the reactor. The first one utilized a Pt heating wire in the hope of attaining long service life. Twelve inch long, 1.4 inch OD ceramic tubes were bundled with Pt wire. This heating element provided a homogeneous temperature distribution, but lasted only three cycles in the first chamber and five cycles in the secondary chamber. This design leaves relatively large "bare" sections of the heating wire at the ends of the ceramic tubes vulnerable to corrosion. This can be improved by using larger ceramic tubes with both ends sealed. The critical areas of these heating elements – the opposite ends and lead connections – were reinforced with Pt wire coiled onto a section of heavy gauge nichrome heating wire. However, none of these heating elements lasted more than two cycles.

Based on these experiences, the heating element design shown in Figure 4 was implemented. Several long ceramic tubes (three in the first chamber and four in the secondary chamber) with one end closed were used to house the heating wires, where only part of the length (10 inches long) is heated. This allows for sealing the cold section of the ceramic tube itself directly onto the flange, thereby preventing reaction product gases from entering the inside of the heater. Using this method, no carbon deposition onto heating wire surfaces occurs. Moreover, providing an inert nitrogen atmosphere inside the ceramic cartridge allows operation of the heating elements at sufficiently high temperatures for an indefinite period of time. Boron nitride, as a good heat conductor in the heated section, enhances heat transfer towards the walls, while the sand filling in the unheated section serves a heat barrier towards the cold seal on the flange. This heating element design has been successfully used for more than 30 reactor cycles.

The current reactor still has a problem with hot spots in the primary pyrolysis zone. This problem will be solved by developing a ceramic and wire mesh basket to suspend the pellets above the heating elements and improve heat distribution.

RESULTS AND DISCUSSIONS

SAMPLE PREPARATION

If the raw waste (wheat straw) is fed into the reactor in finely ground form, the resulting char is very hard to clean from the reactor. However, if the feed was pressed into large pellets beforehand, the reaction resulted in distinct pieces of char easily removable after pyrolysis. A photograph of a raw and pyrolyzed pellet is shown in Figure 5.
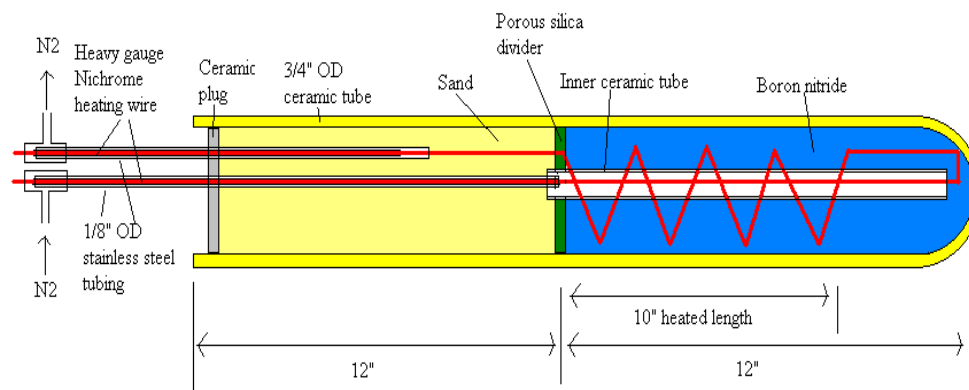
Figure 4. Latest design for ceramic cartridge heaters.

The pellets ($\approx$ 16 g per pellet) were prepared in a 1-inch I.D. die at 10-Ton pressure. Most of the initial moisture in the sample is removed during the pelletization process. 10 wt% lignin (Alcell) was added as binder in most cases. Without a binder, the pulverized straw material used in the experiment does not form as strong a pellet. Lignin, a natural plant material itself, was considered not to significantly influence the pyrolysis of wheat straw. However, it would not be necessary to bring lignin on board, since it is a component of human waste.

PROCEDURE AND RESULTS

Approximately 280 - 400 g of pellets were placed in the reactor and the system was constantly purged with 800 cc/min N_2. First, the secondary pyrolysis chamber was heated up to about 1100 °C. Next the temperature of the primary pyrolysis chamber was raised while the volume and composition of the product gases was constantly monitored. The following gas concentrations are routinely monitored: H_2O, CO, CO_2, CH_4, C_2H_4, NO, NO_2, SO_2, H_2S, NH_3, CH_3OH, C_6H_6, $C_6H_5CH_3$. The main products were CO_2, CO, CH_4, H_2O and some aromatic

Figure 5. Photograph of raw and pyrolyzed wheat straw pellets.

products (C_6H_6, $C_6H_5CH_3$) while the other gases appeared only in trace amounts. Some H2O is produced as a result of pyrolysis and it is also present at some level in the waste as moisture.

Figure 6 shows the concentrations of CO, CO_2, CH_4 as
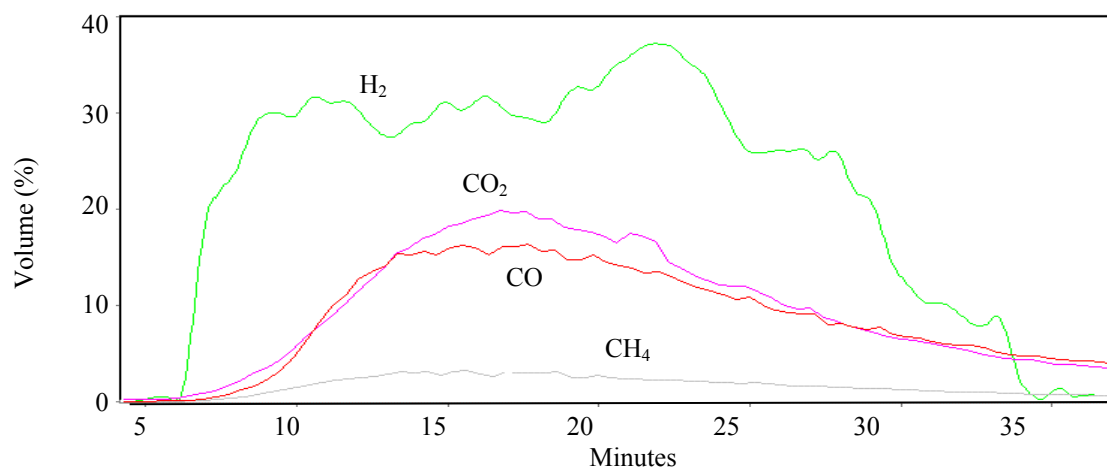
Figure 6. Gas concentration profiles obtained from reactor operation with wheat straw during the pyrolysis step.

well as H_2 in the exhaust gases. The H_2 evolution was estimated by subtracting the three main products and the carrier N_2 flow from the measured volumetric flow at the reactor outlet. The material balances were typically closed to within 90-95%. Individual element balances have not yet been done.

After the pyrolysis reaction (40 minutes), the purge gas was switched to 300 cc/min CO_2 to gasify the carbon deposited in the second chamber. The gas concentration profiles from this step are shown in Figure 7.
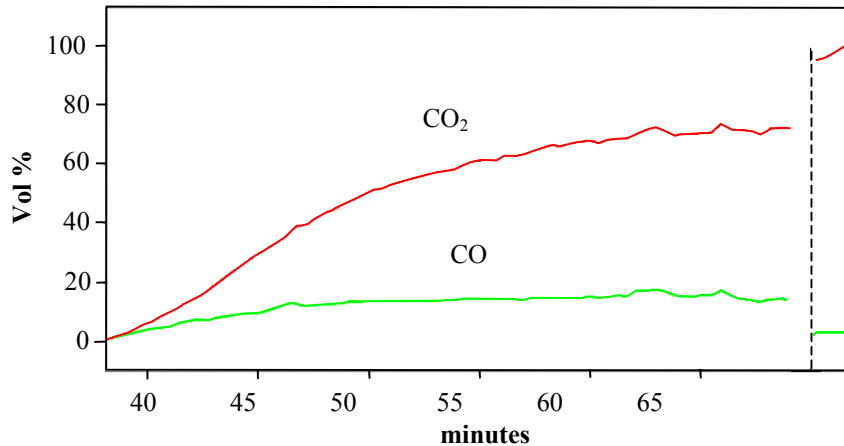
Figure 7. Exit concentration of CO_2 and CO from reactor system during gasification step.

It is seen, that part of the CO_2 is reduced to CO by the carbon. The carbon completely reacted away after about an hour (after the dotted line). However, some small amounts of CO continue to be formed by gasification of the char in the first stage, even at the relatively low temperature of 600 °C. This confirms the high reactivities of the chars that were measured previously [14].

MODELING OF PRIMARY AND SECONDARY PYROLYSIS BEHAVIOR

In order to develop the complicated relationship between the composition of the starting materials, the process conditions and the desired product yields, this study has also investigated the use of artificial neural network (ANN) models. Recently, ANNs have been applied to a variety of similarly intractable problems and have demonstrated a high degree of success [16-20]. The ability of ANNs to learn from observation, together with their inherent ability to model nonlinearity, make them ideally suited to the problem of control in complex pyrolysis processes. It should be possible to use ANNs to adaptively model the pyrolysis process using the process parameters as inputs and the resulting pyrolysis product distributions as outputs. The model will then be used in a feedback control loop to maximize the yields of desirable products while minimizing side reactions. The validation data for the ANN control technology will be the concentrations of pyrolysis species supplied by IR gas

analysis equipment. Additional details are provided in Reference 14.

SUMMARY AND CONCLUSIONS

Pyrolysis processing is one of several options for solid waste resource recovery in space. It has the advantage of being relatively simple and adaptable to a wide variety of feedstocks and it can produce several usable products from typical waste streams. The objective of this study is to produce a prototype mixed solid waste pyrolyzer for spacecraft applications. A two-stage reactor system was developed which can process about 1 kg of waste per cycle. The reactor includes a pyrolysis chamber where the waste is heated to temperatures above 600°C for primary pyrolysis. The volatile products (liquids, gases) are transported by a N_2 purge gas to a second chamber which contains a catalyst bed for cracking the tars at temperatures of about 1000 °C – 1100 °C. The tars are cracked into carbon and additional gases. Most of the carbon is subsequently gasified by oxygenated volatiles (CO_2, H_2O) from the first stage. In a final step, the temperature of the first stage can be raised and the purge gas switched from N_2 to CO_2 in order to gasify the remaining char in the first stage and the remaining carbon deposits in the second stage. Alternatively, the char can be removed from the first stage and saved as a future source of CO_2 or used to make activated carbon. The prototype two stage system has been successfully operated over many cycles. Early problems with heating element life were solved. Future work will include development of a control scheme, probably involving the use of ANN models.

ACKNOWLEDGEMENTS

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