

## GASIFICATION OF WASTE PLASTICS FOR THE PRODUCTION OF FUEL-GRADE GAS

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### INTRODUCTION

Many areas of the United States are experiencing waste disposal problems stemming from both a shortage of landfill space and a public concern for the environmental impacts and the appearance of landfilling. Although it is still the cheapest method of disposal, the rising cost of landfilling is making energy from waste more economically feasible. Incineration, another popular waste disposal method, faces ever more stringent emissions regulations, making it an increasingly less attractive alternative economically. New gasification and pollution control technologies are making it possible for waste materials to be used as environmentally acceptable sources of energy. Two possible waste materials which might be used as a feedstock for energy production, ebonite and automotive shredder residue, are being investigated at the Energy and Environmental Research Center at the University of North Dakota.

Several tests have been conducted with ebonite in a thermogravimetric analyzer (TGA) and a 1 to 4-lb/hr continuous fluid-bed reactor (CFBR) using  $K_2CO_3$  and Paris limestone catalysts. Tests are scheduled for the automotive shredder residue. Data from the tests include carbon conversion, gas production, wastewater production, heavy metal analysis, and chlorine analysis. Analysis of the data includes discussion of the effects of the benefits of producing a fuel gas and the decrease in landfill volume, the environmental impacts of heavy metal disposal from the ash produced in the system, and the technological requirements for gas cleanup.

### WASTE FEED MATERIAL

Automotive shredder residue is a waste product generated in the dismantling of automobiles. After removal of the gas tank and battery, the automobile is shredded to provide a material approximately less than 4 inches in size and composed of approximately 50% organic and 50% inorganic fractions. Magnetic separation is then used to separate out ferrous scrap. Air cyclone separators isolate a low density "fluff" from the nonferrous fraction (aluminum, copper, etc.). This fluff (shredder residue) is composed of a variety of plastics, fabrics, foams, glass, rubber, and an assortment of contaminants<sup>1</sup>. This waste product contains a wide variety of heavy metals and halogens, making it an excellent test material, as it will present many of the common problems to be considered when using waste as a gasification feedstock. Tests on automotive shredder residue are scheduled in the TGA and in the 1 to 4-lb/hr CFBR to investigate its gasification potential.

Ebonite, a hard rubber material used primarily in car battery casings, was tested both in a TGA and in the CFBR. Three tests in the TGA included one test at 800°C, with potassium carbonate as a catalyst, and two tests at 900°C, one of these with potassium carbonate and one with Paris limestone. The tests in the 1 to 4-lb/hr CFBR were all carried out using potassium carbonate as a catalyst, since it accelerated the process to the greatest degree. Table 1 shows the proximate and ultimate analyses of the ebonite.

## EBONITE TGA GASIFICATION TESTS

Tests were conducted in the thermogravimetric analysis (TGA) instrument to determine test matrix conditions for further experiments to be run in the 1 to 4-lb/hr bench-scale unit. Ebonite reactivity with steam and two catalysts were investigated at temperatures of 800° and 900°C (Figure 1-4).

In all tests, the reactant mixtures containing -60-mesh ebonite were heated to the desired reaction temperature and held at temperature until approximately half of the fixed carbon in the sample had been converted to gas, at which point the reaction was terminated by cutting off the steam and heat supply. A -60-mesh ebonite was used due to the difficulty in obtaining samples of reproducible size distribution from the bulk samples. The +60-mesh-size fraction had the same TGA proximate analysis as the -60-mesh fraction, implying the difference (if any) in their reactivities would likely not be chemical, but due to a difference in surface area. All tests were performed under flowing argon gas.

To determine the point at which half of the fixed carbon had been converted, TGA proximate analyses were carried out on each sample prior to the reactivity tests. These analyses (Table 2) showed that volatiles are removed from the reactant mixtures, and the remaining material consists of about 63% fixed carbon and 37% ash for ebonite with catalyst and about 76% fixed carbon and 23% ash for ebonite without catalyst.

The TGA graphs start at time = 0. This point marks the beginning of the heat-up period. Weight loss during the heat-up period (as measured by a decreasing weight percent value) is due to moisture loss and devolatilization. When the reaction temperature is achieved (at which point devolatilization is essentially complete), the weight percent value is manually reset to a y-value of 100%, and steam is added. When 50% of the fixed carbon is converted, heat is turned off and the steam flow terminated. The point at which 50% of the fixed carbon is converted is determined by examination of proximate analysis data. As stated, each reactivity test was terminated when about half of each devolatilized sample had been converted to gas: 31.5 weight percent of the sample in the case with catalyst and 38.1 wt% of the sample in the case with no catalyst. After the termination of heat and steam, the conversion line still continued until the instrument was turned off, since some residual steam was still present, but it was not linear.

The catalysts investigated were Paris limestone (calcium carbonate) and potassium carbonate. All catalyst tests were performed using mixtures of ebonite and 10 weight percent-added catalyst. The ebonite/limestone test was performed at 900°C, and ebonite/potassium carbonate tests were performed at 800° and 900°C. The TGA data indicated that Paris limestone had a minor effect on the reactivity of the ebonite at 900°C (Figure 2), compared with the reactivity of ebonite without catalyst at the same temperature (Figure 1). Potassium carbonate, however, significantly affected reactivity. Conversion at 800°C (Figure 3) and at 900°C (Figure 4) with a potassium carbonate catalyst occurred quite rapidly. The residence time required for complete conversion at 800°C is 5.5 minutes and at 900°C is 2 minutes, whereas conversion time at 900°C is 18 minutes. Residence times for 50% and 100% conversion were found graphically. The point for 100% conversion was found by extrapolating the linear portion of the conversion line. The reaction appears to be zeroth order with respect to carbon. As conversion approaches 100%, the reaction is no longer strictly zeroth order because unreactable material (ash) limits access to carbon, but the order goes up only to approximately 0.2, introducing a very small error into the calculated time for total conversion.

## EBONITE CFBR GASIFICATION TESTS

Bench-scale testing was performed in a 1 to 4-lb/hr fluid-bed reactor system, shown in Figure 5. Preheated gas and steam are introduced into the bottom of a 3-inch-

diameter reactor. The lower section of the reactor, which is attached to the coal feed system, is made of 3-inch pipe and is 33 inches in length. The freeboard section is made of 4-inch pipe, 18.75 inches in length. Solids remain in the bed until, through weight loss from gasification, they reach the top of the 3-inch section and fall out through the top bed drain leg, where they are collected in an accumulation vessel. Unreacted fines and some ash particles are entrained and separated from the gas stream by a 3-inch cyclone. Liquids are condensed in one of two parallel indirect cooled condensation trains. Gas is then metered and sampled by an on-line mass spectrometer.

The particle-size distribution of the ebonite was determined by sieve analysis; the results of which are shown in Table 3. Cold flow fluidization tests indicated a well-fluidized bed at 0.6 to 0.8 ft/s.

Carbon conversion for the ebonite was found to be approximately 90% at 900°C, with most of the unreacted ebonite found in the condensation train, indicating that fines blew out of the bed before having sufficient residence time for complete conversion. A narrower particle size for the feed, a lower fluidization velocity, or a larger diameter freeboard section would most likely raise this conversion by reducing fines entrainment. Alternatively, a reactor/cyclone recycle system that is designed for this particular feedstock would also produce higher conversions. Comparing the amount of material in the bed with the feed rate indicates that the residence time for the test was less than 1 hour. The residence time is extremely dependent on temperature and heat-up rate. Ebonite agglomerates at temperatures below about 800°C. If the reactor is not above 850°C and at a high heat-up rate, the ebonite will agglomerate, and the reaction rate and overall conversion are greatly reduced.

Gas produced from gasification and from water-gas shift reactions is between 220 to 280 lbs per 100 lbs of MAF ebonite feed material. Average composition of the product gas is shown in Table 4. Gas produced has a Btu content of approximately 260 Btu/scf. This number does not include nitrogen used in fluidization.

Water conversion was found to be 1.5-2.0 mole water/mole fixed carbon based on material balance data. Trace-element analysis showed considerable loss of lead from the ebonite, going from 660 ppm in the feed to 257 ppm in the product char. Antimony also decreased considerably, starting off at 696 ppm and ending up at 129 ppm. Chlorine content went from 160 ppm to 149 ppm.

#### ENVIRONMENTAL IMPACTS OF GASIFYING WASTE MATERIAL

Gasification of ebonite offers not only the benefit of energy production, but also decreases waste volume that needs to be landfilled. Density of the feed material (ebonite) is approximately 0.73 g/mL. Density of the reacted material (top bed drain) is approximately 0.56 g/mL. On an as-received basis, 12.8 ft<sup>3</sup> out of 100 ft<sup>3</sup> fed will be left over for landfill (assuming the 90% conversion). If 100% conversion is achieved, 14.5 grams per 100 grams of feed will be left over to landfill, resulting in a volume decrease of 87%.

Wastewater from the process may contain some heavy metals, including lead and antimony. Acid leaching the ebonite prior to gasification would be desirable to eliminate as much of the heavy metals as possible in downstream operations. Additionally, leachability studies will need to be conducted on the unconverted material. Gas cleanup problems will include the need to eliminate sulfur- and chlorine-containing compounds such as H<sub>2</sub>S and HCl from the gas stream, as well as trace metals that may vaporize and recondense as particulates. The ebonite feed material is fairly high in sulfur, having an as-received sulfur content of 3.9%.

## FUTURE TESTS

Further tests are planned to determine:

- the yield structure for automotive shredder residue and to verify the yield structure for ebonite
- optimal fluidization velocity
- carbon conversion with reduced fluidization velocity
- the effect of steam to carbon ratio
- the effect of increased pressure on gas yields
- the fate of vaporized heavy metals
- methods of ash stabilization
- the feasibility hot-gas cleanup
- leachability properties of unreacted material

Two of the key reactor design parameters that need further investigation include the fluidization velocity and the steam to carbon ratio. Carbon conversion could be increased if the fines could be kept in the reactor. The steam to carbon ratio coupled with the reactor pressure could change the output of carbon monoxide and hydrogen produced in the system. The heavy metals that are vaporized will either condense in the condensate train, which will cause scaling over a long period of time, or possibly recondense as particulates in the gas stream. More information will be needed on where these metals condense in order to determine the best way to deal with them.

## SUMMARY

The future of waste disposal appears to be moving away from landfilling and incineration and toward recycling and using waste materials as a source of energy. New technology in pollution control and in energy generation techniques, such as gasification, make energy production from waste materials an environmentally acceptable alternative. Testing on ebonite, a hard rubber waste material, indicates that a high Btu gas can be produced in a reasonable residence time. Some work remains to be done to optimize operating conditions and to determine how to deal best with heavy metals and chlorine and sulfur compounds.

## REFERENCES

1. Schmitt, R.J. "Automobile Shredder Residue-The Problem and Potential Solutions," Center for Materials Production, January 1990.

TABLE 1

## EBONITE ANALYSIS

	As Det.	As-Received	MF	MAF
<u>Proximate</u>				
Moisture	1.98	2.00	N/A	N/A
Volatile Matter	37.1	37.1	37.85	44.4
Fixed Carbon	46.45	46.43	47.39	55.59
Ash	14.46	14.46	14.73	N/A
<u>Ultimate</u>				
Hydrogen	4.82	4.82	4.69	5.5
Carbon	70.34	70.34	71.76	84.18
Nitrogen	1.12	1.12	1.14	1.34
Sulfur	3.91	3.91	3.99	4.68
Oxygen	5.34	5.34	3.65	4.28
Ash	14.46	14.46	14.76	N/A

TABLE 2

## PROXIMATE ANALYSES OF EBONITE/CATALYST MIXTURES

	Ebonite/10% CaCO <sub>3</sub>	Ebonite/10% K <sub>2</sub> CO <sub>3</sub>
Moisture	1.70	2.76
Volatile Matter	36.53	36.97
Fixed Carbon	39.77	37.64
Ash	22.00	22.66

TABLE 3

## EBONITE PARTICLE-SIZE DISTRIBUTION

Tyler Mesh Size	Weight Percent Retained
4	1.38
6	8.01
8	15.73
20	31.00
60	21.32
325	14.79
-325	7.71

TABLE 4

GAS ANALYSIS<sup>1</sup>

H <sub>2</sub>	50.1
CO <sub>2</sub>	28.8
H <sub>2</sub> S	0.9
CH <sub>4</sub>	4.5
CO	15.0

<sup>1</sup> Without nitrogen fluidizing gas.

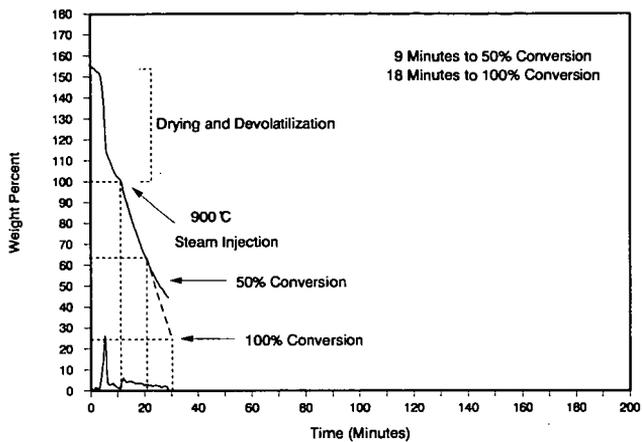


Figure 1. Steam reactivity of ebonite at 900°C.

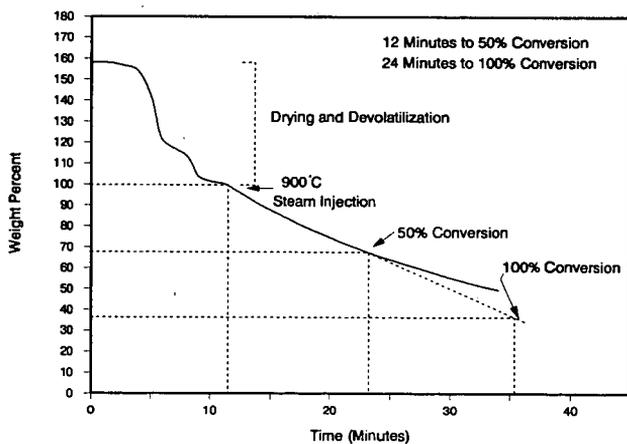


Figure 2. Steam reactivity of ebonite and calcium carbonate catalyst at 900°C.

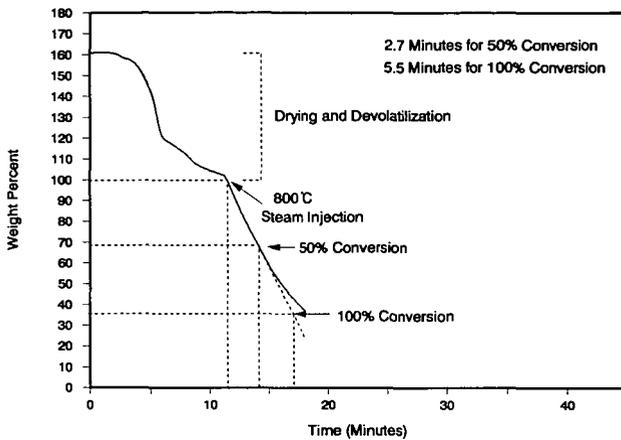


Figure 3. Steam reactivity of ebonite and potassium carbonate catalyst at 800°C.

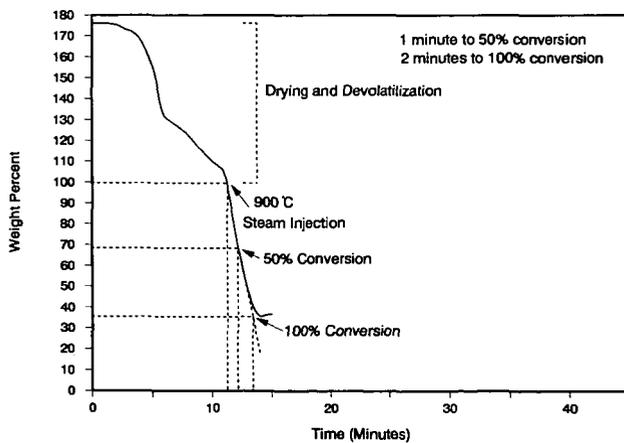


Figure 4. Steam reactivity of ebonite and potassium carbonate catalyst at 900°C.

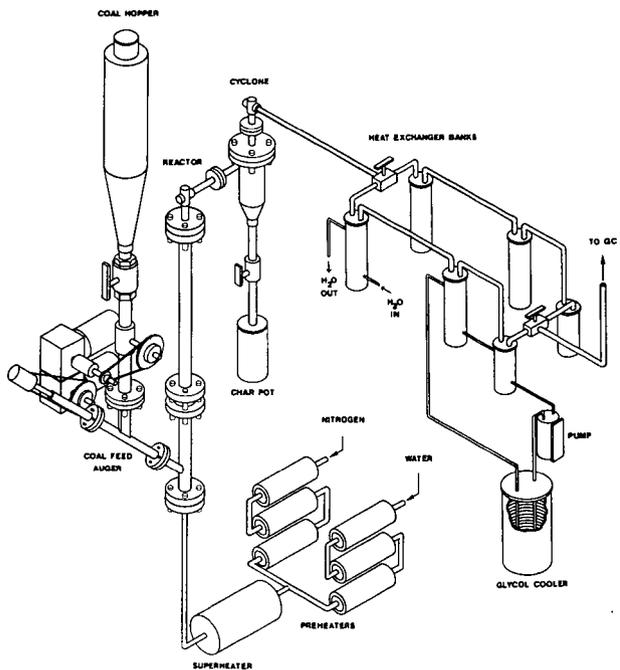


Figure 5. 1-4 lb/hr CFBR schematic.