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AN INVESTIGATION INTO THE SYNGAS PRODUCTION FROM MUNICIPAL SOLID WASTE (MSW) GASIFICATION UNDER VARIOUS PRESSURES AND CO_2 CONCENTRATION ATMOSPHERES

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ABSTRACT

The Municipal Solid Waste (MSW) gasification process is a promising candidate for both MSW disposal and syngas production. The MSW gasification process has been characterized thermo-gravimetrically under various experimental atmospheres in order to understand syngas production and char burnout. This preliminary data shows that with any concentration of carbon dioxide in the atmosphere the residual char is reduced about 20% of the original mass (in an inert atmosphere) to about 5%, corresponding to a significant amount of carbon monoxide production (0.7% of CO was produced from a 20mg sample with 100ml/min of purge gas at 825°C).

Two main steps of thermal degradation have been observed. The first thermal degradation step occurs at temperatures between 280~350°C and consists mainly of the decomposition of the biomass component into light C_{1-3}-hydrocarbons. The second thermal degradation step occurs between 380~450°C and is mainly attributed to polymer components, such as plastics and rubber, in MSW. The polymer component in MSW gave off significant amount of benzene derivatives such as styrene. In order to identify the optimal operating regime for MSW gasification, a series of tests covering a range of temperatures (280~700°C), pressures (30~45 Bar), and atmospheres (100% N2, 0~20%CO_2+Bal. N_2 with/without steam) have been done and the results are presented here.

1. INTRODUCTION

As the world looks to manage solid waste and reduce greenhouse gases, an integrated approach to waste management should be considered. In 2006, 251 million tons of MSW was generated in the U.S. 138.2 million tons of this waste (55.1% of total generation) was landfilled and more than 31 million tons (12.4% of total) of materials were combusted with energy recovery[1, 2]. In 2003 Waste-to-Energy (WtE) facilities converted MSW into 440 trillion BTU of usable energy, which was approximately 0.4% of total U.S. demand. While Combustion techniques are widespread and well known throughout the WtE industry, gasification is a promising alternative technology, which may be attractive in that the products other than heat and energy are produced.

The gasification process transfers some of the heating value of the solid fuel to a gaseous energy carrier, due to the advantages of a gas over a solid fuel[3]. For example, gases are easy to clean, transport and to combust efficiently with less excess air and less lower levels of some types of pollutants[4]. Many studies have been carried out on gasification of various feedstocks from biomass[5, 6] and coal[4, 7-12]. Recently, according to tremendous consumption of polymer (plastics & rubbers), the gasification is appearing as an interesting solution for utilization of plastic and rubbery wastes even though there has not been much work done at the pilot scale. For example, Sumitomo Metals in Japan successfully produced dioxin-free and high calorie purified gas via Poly-Vinyl Chloride (PVC) gasification[12].

Due to the heterogeneous MSW matrix, however, only limited information on MSW gasification is available even though the gasification process for each components of MSW has been investigated[13-15]. Indeed, MSW is composed of ~60% biomass or biomass derived components including yard trimmings, wood, food scraps, and paper, which can be an advantage in terms of carbon credit. Thus, MSW conversion via gasification or combustion should be encouraged as part of a strategy for CO_2 abatement.

The objective of this work is to investigate the MSW gasification process, and enhance the syngas production using CO_2 as a feedstock[16]. Thus, MSW samples have been investigated thermo-gravimetrically under various CO_2 concentrations. In order to extend this understanding to a more

practical level, MSW was gasified using a Drop Tube Reactor (DTR) by controlling experimental parameters including temperature (500~1000˚C) and atmosphere (0~30% CO2 with steam). In addition, the MSW gasification under various pressures (30~50 Bar) with a Parr pressure reactor was assessed.

The release of all chemicals from the TGA, DTR and Parr Pressure Reactor have been analyzed using a Gas Chromatograph/Mass Spectrometry (GC/MS) and μ-GC in order to determine not only the overall MSW gasification process, but also syngas yield enhancement by CO_2 injection. Lastly, the liquid portion of the gasification products including tar and oil was analyzed and quantified using the GC/MS.

2. EXPERIMENTAL

MSW collected from NYC was manually separated, dried and pulverized by Thomas® Wiley Mill. Individual components were mixed according to the average MSW composition outlined by the Department of Energy (DOE) report and summarized in Figure 1. The volatile matter content in the dry MSW sample using ASTM D-3174 was 60.89%.

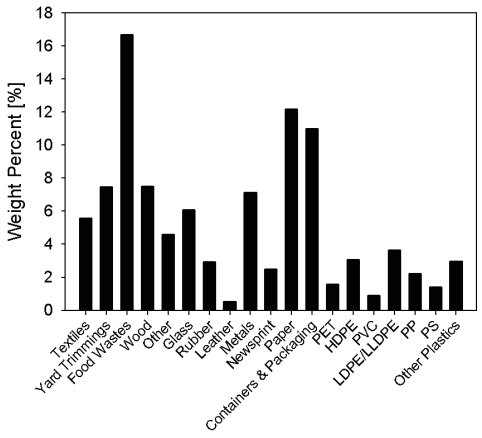

Figure 1.MSW weight percents by categories

Samples of 20 mg to 25 mg of the mixed waste were first thermo-gravimetrically analyzed with a Netzsch STA 409 PC/4/H TGA unit with atmospheres ranging from 0% to 20% CO_2 with a balance of N_2 for a total flow of 100 ml/min. The sample was heated from ambient temperature to 1000°C at a rate of 10°C/min. After the decay curves were determined the TGA gas outlet was connected to a GC/MS (Agilent 9890/5973) and μ-GC (Agilent 3000). The sample gas outlet from the GC/MS was attached to a valve followed by a sample pump to ensure an end flow rate of 100 ml/min to avoid major pressure drops along the system.

The Drop Tube Reactor (DTR) used was made of quartz tubing (GE type 214, *National Scientific Company*) and was 2 m long, 25.4 mm OD (1inch) and 19 mm ID (0.75inch). 25.4mm OD Stainless Ultra Torr® Vacuum Fitting (Swagelok SS-16-UT-6) was used for airtight connections. The DTR was vertically secured in the center of a furnace using a 25.4 mm OD bulkhead union (Swagelok ss-1610-61). The furnace used was a split-hinged vertical furnace with 5 temperature zones (*SV Furnace MA #100087, Mellen Inc.*). The temperature was simultaneously compared with S-type thermocouples implemented in each zone of the furnace to maintain the target temperature. In order to minimize heat transfer from the reactor and secure the quartz tubing an insulation collar (*Duraboard high temperature insulation*) was inserted into the top and bottom of the furnace. The overall experimental scheme is illustrated in Figure 2, and the temperature profiles of DTR are shown in Figure 3. The temperature deviation in the DTR is less than ±8˚C and the temperature deviation between the DTR and furnace wall is less than ±3˚C. The MSW sample was introduced continuously to the DTR using screw feeder (WLS-0.3).

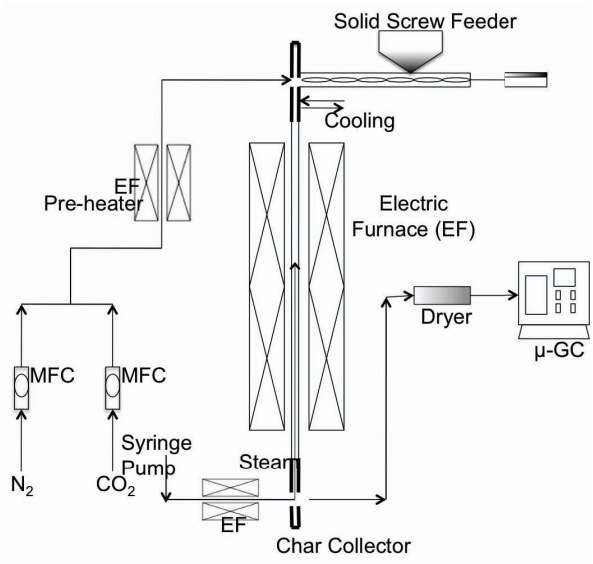

Figure 2.Schematic diagram of drop tube reactor

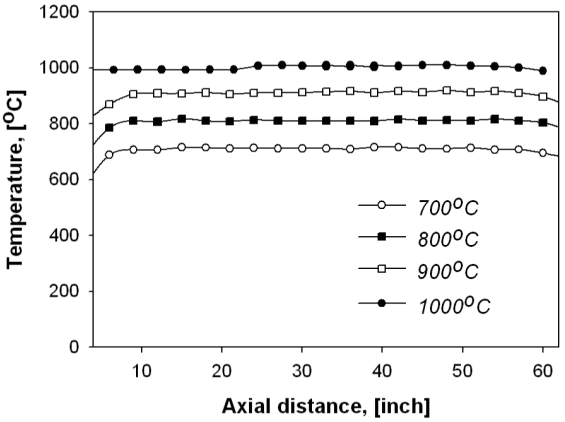

Figure 3.Temperature profiles in the DTR reactor

All gases used for the experiments were ultra high purity from *TechAir* (New York). All gas flow rates were set using an Aalborg Thermal Mass Flow Meter (GFCS-01038) certified by *Alborg ® Inc* and the flow rate were also checked with Bubble-O-Meter and Alltech Digital Flow Check™ to ensure accurate flow control. The steam was generated using an electric furnace at a temperature of 270˚C and the steam flow rate was controlled using syringe pump (*Cole-Parmer® single syringe infusion pump, EW-74900-5*).

The gasification under pressure (35~45 Bar) was carried out with Parr Instruments Model 4642 vessel assembly. 5g of MSW sample and 5g of distilled water were initially loaded in the reactor vessel. A pressure transducer atop the vessel reads the reactor pressure and the reactor temperature is read by a J-type thermocouple inserted into a thermo-well inside of the vessel. The thermocouple also serves as the reference for the PID temperature controller, Par Instrument Model 4835. The temperature controller serves to heat and control the temperature via a Parr Instruments heater assembly Model 4913 which encases the reactor vessel.

3. RESULTS AND DISCUSSION

Figure 4 depicts representative data obtained from a series of TGA experiments with the MSW sample over a temperature range from ambient and 1000˚C at a heating rate of 10˚C/min under various concentrations (0~20% CO_2/Bal. N_2).

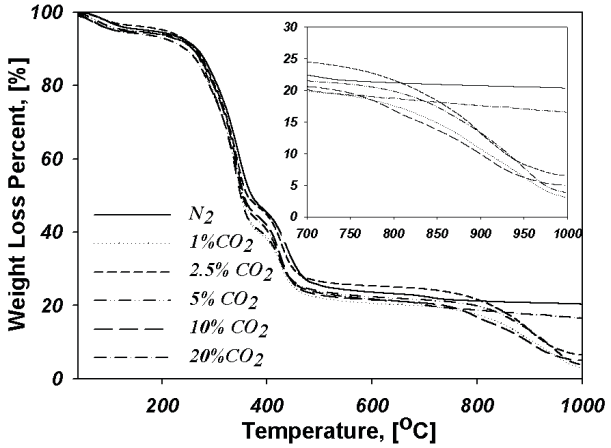

Figure 4.Representative thermograms with MSW under various CO_2 concentrations

As shown in Figure 4, there are two main thermal degradation steps and there is ~20% residual char from MSW in a N_2 atmosphere. The first thermal degradation step at temperature of 280~350˚C consist of the decomposition of the biomass component in MSW and light $C_{1\text{-}3}$-hydrocarbons are observed in the product gas[6]. The second thermal degradation step at temperature 380~450˚C is mainly attributed to the polymer components, such as plastics (Poly-Styrene) and rubber (Styrene-Butadiene Rubber), in MSW[17-22]. The polymer component in MSW gave off significant amounts of benzene derivatives such as styrene. In addition, the residual char was burned in with air in the TGA. The black residual was clean after that test and GC measurement taken during the test yield only CO and CO_2, which indicate the black residual is indeed carbon.

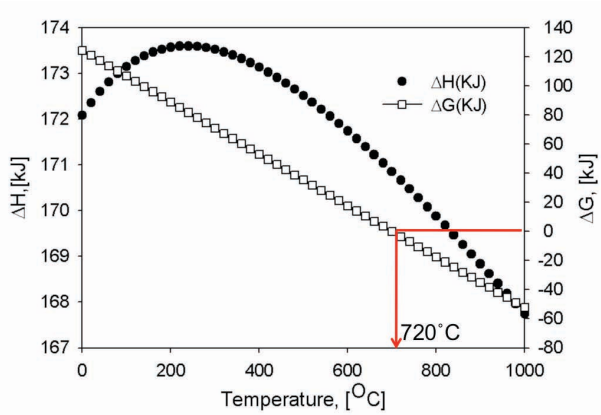

Figure 5.Gibbs free energy calculation using HSC

As shown in Figure 4, the black residual, however, decreases significantly under CO_2 atmosphere. The insect in Figure 4 shows a zoomed in section of the high temperature decay. In addition, the decomposition rate of carbon is proportional to CO_2, indicating a reaction between CO_2 and carbon, Boudouard reaction

$$C + CO_2 \leftrightarrow 2CO \qquad \text{Equation 1}$$

This can be evidenced by the Gibbs free energy calculation using HSC software package (chemical reaction and equilibrium software) in that negative Gibbs free energy indicates a spontaneous reaction. Moreover, the temperature of carbon decomposition (≥720˚C) in Figure 4 corresponds very well to that shown in Figure 5.

However, this TGA experiment does not truly represent MSW gasification conditions due the inability of the TGA to handle large sample sizes, continuous MSW feed, steam injection, and ballistic MSW heating rate (500˚C/sec). Thus, a Drop Tube Reactor (DTR) has been utilized in order to overcome these limitations. The MSW was fed continuously at the rate of 0.5g/min along with 0.5 g/min of water in order to meet a 1:1 MSW to steam mass ratio under various CO_2 concentration (10~30%) atmospheres. A typical gas evolution plot showing the distribution of the four gases that are monitored (hydrogen, methane, carbon monoxide, and ethylene) under various CO_2 concentration atmospheres with DTR were shown in Figure 6.

One interesting feature in Figure 6 is the concentration of CO when CO_2 is present. For example, the concentration of CO under CO_2 (10~30%) atmospheres is higher than that of CO under N_2 atmosphere, which is more apparent (~factor 2) in lower temperature range from 500˚C to 700˚C. CO generation enhancement at a low temperature range is

indicative of a significant reaction generating CO and H_2, which can be a reforming reaction

$$C + H_2O \rightarrow CO + H_2 \qquad \text{Equation 2}$$

However, the H_2 concentration is not much different in the CO_2 addition experiment atmospheres. This observation has two explanations. First, the various metals (iron, zinc, nickel, copper, aluminum) in the MSW sample catalyze the Boudouard reaction. Second, the char-burnout reaction due to oxygen from MSW

$$C + \tfrac{1}{2}O_2 \rightarrow CO \qquad \text{Equation 3}$$

should be considered. In addition, the generation of CH_4 from the gasification of MSW could be explained three reactions as follow;

$$2CO + 2H_2 \rightarrow CH_4 \qquad \text{Equation 4}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \text{Equation 5}$$

$$C + 2H_2 \rightarrow CH_4 \qquad \text{Equation}$$

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The most interesting observation in Figure 6 is the concentration of CO and H_2. For example, high temperature is a favorable condition for generating CO. In addition, the generation of H_2 (Equation 2) should be suppressed by the generation of CO (Equation 1). However, the concentration profiles of CO and H_2 in Figure 6 do not reflect the Boudouard reaction, which means that the MSW sample size is too coarse to have enough a residence time in the DRT. In order to further investigate this observation, steam gasification under CO_2 atmosphere with Montana coal (Sub-Bituminous coal, 170 mesh size (0.0088mm)) having a 5-6 second residence time has been carried out in order to investigate the char reaction under CO_2 atmosphere. The experimental conditions were 0.5g/min of MSW, water, and CO_2 each.

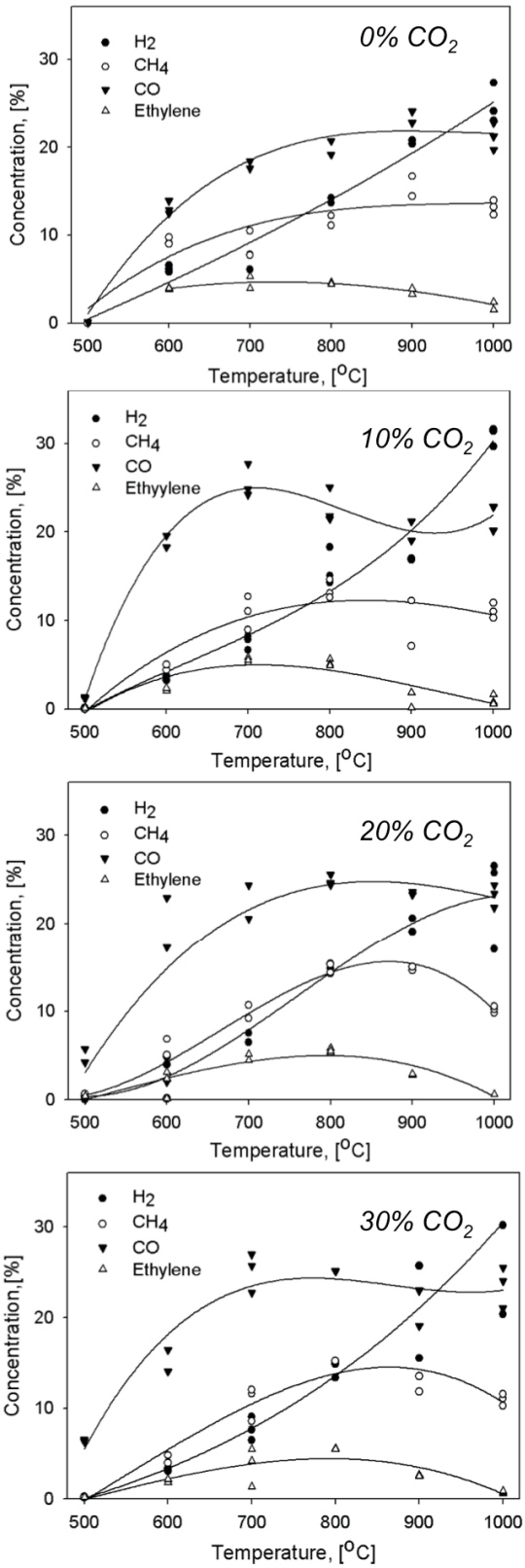

Figure 6.Concentration profiles of H_2, CH_4, CO, and Ethylene in various CO_2 Concentrations

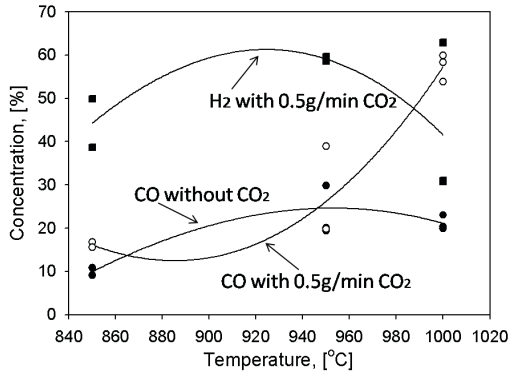

Figure 7.Concentration profiles of CO and H_2 with/without CO_2

As evidenced in Figure 7, the concentration profile of CO exponentially increases when CO_2 is present, which can be a solid evidence of the Boudouard reaction. In addition, the Boudouard reaction (Equation 1) competes with the Reforming reaction (Equation 2) as discussed above. Thus, this observation shows that the CO_2 injection can enhance the MSW gasification. Especially in char burnout modifications are being made to the DTR and MSW sample size to achieve longer residence time. Moreover, all experimental findings suggest that the MSW gasification could be an environmentally benign way of managing waste, and producing a syngas which gives options for the abatement of Green House Gas emissions (GHG) using CO_2 as a feedstock.

Lastly, MSW gasification tests under high pressure (35~45 Bar) were done to investigate the pressure dependence[9, 11, 23]. The high-pressure tests were done at a temperature of 680˚C with a batch feeding of 5 g of MSW and 5 g of water with various CO_2 (0~30%) concentrations. The final pressure was varied even though the initial condition (10 bar) for all experiments were the same. This observation means that the reaction rate is proportional to the reaction rate.

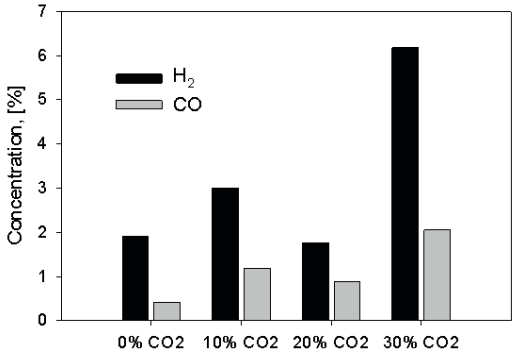

Figure 8.Concentration of H_2 and CO under pressure and various CO_2 concentrations

As shown in Figure 8, the concentration of H_2 and CO increases when CO_2 is present even in high pressure, which is consistent with the observations from low-pressure tests in Figure 6. These tests produced a liquid oil as well as gaseous product. The liquid oil from the Parr pressure reactor has been analyzed using a GC/MS and the representative chromatograms are presented in Figure 9.

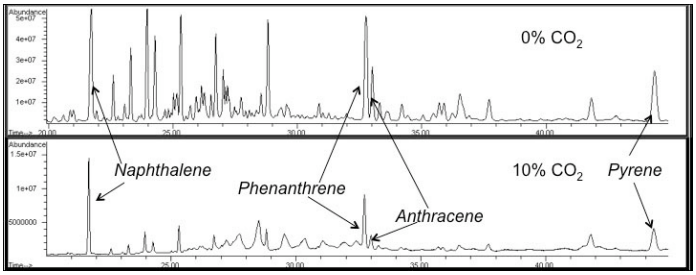

Figure 9.Representative chromatograms of liquid oil from the Parr pressure reactor

Two representative chromatograms of liquid oil under 0% CO_2 and 10% CO_2 are shown in Figure 9. All chemical species in the chromatogram in Figure 9 are Polycyclic Aromatic Hydrocarbons (PAHs) or substituted PAHs. For example, naphthalene, 1H-indene, 1-methyl-naphthalene, biphenyl, acenaphthylene, fluorene, phenanthrene, and pyrene are observed. No paraffin and olefin hydrocarbons are observed from the liquid oil. One significant observation is the relative concentration of two-, three-, four-ring PAHs. As evidenced in Figure 9, the peaks (substituted naphthalene, 1H-indene, biphenyl, acenaphthylene, and fluorene) between naphthalene and phenanthrene are significantly reduced in that peak area is proportional to the concentration of chemical species. This observation suggests that CO_2 injections during the MSW gasification could be a way to reduce the generation of tar or coke. Moreover, this observation indicates that the CO_2 injection in the MSW gasification process may block the pathway of the growth of PAHs by inhibiting the Reforming reaction in Equation 2.

4. CONCLUSIONS

The MSW gasification process under various CO_2 conditions has been investigated in order to enhance the gasification product yield. All experimental findings evidenced that CO_2 injection enables further char reduction, and produces a significantly higher concentration of CO. In addition, CO_2 injection decreases the levels of PAHs, which can be directly related to tar and coke formation during the gasification process. Thus, the enhancement of MSW gasification by utilizing CO_2 provides for significant improvements for the Integrated Gasification Combined Cycle (IGCC) in the Waste-to-Energy industry

5. AKNOWLEGEMENT

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