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## Transforming Municipal Solid Waste (MSW) into Fuel via the Gasification/Pyrolysis Process

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### ABSTRACT

Municipal solid waste (MSW) gasification/pyrolysis enhancement using CO<sub>2</sub> as gasification medium has been studied to understand the performance under various reaction conditions. MSW gasification/pyrolysis has been characterized thermo-gravimetrically under various atmospheres covering the gasification/pyrolysis process, which has been used as a basis for scale-up experimental work using a flow-through reactor (FTR) and drop tube reactor (DTR) (0.5 g/min of sample, 4-5 sec residence time, 500°C-1000°C). For example, FTR has been used to carry out the fast pyrolysis process having a nominal heating rate of 800°C/min. Oils produced from the FTR have been condensed and analyzed with GC/MS. Among identified chemical species in the pyrolysis sample, the 10 most abundant compounds (benzene, toluene, styrene, limonene, 2,3-dimethyl-1-heptene, benzoic acid, ethylbenzene, indole, xylene, and d-allose) in the pyrolysis oil sample were determined and quantified. These 10 abundant chemical species are substantially reduced in the presence of CO<sub>2</sub>. This leads to a substantial increase of C<sub>1-5</sub> hydrocarbons in gaseous (non-condensable) products and a reduction of pyrolysis oil (~20%) as well. In addition, MSW samples have been tested in the DTR at a temperature range from 500°C and 1000°C under various atmospheres with CO<sub>2</sub> concentrations of 0% and 30%. The release of all chemical species from the DTR was determined using  $\mu$ -GC. For example, CO (~30%), H<sub>2</sub> (~25%), and CH<sub>4</sub> (~10%) under the presence of CO<sub>2</sub> were generated and introducing CO<sub>2</sub> into the gasification process substantially enhanced syngas production.

Finally, steam gasification using different ratios of biomass to polyethylene has been explored to better understand the enhanced steam gasification of MSW that is mostly composed of biomass and polymer. Overall thermal degradation trend is the similar, but steam gasification of MSW needs a relatively long residence time and high temperature as compared to biomass.

### INTRODUCTION

The amount of MSW generated worldwide in 2006 was 2.02 billion tons, 251 million tons of which was generated in the U.S., with 138.2 million tones (55.1% of total generation) landfilled[1]. Landfills are reported as the largest single source of anthropogenic methane emission in the U.S., accounting for 132 million tons of CO<sub>2</sub> equivalents in 2005, which was nearly 2% of total GHG emission[1-3].

The shortage of fossil fuel and the environmental problems arising from their use in combustion processes have attracted great attention in relation to the exploitation of clean renewable energy sources[4-7]. For example, thermo-chemical transformation via pyrolysis/gasification of MSW is desirable in terms of an essential part of greenhouse-gas-neutral energy production as well as sustainable waste management.

Pyrolysis[8-12], the thermal decomposition of materials in absence of oxygen, has been used to convert MSW to a blend of solid, liquid, and gaseous products. The role of pyrolysis is important in the thermal processes as it converts the raw material into reactive intermediate products: char, light molecular weight gases and heavy molecular weight compounds that condensed when cooled down. For example, in conventional slow

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pyrolysis, a solid (char) is obtained; however, the rapid heating of a carbonaceous feedstock (fast pyrolysis) [13-15] results in a liquid fuel.

Gasification[8, 16-18], the transformation of the combustion value of the solid fuel to a gaseous carrier, is also an attractive technology. For instance, organic matters in MSW are volatilized but not combusted, and the inorganic remains form an inert residue. The resultant gas, or synthetic gas, is a mixture of primarily CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, and non-methane hydrocarbons. It can be used directly as a fuel, or as feedstock for production of chemical such as hydrogen or methanol.

While pyrolysis/gasification of coal and woody biomass are in commercial use, pyrolysis/gasification of MSW for feedstock production is not yet to be commercially utilized due to the heterogeneous matrix of MSW. Thus, the objective of this study is to characterize properties of pyrolysis/gasification products from MSW, as part of fundamental investigation for pyrolysis of MSW. In addition, the impact of CO<sub>2</sub> co-feed on the thermal process was also investigated for the enhancement or modification of the products from the pyrolysis/gasification process.

## EXPERIMENTAL

All gases used in the experiments were of ultra high purity and obtained from TechAir (New York). All gas flow rates were set using an Aalborg Thermal Mass Flow Meter (GFCS-01038). The steam flow rate was controlled using a syringe pump (Cole-Parmer® single syringe infusion pump, EW-74900-5), with the steam generated using a heat tape (Omega STR201-060) and cartridge heater (CIR-1013/120V) at the temperature of 300°C.

A Netzsch STA 409 PC/4/H TGA unit and Du Pont 951 capable of TG and differential temperature analysis (DTA) measurements were used. The TGA test was performed over the temperature range 20 to 1000°C under various atmospheres and heating rates.

A tubular reactor (TR), made of 1 inch OD quartz tubing (Chemglass® CGQ-0800T-13) and 1 inch Stainless Ultra-Torr® Vacuum Fitting (Swagelok SS-4-UT-6-400), was used to maintain airtight conditions. The required experimental temperature was achieved using a split-hinged furnace (Multiple Unit, Hevi Duty Electric Company) over the temperature range 500 to 1000°C, with the temperature simultaneously compared with an S-type thermocouple reading to ensure the target temperature had been met.

A DTR, made of 2m long, 25.4mm OD, and 19mm ID quartz tubing (Chemglass® CGQ-0207), was used. 25.4mm OD stainless Ultra Torr® Vacuum fitting (Swagelok SS-16-UT-6-400) was used to construct the airtight connections. The DTR was vertically secured in

the center of a furnace using a 25.4mm OD bulkhead union (Swagelok SS-1610-61). An insulation collar (Duraboard high temperature insulation) at the top and bottom of a furnace was used to block heat transfer during operation and to secure quartz tubing. The required experimental temperature was achieved using a split-hinged vertical furnace containing 5 temperature zones (SV Furnace MA #100087, Mellen Inc.), with the temperature simultaneously compared with S-type thermocouples located in each zone of the furnace to maintain the target temperature. The MSW sample was introduced continuously to the DTR using a screw feeder (WLS-0.3).

The effluent from the TGA unit, TR and DTR was sent to either a  $\mu$ -GC (Agilent 3000A) or GC/MS (Agilent 9890/5973) for identification and quantification of chemical species. A sampling pump (B19310TM5, Air Dimensions Inc.) capable of 100ml/min was used. The residual from a series of TGA tests was analyzed using energy dispersive x-ray spectroscopy (EDX or EDS) to detect the elements.

MSW, collected from New York City (NYC), was manually separated, dried and pulverized using a Thomas® Wiley Mill (size of ~0.5mm). Individual components were mixed according to the average MSW composition outlined by the department of energy (DOE) report; 5.57% textiles, 7.56% yard trimming, 16.68% food waste, 7.51% wood, 4.85% rubber, 0.88% leather, 11.85% metals, 4.13% news print, 20.2% paper, 18.24% containers and packaging, 2.58% PET, 5.11% HDPE, 1.15% PVC, 6.07% LDPE, 3.36% PP, and 2.34% PS. Processing of the biomass (oak wood) and coal (sub-bituminous coal) followed the same procedure as that used for the MSW.

## RESULTS AND DISCUSSION

Representative thermo-grams from a series of TGA experiments with MSW over a temperature range from 20°C to 1000°C at a heating rate 10°C/min under various CO<sub>2</sub> concentrations.

There are two main thermal degradation steps. For example, the first and second thermal degradation step are at the temperature range of 280~350°C and 380~450°C, respectively. These two thermal degradations steps are distinctive in terms of chemical species evolved from each step. For example, the first step mainly gave off light hydrocarbons (C<sub>1-3</sub>). The benzene derivatives, such as styrene, was evolved from the second step. These benzene derivatives would be mainly attributed to the polymer components, such as plastics (poly-styrene (PS)) and rubber (styrene-butadiene rubber (SBR)), in MSW. Thus, the first and second thermal decomposition step are mainly attributed from biomass and polymer, respectively, in MSW[19, 20].

One noticeable feature in Figure 1 is ~20% residual only in a N<sub>2</sub> atmosphere. EDX analysis with the residual has been carried out and EDX test confirms that the residual is mostly carbon. The black residual, however, decreases significantly under a CO<sub>2</sub> atmosphere, which is proportional to CO<sub>2</sub> concentration. This can be indicative of a reaction between CO<sub>2</sub> and carbon, such as Boudouard reaction.

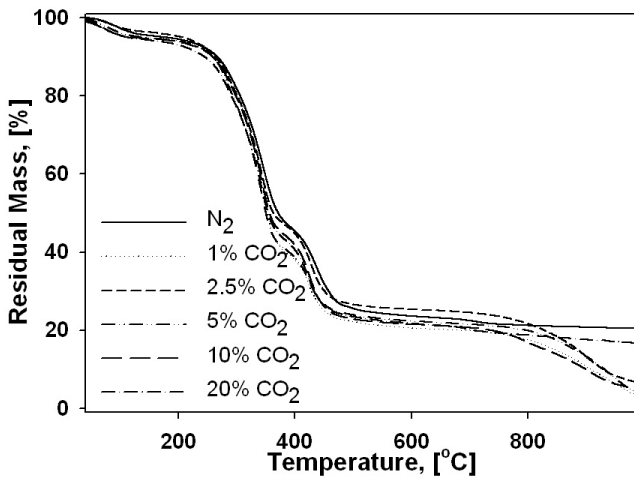


Figure 1. Representative thermograms with MSW under various CO<sub>2</sub> atmospheres

More achievable mass conversion through the Boudouard reaction is desirable because CO<sub>2</sub> can be used as a chemical feedstock to achieve high thermal efficiency, which directly leads to an environmental benefit. However, as shown in Figure 1, no discernible impact of CO<sub>2</sub> co-feed was observed on the pyrolysis of MSW due to the small MSW sample used in the TGA analysis.

In case of the pyrolysis of coal, the thermal degradation rate shown in Figure 2 is discernibly slower than that of MSW. For example, the final mass conversion of coal, even at a heating rate of 2 °C/min cannot reach the maximum achievable mass conversion. This is very apparent compared with the thermogram of coal under a pure oxygen environment and the same TGA conditions. Thus, exploiting MSW as pyrolysis and gasification feedstock can be a feasible alternative to coal as the pyrolysis can be carried out at a relatively low temperature and with a short residence time. This advantage over coal can be directly connected with environmental benefits.

Thus, in order to obtain more detailed information of the pyrolysis of MSW, a scale-up experiment with a tubular reactor (TR) has been carried out to overcome the uncertainty arising from the heterogeneous matrix of MSW. The 10 most abundant chemical species, based

on peak areas, in the pyrolysis oil samples were determined and analyzed. The most abundant identified chemical species, based on peak areas, in the pyrolysis oil samples were determined and analyzed; benzene, styrene, toluene, limonene, 2, 3-dimethyl-1-heptene, benzoic acid, ethyl benzene, indole, p-xylene and d-allose. Most of these compounds are aromatic hydrocarbon compounds. Especially, 2, 3-dimethyl-1-heptene is the closest candidate for a gasoline type fuel. While aromatics may not be the best starting point for fuel oil, this process may be better suited for manufacturing feedstock chemicals.

In addition to these chemical species, other complex aromatic compounds, having two, three and four-ring, were also observed. One interesting observation was that the introduction of CO<sub>2</sub> to the pyrolysis process served to minimize the formation of char and tar (~30%). A significant amount of ring structure breakdown occurred in the presence of CO<sub>2</sub>, which suggests that the pyrolytic products can be tailored to meet any purpose.

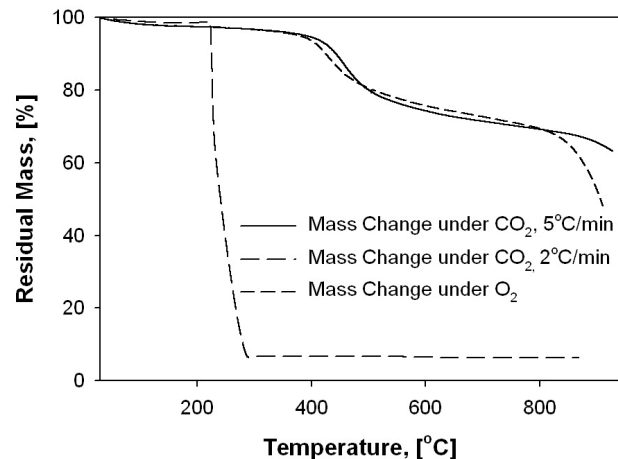


Figure 2. Representative thermograms with coal under different heating rates and atmospheres.

Pyrolysis is the first step in the gasification process, which can then be followed by partial oxidation of the primary product. In addition, the identified impact of the CO<sub>2</sub> co-feed on the pyrolysis would enhance the gasification process. Thus, the steam gasification of biomass (oak wood) was followed thermo-gravimetrically to investigate the impact of the CO<sub>2</sub> co-feed on the gasification process. For example, the TGA test with biomass (oak wood) was carried out a heating rate of ~950 °C min<sup>-1</sup> and temperature of 950 °C. The thermograms in Figure 3 indicate that the mass decay patterns were not much different compared to pyrolysis. However, no further information on the thermograms can be procured without quantifying the chemical species.

Thus, to obtain more detailed information on the impact of the CO<sub>2</sub> co-feed on the gasification process; scale-up work was performed using a TR. The scale-up experimental work was conducted under the same experimental conditions used in Fig. 3. The observed concentration profiles of major chemical species (H<sub>2</sub>, CO, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub>) are illustrated in Fig. 4.

The most interesting observation in Fig. 4 is the substantial enhancement of CO, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> produced in the presence of CO<sub>2</sub>. For example, the concentration of CO in the presence of CO<sub>2</sub> increases by a factor of 2. The generations of CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> were also enhanced, albeit it not discernibly. In addition, the tar collected in the presence of CO<sub>2</sub> was substantially decreased (~40%). This substantial reduction in the production of tar can be directly related to the enhanced production of CO, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub>. For example, carbon dioxide expedites to crack condensable hydrocarbons, such as tar. In addition, this cracking behavior is consistent with the previous discussion. However, the concentration profile of H<sub>2</sub> did not show any enhancement, which was similar to the other major chemical species. This can be explained by the generated C<sub>1-2</sub> hydrocarbons consuming the generated hydrogen during the gasification process; also, the

dilution factor cannot be excluded.

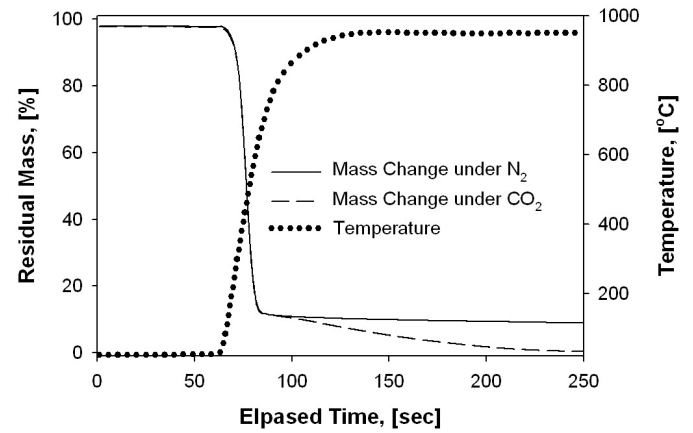


Figure 3. The thermogram of the steam gasification of biomass (oak wood) at a heating rate of ~950°C min<sup>-1</sup> and temperature of 950°C under a N<sub>2</sub> and (30%CO<sub>2</sub>/Bal.N<sub>2</sub>) atmospheres.

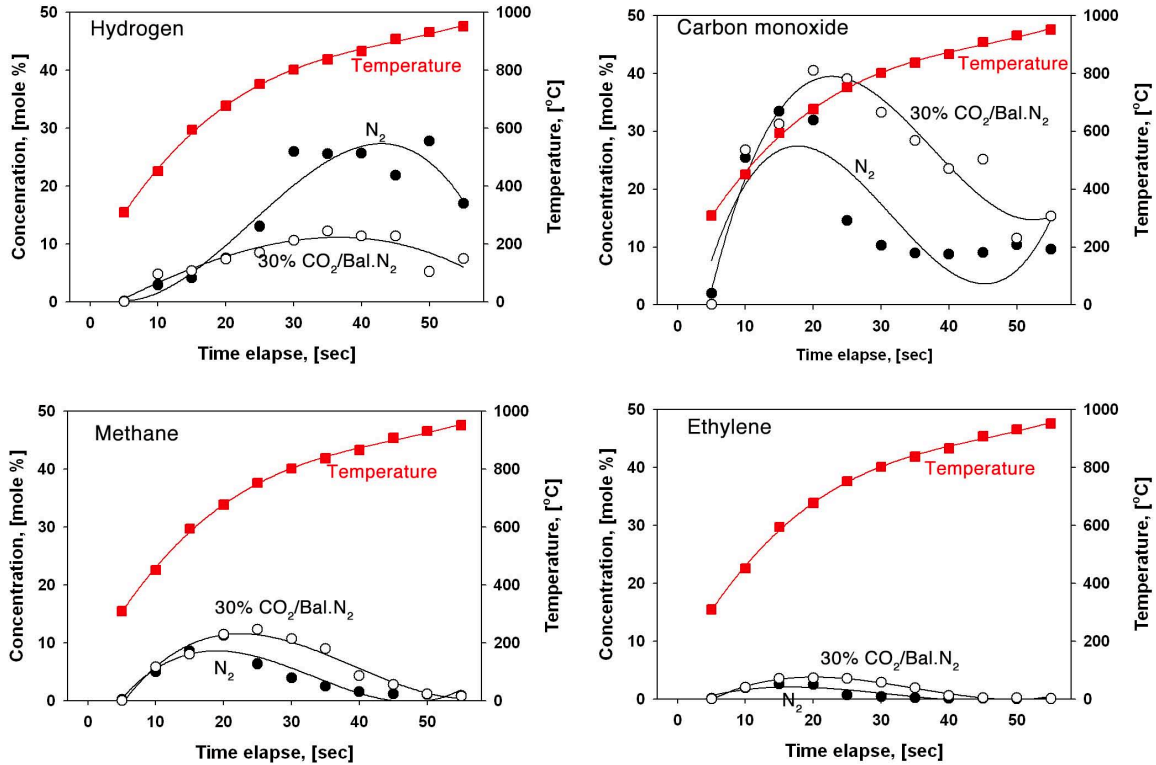


Figure 4. The concentration profiles of major chemical species from the gasification of biomass (oak wood) at a heating rate of ~950°C min<sup>-1</sup> under N<sub>2</sub> and 30% CO<sub>2</sub>/Bal.N<sub>2</sub> atmospheres

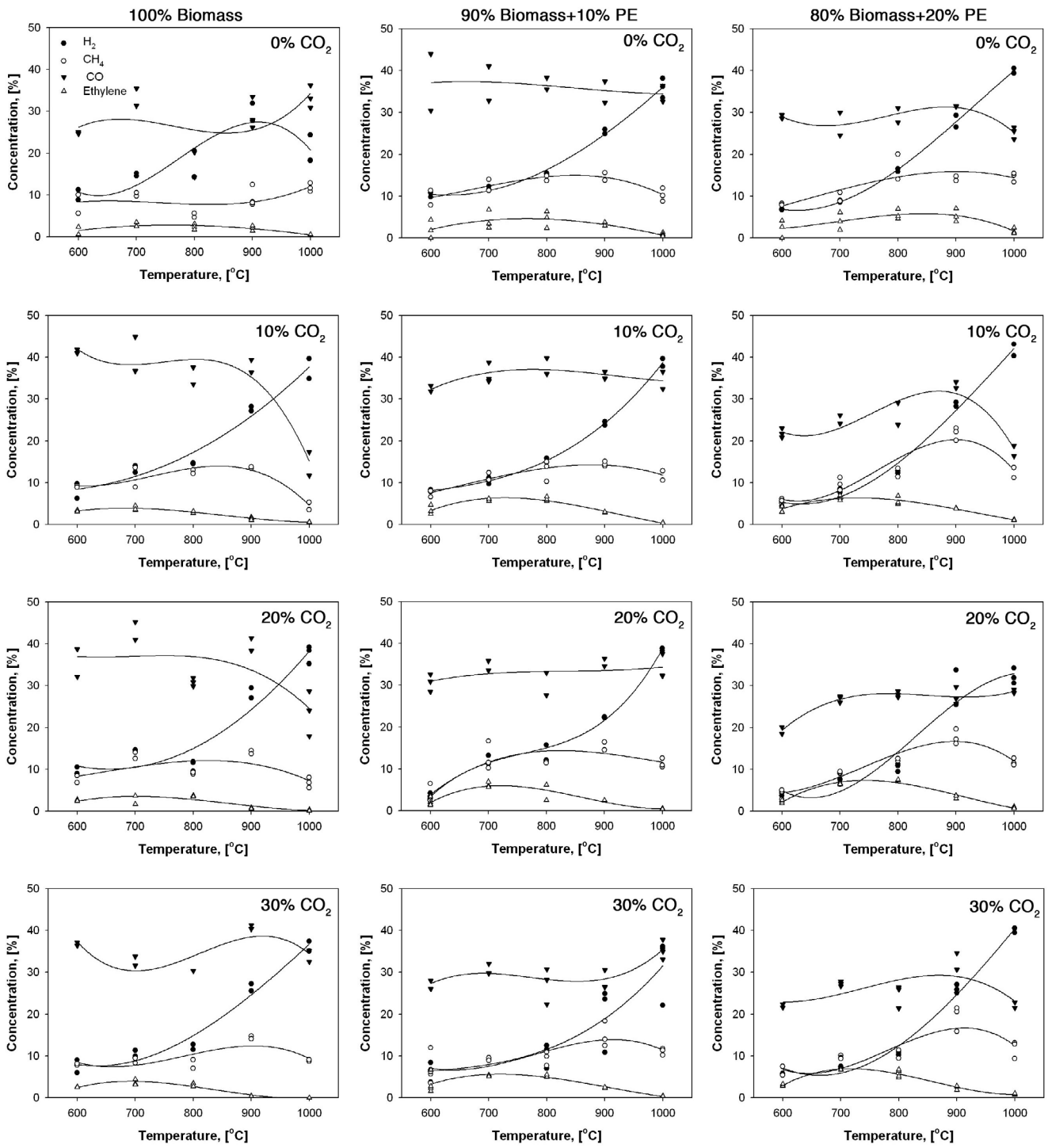


Figure 5. Concentration profiles of H<sub>2</sub>, CH<sub>4</sub>, CO, and C<sub>2</sub>H<sub>4</sub> from steam gasification of different ratios of biomass to polymer (PE) in various CO<sub>2</sub> atmospheres

All the experimental work undertaken using TGA and TR does not fully represent the real gasification conditions due to the inability of the TGA and TR to handle continuous feedstock feed and because of the ballistic heating rate ( $\sim 900^{\circ}\text{C sec}^{-1}$ ). Thus, a drop tube reactor (DTR) was utilized in order to overcome these experimental limitations. A biomass sample (oak wood) was fed continuously at a rate of  $0.5\text{g min}^{-1}$ , along with  $0.5\text{g min}^{-1}$  of water, under various  $\text{CO}_2$  concentration (0~30%) atmospheres. Typical gas evolution plots, showing the distribution of the four monitored gases ( $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$ ) within the DTR are shown in Fig. 5.

The concentration profiles of the major chemical species were almost consistent with the experimental work conducted using a TR. For example, the substantially enhanced generation of  $\text{CO}$  also occurred in the presence of  $\text{CO}_2$ . In addition, Fig. 5 shows that the

generation of  $\text{H}_2$  was favorable with a high temperature regime, which is also consistent with the experimental findings shown in Fig. 4. However, one interesting observation in Fig. 5 is the concentration of  $\text{CO}$  with a high temperature regime, which decreases significantly as the concentration of  $\text{H}_2$  increases, as shown in Fig. 5. However, the magnitude of this  $\text{CO}$  reduction substantially decreases as more  $\text{CO}_2$  is introduced to the gasification process, as introducing  $\text{CO}_2$  to the gasification process can enhance the generation of  $\text{CO}$ . Thus, the modification of gasification products is possible by means of using different  $\text{CO}_2$  concentrations. In order to get more detailed information, all residual from DTR were analyzed with thermo-gravimetrically and all results are summarized in Table 1.

Table 1. Gasification carbon conversion efficiency at various experimental conditions

Experimental Conditions	Temperature ( $^{\circ}\text{C}$ )	Gasification Carbon Conversion Efficiency		
		100% Biomass	90% Biomass +10% PE	80% Biomass +20% PE
0% $\text{CO}_2$ + 100% $\text{N}_2$	600 $^{\circ}\text{C}$	91.59%	88.31%	87.99%
	700 $^{\circ}\text{C}$	94.76%	95.39%	92.62%
	800 $^{\circ}\text{C}$	90.87%	92.33%	93.12%
	900 $^{\circ}\text{C}$	92.70%	93.19%	93.12%
	1000 $^{\circ}\text{C}$	91.31%	92.54%	91.19%
10% $\text{CO}_2$ + 90% $\text{N}_2$	600 $^{\circ}\text{C}$	89.23%	92.82%	84.33%
	700 $^{\circ}\text{C}$	90.02%	90.23%	85.81%
	800 $^{\circ}\text{C}$	91.15%	94.90%	93.12%
	900 $^{\circ}\text{C}$	89.87%	94.48%	95.49%
	1000 $^{\circ}\text{C}$	92.78%	92.71%	91.42%
20% $\text{CO}_2$ + 80% $\text{N}_2$	600 $^{\circ}\text{C}$	87.95%	90.14%	89.51%
	700 $^{\circ}\text{C}$	93.06%	85.20%	83.51%
	800 $^{\circ}\text{C}$	92.91%	94.59%	89.98%
	900 $^{\circ}\text{C}$	92.45%	95.32%	90.27%
	1000 $^{\circ}\text{C}$	93.89%	89.10%	90.75%
30% $\text{CO}_2$ + 80% $\text{N}_2$	600 $^{\circ}\text{C}$	88.80%	93.10%	88.32%
	700 $^{\circ}\text{C}$	91.53%	89.41%	93.16%
	800 $^{\circ}\text{C}$	91.94%	87.91%	94.90%
	900 $^{\circ}\text{C}$	92.18%	93.89%	90.95%
	1000 $^{\circ}\text{C}$	92.46%	89.90%	90.23%

As shown in Table 1, all gasification conversion efficiencies indicate very small deviation even at various temperature and atmospheres. Thus, this observation suggests that more condensible hydrocarbons are generated during the gasification process with 10% and 20% polymer/Bal. biomass. The observation in Figure 5 and Table 1 suggest very important information on MSW gasification. For example, the MSW steam gasification

can be enhanced by introducing  $\text{CO}_2$  and the gasification process can be done relatively low temperature compared to conventional fuel, such as coal. In addition, MSW steam gasification can be enhanced by means of recycle or using fluidized reactor in order to increase residence time due to condensible hydrocarbon evolved from polymers in MSW.

## CONCLUSION

The impact of the CO<sub>2</sub> co-feed on the pyrolysis/gasification process of MSW has been investigated to enhance and modify the end products from the pyrolysis/gasification process. First, the CO<sub>2</sub> injected into the pyrolysis/gasification process substantially increase the final mass conversion. In addition, the introduction of CO<sub>2</sub> into the pyrolysis/gasification process enabled the hydrocarbons (tar) to be considerably reduced by means of expediting cracking; thus, exploiting CO<sub>2</sub> as a chemical feedstock for the pyrolysis/gasification process leads not only to higher thermal efficiency, but also has environmental benefits. Finally, biomass and MSW can be promising candidates as chemical feedstocks compared to coal for the pyrolysis/gasification process.

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