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Thermodynamic Simulation of Plasma Gasification for the Treatment of Solid Wastes

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Abstract Plasma gasification is an effective and environmentally friendly process for solid waste treatment and energy utilization. This study presents the extension of a model developed in our laboratory, which is able to perform a complete thermodynamic analysis of the plasma gasification process. This analysis includes prediction of the main gaseous components produced (CO, H_2, CH_4, H_2O, CO_2 and N_2), prediction of the concentrations of the impurities in the raw synthesis gas (HCl, H_2S and Cl_2) as well as energy calculations. The results of the new model, called as Modified Gasifeq, are compared against two sets of experimental data taken from the literature. In the first case the model predictions are compared against experimental data for wood gasification, while in the second with real operational experimental data from a commercially-available plasma gasification process of MSW. The comparison between the model predictions and the experimental data shows a close agreement between them. The Modified Gasifed model can be thus used as a tool for predicting the composition of the synthesis gas and serve in the design of a complete plasma gasification process of solid wastes.

Keywords: Plasma; gasification, solid waste; waste to energy.

1. Introduction

The rapid economic development has led to an annual increase in municipal solid waste (MSW), making its disposal a serious problem throughout the world. Sustainable and successful treatment of MSW should be safe, effective, and environmentally friendly. The priority sequence for an integrated MSW management is typically governed by the so-called “ladder of Lansink” (Parto *et al.*, 2007) that specifies a generally accepted hierarchy of preferred methods for dealing with waste. The top of the ladder shows prevention of waste followed by material re-use. Next is recycling -including organic treatment in case of MSW- and then is thermal treatment with energy recovery, while the lowest rung of the ladder is disposal through landfill, which is a last resort option. Unfortunately, landfill has been the practice most widely adopted. There are two main drawbacks of landfill. One is that surrounding areas of landfills are often heavily polluted since it is difficult to keep dangerous chemicals from leaching out into the surrounding land. The other is that landfill can increase chances of global warming by releasing CH_4, which is 20 times more dangerous as a greenhouse gas than CO_2. Therefore, alternative environmentally friendly methods should be established for MSW treatment. Sustainable MSW management offers the opportunity to select the most suitable way to valorise – either as materials (Waste-to-Product, WtP) or as energy (Waste-to-Energy, WtE) – certain waste streams.

WtE can play an important role in an integrated waste management system, since it can: (a) reduce the volume of waste, therefore preserving landfill space, (b) allow for the recovery of energy from the solid waste stream, (c) allow for the recovery of minerals and chemicals from the solid waste stream which can then be reused or recycled, (d) destroy a number of contaminants that may be present in the waste stream.

Thermal treatment covers a range of technologies that extract energy from the waste while reducing its volume and rendering the remaining fraction mostly inert. These technologies can be generally grouped into two main categories: conventional combustion and advanced thermal treatment. Conventional combustion technologies include mass burn incineration and fluidized bed incineration among others. Mass burn incineration is the most common type of WtE technology used worldwide. Advanced thermal treatment technologies include gasification, pyrolysis and plasma gasification. These technologies tend to be less proven on a commercial scale and involve more complex technological processes.

Thermal plasma technology has been applied in various industrial applications such as cutting, welding, spraying, metallurgy, mass spectroscopy, nano-sized particle synthesis, powder spheroidization, and waste treatment. Over the past decade, thermal plasma process has also been regarded as a viable alternative to treat highly toxic wastes such as ash and air pollutant control residues, radioactive, medical wastes as well as MSW (Moustakas *et al.*, 2005; Bryden, 2006; Cyranoski. 2006).

Plasma gasification is a technologically advanced and environmentally friendly process of disposing of waste and converting them to usable by-products. It is a non-incineration thermal process that uses very high temperatures in an oxygen starved environment to decompose completely the input waste material into very simple molecules (Littlewood, 1977; Orr and Maxwell, 2000). The products of the process are a combustible gas mainly composed of H_2 and CO known as synthesis gas, while inorganic components are vitrified into inert glass-like slag. It has been demonstrated that the thermal plasma process is environmentally friendly, producing only inert slag and minimal air pollutants that after appropriate cleaning are well within regional regulations (Moustakas *et al.*, 2008).

Mountouris *et al.* (2006) developed the GasifEq equilibrium thermodynamic model that describes thoroughly the plasma gasification process. Later, Montouris *et al.* (2008) used the Gasifeq model for energy analysis of the plasma gasification process using as case study the sewage sludge producesd from the main wastewater treatment plant of Athens at Psittalia. In the present study the Gasifeq model is extended to include formation sulfur and chlorine components. The results of the new model, called as Modified Gasifeq, are compared against experimental data for wood gasification and, most important, with real operational experimental data from a commercially-available plasma gasification process of MSW.

2. Description of the complete plasma gasification process for the treatment of MSW

A typical plasma gasification processing unit includes a waste preparation step, a gasification/vitrification furnace equipped with plasma torches, a heat exchanger, a gas cleaning system and an energy recovery system.

Waste Preparation System

The purpose of the waste preparation is to reduce the size of waste and its moisture content if needed. The waste is first shredded to make the particle size suitable for feeding into the furnace so as to accelerate the gasification reactions. The shredded waste is then dried, if needed, to reduce the moisture content aiming to improve the energy efficiency of the gasification process.

Gasification/vitrification furnace

The waste is introduced into the gasification and vitrification furnace, along with controlled amounts of air. Depending on the energy recover requirements, pure oxygen can be used instead of air. The molten metal and slag within the furnace are maintained at temperatures in the order of 1200-1500 K. At these temperatures within the gasification and vitrification furnace, the organic molecules contained in the waste break down and react with the air and water contained in the waste feed to form synthesis gas, which consists mainly of carbon monoxide and hydrogen. The inorganic components of the waste are either metal or oxides, coming from items such as glass and ash present in the waste. These materials melt and separate, with the metal forming a layer at the bottom of the furnace and the oxides forming a separate layer on top of the metal layer. When the oxides melt together, they form a type of glass that is extremely stable and inert. The process is called vitrification and is an excellent method of permanently trapping environmentally hazardous materials, including heavy metals, in an inert matrix. The molten vitrified oxides are called slag and are recovered from the furnace continuously and automatically in the form of fine gravel, perfectly suited for use as construction material. The most important part for the plasma gasification furnace is the thermal plasma generator. Usually, direct current (DC) arc plasma is used generated through plasma torch, which is a device that converts electrical energy into thermal energy. Plasma is an ionized gas that is that is conditioned to respond to electro-magnetic forces. The plasma arc is created when high voltage is established between two points. Plasma torches operate at much higher temperatures, higher enthalpies, and efficiencies much greater than those of fossil-fuel burners do. In addition, plasma torches require only about 20-30 percent of the air necessary for fossil-fuel burners; therefore waste effluent gases are greatly reduced.

Heat exchanger

A heat exchanger is usually installed after the thermal plasma furnace to recover the heat from the gas. The recovered heat can be utilized as an energy source, e.g. using a steam turbine. It is noted that only part of the thermal energy of the hot synthesis gas produced in the plasma furnace is utilized because the temperature of the gas exit the heat exchanger must not be reduced below 500 ^{o}C to avoid the possibility of dioxin reformation.

Synthesis Gas Cleaning System

The synthesis gas leaving the gasifier contains a number of pollutants, including fine particles, chlorides and sulfur. These pollutants are removed prior to introduction in an energy recovery system. Typically a syngas cleaning system includes: a quench chamber that is used for rapid gas cooling, a cooling absorber that is used for water removal along with soluble acid gases, eg. HCl, a Venturi scrubber that is used for particulate removal and an H_2S absorber that is used for removal of H_2S and sulphur recovery. The water quench is the first step and very important part of the synthesis gas cleaning system. The quench is used to freeze the high temperature thermodynamic equilibrium of the gases, eliminating the possibility of reformation of dioxins and furans. Typical off-gas outlet temperatures range from 70 °C to 90 °C. Cooling the gas to this temperature makes it suitable for further processing in the packed-bed scrubber or cooling absorber. The quench utilizes recycled scrubber water, reducing the amount of fresh-water makeup required.

Energy recovery system

Although many alternative energy recovery systems can be utilized, the clean synthesis gas can be ideally used as fuel in a gas engine, which offers the advantage of high energy efficiency. Furthermore, gas engines are suitable for producing electricity from low-BTU gas, such as the synthesis gas produced from plasma gasification of MSW. Because the synthesis gas has been cleaned prior to its introduction in the engine, there is no need to quench the off-gas and a heat recovery boiler can be used to recover all the sensible energy from the hot combustion gases exiting the engine in the form of steam. This steam can be used for drying of the waste.

3. Extension of the Gasifeq model

Mountouris *et al*. (2006) developed a simple and reliable thermodynamic equilibrium model, called GasifEq, which describes the plasma gasification process. In the present study the Gasifeq model is extended to include formation of sulfur and chlorine compounds at equilibrium. In the new model, called as Modified Gasifeq, ten compounds were assumed to be present in the gasifier at equilibrium: CO, H_2, CO_2, H_2O (g), CH_4, N_2, S(g), Cl_2, H_2S, HCl. Using the Gibbs rule, it is calculated that four independent reactions are required to describe the thermodynamic equilibrium of the system. The following reactions were considered in the Modified Gasifeq model:

$CO + H_2O \leftrightarrow CO_2 + H_2$ (Water gas shift)

$CH_4 + H_2O \leftrightarrow CO + 3H_2$ (Methane decomposition)

$H_2 + S \leftrightarrow H_2S$ (H_2S formation)

$H_2 + Cl_2 \leftrightarrow 2HCl$ (HCl formation)

The thermodynamic properties needed for development of the equilibrium gasification model are the Gibbs energies of formation at 298 K, the enthalpies of formation at 298 K and the temperature dependent heat capacities. The database used for the evaluation of these properties is the Chemical Properties Handbook (Yaws, 1999).

For the description of the complete gasification process, the Modeified Gasifeq model includes a system of eleven equations: the four are the chemical equilibrium equations, six mass balances and the energy balance.

4. Model validation

In order to validate the Modified GasifEq model, experimental data taken from the literature were used. Table 1 presents such a comparison for gasification wood waste that is a common waste material, using the data reported by Zainal *et al*. (2001). In this case no sulfur or chlorine is present in the feed waste so no sulfur or chlorine compounds are present in the gaseous products. For comparison purposes results are also presented by two other models: the model proposed by Zainal *et al*. and the one presented by Karamarkovic and Karamarkovic (2010). As shown the Modified Gasifeq model gives very satisfactorily results. The observed difference between the Modified GasifEq model prediction and the experimental value for methane may be due to the fact that equilibrium is not attained in the experiments, since practically only traces of methane are expected at the equilibrium state for the reported gasification temperature of the experiments (800 ^oC). Note also that in the model of Zainal *et al*. the enthalpy of formation of gaseous water is erroneously used, while the enthalpy of formation of liquid water should be used instead.

More important, the model predictions were compared against real operational experimental data from a commercially-available plasma gasification process of Thermoselect that is one of the few MSW plasma gasification technologies operating at large scale (Hau *et al*., 2008). The ultimate analysis of the MSW treated by Thermoselect as well as the operational parameters of the process are shown in Table 2. Also, Table 3 presents the predictions of the Modified Gasified model for the gaseous product composition along with the experimental data reported by Hau *et al*. (2008). In this case both sulfur and chlorine are present in the feed MSW, so sulfur and chlorine compounds should be present in the gaseous products. Hau *et al*. have also developed a thermodynamic equilibrium model that is much more complicated than Modified Gasifeq and the results obtained by this model are also presented in Table 3. As shown the agreement between the experimental data and the Modified Gasifeq model predictions is remarkably good. As no HCl experimental data have been available to validate these results, it is not possible to comment on the reliability of the model for this species.

The model validation results are also presented graphically in a scatter plot (Figure 1), where the Modified Gasifeq predictions of the gaseous product compositions are plotted against the experimental ones. The small deviations of the points from the 45-degree line indicate the high accuracy of the Modified Gasifeq model.

Table 1. Comparison between experimental (Zainal *et al*., 2001) and model predictions for wood waste gasification.

Gaseous products	**Experimental**	**Modified Gasifeq**	**Zainal *et al*.**	**Karamarkovic**
	% v/v dry basis			
CO	23.0	19.9	19.6	20.3
H_2	15.2	21.0	21.1	22.6
CH_4	1.6	0.00008	0.64	0.0002
CO_2	16.4	12.1	12.0	12.2
N_2	42.3	47	46.7	44.9

Table 2. Ultimate analysis of the waste and operational parameters of the Thermoselect process (Hau *et al*., 2008).

Element	**%w/w dry ash free waste**
C	39.8
H	4.4
O	47.5
N	6.9
S	0.33
Cl	1.3
Moisture (% w/w in waste as received)	22.6
Ash (% w/w in waste as received)	16.6
Gasification temperature (^oC)	1200
Oxygene (kmol O_2 per kmol dry ash free waste)	0.37

Table 3. Comparison between experimental (Hau *et al*., 2008) and model predictions (% v/v) for the Thermoselect process.

Gaseous products	**Experimental**	**Modified Gasifeq**	**Hau *et al*. model**
CO	29.4	30.8	30.8
H_2	2.1	1.66	1.98
CO_2	35.9	34.3	34.2
H_2O	27.9	28.5	28.7
N_2	3.4	3.9	3.4
HCl	0	0.571	0.0151
S+H2S	0.158	0.199	0.168

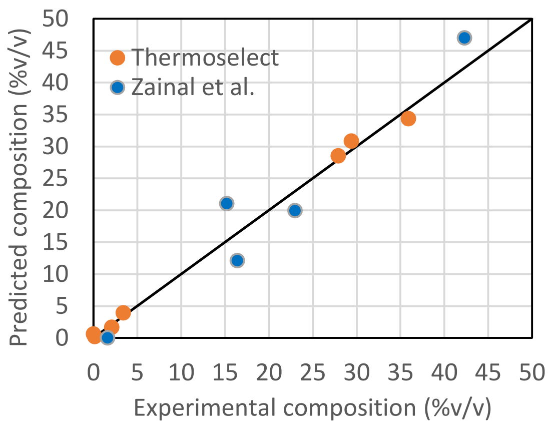

Figure 1. Modified Gasifeq gaseous product composition predictions vs experimental ones. Detailed results are shown in Tables 1 and 3.

5. Conclusions

This paper presents a model, Modified Gasifeq, which is able to perform a complete thermodynamic analysis of the plasma gasification process. This analysis includes prediction of the main gaseous components produced (CO, H_2, CH_4, H_2O, CO_2 and N_2), prediction of the concentrations of the impurities in the raw synthesis gas (H_2S, HCl and Cl_2), and energy calculations. The results of the new model were compared against two sets of experimental data taken from the literature. The agreement between the results of the model and the reported experimental data is remarkably good, especially with the real operational experimental data from a commercially-available plasma gasification process of MSW. This indicates that the Modified Gasifed model can be used as a tool for assisting the design of a complete plasma gasification process of solid wastes.

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