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## **A Thermodynamic Model of the Outputs of Gasification of Solid Waste**

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# A Thermodynamic Model of the Outputs of Gasification of Solid Waste\*

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## Abstract

This paper presents a thermodynamic model for the estimation of impurities in the raw synthesis gas and in the slag resulting from gasification of solid waste. Based on thermodynamic equilibrium calculations and mass balances, the model takes into account the possibility of each impurity becoming an oxide, a chloride, or remaining in its elemental form. The model includes a comprehensive set of thermodynamic data for a wide variety of chemical species used to estimate the equilibrium constants. By solving the equilibrium reaction equations, the model predicts which pollutants are formed and in what amounts as well as their distribution in the raw synthesis gas and in the slag. Predicting the distribution and fate of these pollutants is particularly important for the design of a gas cleaning system for the raw synthesis gas and for deciding on the disposal options of the slag. The model can be applied to different waste materials, including municipal solid waste, mixed plastics waste, auto-shredder residue (ASR) and biomass. A comparison between the model predictions and the operational data from a commercially-available gasification process (Thermoselect) shows a close agreement between the estimated and real data.

**KEYWORDS:** gasification, solid waste, synthesis gas, thermodynamic model, Thermoselect process

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## 1. INTRODUCTION

Depletion of fossil fuels, the rising demand for and cost of energy as well as the issue of global warming have led to an increased activity by national governments and industries to identify more sustainable energy resources. Municipal Solid Waste (MSW) represents one such potential source of energy. For instance, England and Wales already produce over 100 million tonnes of combined industry, commerce and household waste annually (Defra, 2007). However, currently, a large fraction of MSW is landfilled (Kirkby and Azapagic, 2004). Apart from the odour, leachates and release of methane from landfills, there is also the problem that the space available for landfilling is diminishing. Moreover, as the new EU Landfill Directive (EC, 1999) sets stricter requirements on the amount of waste to be diverted from landfill (e.g. 65% biodegradable waste reduction by 2020 from the 1995 levels), it is becoming clear that landfill will eventually cease to be an option for solid waste disposal. This is already the case, for example, in Sweden, where the ban on landfilling combustible and organic waste has been in existence since 2002 and 2005, respectively.

Using MSW as an energy source rather than landfilling it has several advantages, including reduction of the amount of waste going to landfill, reduction in the use of fossil fuels and the related emissions of greenhouse gases. However, depending on the technique used, energy recovery from waste can generate emissions to air (e.g. SO<sub>x</sub>, NO<sub>x</sub> in the flue gas), water (e.g. effluent from the flue-gas cleaning system) and solid waste (ash or other solid waste). Incineration is currently the method most-commonly used for energy recovery from MSW. However, incineration has significantly lower thermal efficiencies than fossil-fuel combustion and thus higher greenhouse gas emissions per unit of energy produced (although a portion of these emissions is from renewable sources and can therefore be considered as carbon-neutral). Moreover, incinerators can produce harmful emissions, including SO<sub>x</sub>, NO<sub>x</sub>, HCl, HF, polyaromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), dioxins and furans, and a wide range of heavy metals which need to be removed in the gas cleaning equipment (Kirkby and Azapagic, 2004; Malkow, 2004). Although new incineration plants have greatly reduced emissions due to improved operation and gas cleaning, a strong public opposition to incineration still persists and the flue gas cleaning systems continue to be costly. Consequently, there is still a need for a better technology than incineration.

Gasification is emerging as a potentially more sustainable technology for energy recovery from waste (Azapagic, 2007). During gasification, waste is converted into synthesis gas by partial oxidation of waste at high temperatures (above 1100°C). The synthesis gas consists mainly of carbon monoxide, hydrogen, carbon dioxide and methane. In general, gasification has several

advantages over incineration. It takes place in a reduced-oxygen environment that limits the emissions of SO<sub>x</sub> and NO<sub>x</sub> and helps to capture most of the alkali and heavy metals in the ash (Malkow, 2004). In most cases, the formation of dioxins and furans during gasification is also prevented. Nitrogen and sulphur may still be present in the synthesis gas, but as N<sub>2</sub>, HN<sub>3</sub> and H<sub>2</sub>S, which are easier to clean up (Rezaiyan and Cheremisinoff, 2005). Furthermore, it requires just a fraction of the stoichiometric amount of oxygen necessary for combustion. As a result, the volume of gas is greatly reduced, requiring smaller and less expensive gas cleaning equipment. Finally, gasification generates fuel gas that can be used in combined-cycle turbines, reciprocating engines and, potentially, with fuel cells that convert fuel energy to electricity.

In general, synthesis gas from a waste gasifier contains several impurities such as halogen halides and volatile heavy metals as well as particulates and alkaline compounds. The amount of each depends not only on the composition of the waste but also on the operating mode of gasification and the type of gasifier used. Moreover, considering different types of waste and the seasonal changes in their composition, the amount of impurities in the synthesis gas can fluctuate significantly. Consequently, predicting the average amounts of impurities and the fluctuation in the composition of both the synthesis gas and the remaining slag is important in order to prevent the adverse impact on the environment.

To contribute towards a better understanding of the potential impact on the environment of energy recovery from MSW by gasification, this paper presents a model for calculating the composition of impurities in the synthesis gas and in the gasification slag. Based on thermodynamic equilibrium calculations and mass balances in the gasification step, the model takes into account the possibility of each impurity forming an oxide, a chloride, or remaining in its elemental form. Although the emphasis here is on gasification of MSW, the model can be used for different types of wastes and their compositions, provided the latter is known.

## 2. GASIFICATION MODEL

The gasification model is based on thermodynamic equilibrium calculations and elemental mass balances. The model considers 89 chemical species and 59 equilibrium reaction equations. It includes the thermodynamic data for a wide variety of oxides, chlorides and some hydrides, enabling estimation of the equilibrium constants and solving the equilibrium reaction equations.

The elements considered in the model are those commonly present in MSW. These are C, H, O, N, S, Cl, Br, F, Ag, Al, As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, N, Na, Ni, P, Pb, S, Sb, Si, Ti, Tl and Zn. This work has been particularly concerned with the fate of the trace elements. The species considered by the model are C, CH<sub>4</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, Cl<sub>2</sub>, HCl, Br<sub>2</sub>, HBr, F<sub>2</sub>, HF, Ag,

Ag<sub>2</sub>O, Al, AlCl<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, As, As<sub>2</sub>O<sub>3</sub>, As<sub>2</sub>O<sub>5</sub>, AsCl<sub>3</sub>, Ca, CaCl<sub>2</sub>, CaO, Cd, CdO, CdCl<sub>2</sub>, Cr, CrCl<sub>2</sub>, CrCl<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Cu, CuO, Cu<sub>2</sub>O, Fe, FeCl<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, FeO, Hg, HgCl, HgCl<sub>2</sub>, K, K<sub>2</sub>O, Mg, MgCl<sub>2</sub>, MgO, Mn, MnCl<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, Mo, MoCl<sub>5</sub>, MoO<sub>3</sub>, N<sub>2</sub>, NO, NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, Na, NaCl, Na<sub>2</sub>O, Ni, NiCl<sub>2</sub>, NiO, P, PCl<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, Pb, PbCl<sub>2</sub>, S, H<sub>2</sub>S, S<sub>2</sub>Cl<sub>2</sub>, SO<sub>2</sub>, SO<sub>3</sub>, Sb, SbCl<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, Si, SiCl<sub>4</sub>, SiO<sub>2</sub>, Ti, TiCl<sub>4</sub>, TiO<sub>2</sub>, Tl, TlCl, Zn, ZnCl<sub>2</sub>, ZnO.

Since this study is concerned with the fate of the impurities, other species that could be formed during gasification, such as COS, HCN and alkanes other than methane, are not considered. Exclusion of such species can be justified on the basis of the results from previous work. For instance, Li et al. (2001) and Higman and van der Burgt (2003) show that there is no significant amount of hydrocarbons, apart from methane, present at the temperatures typical for gasification. However, other species such as COS and HCN have been excluded for simplification.

In general, there are no limits as to how many species can be included in a gasification model. For instance, Li et al. (2001) considered 44 species related to C, H, O, N and S. Kosminski et al. (2006) considered sodium-species only: Na, NaCl, NaOH, Na<sub>2</sub>Cl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>O, Na<sub>2</sub>S, Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>SiO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>4</sub>SiO<sub>4</sub>, Na<sub>6</sub>Si<sub>2</sub>O<sub>7</sub>, NaAlO<sub>2</sub>, NaAlSi<sub>2</sub>O<sub>6</sub>, NaAlSi<sub>3</sub>O<sub>8</sub> and NaAlSiO<sub>4</sub>. Wei et al. (2005) conducted a study to determine the fate of chlorine in the gasification of biomass, in which they considered 611 species, related to the elements C, H, O, N, S, Cl, Si, P, Ca, K, Na, Mg, Al, Fe, Ti, and Mn. In this study, 89 species were considered, as listed above – however, the model is sufficiently generic to allow the inclusion of further species and the related thermodynamic data.

The model presented here requires specification of waste composition as an ultimate analysis (elemental mass composition) as well as its moisture content. The calculation of the thermodynamic properties is carried out assuming ideal but mixed gases, unmixed liquids and unmixed solids. No fugacity coefficients have been used because the model is intended for gasification at atmospheric pressure. Nonetheless, the model could be used for high-pressure gasification since Higman and van der Burgt (2003) state that the assumption of ideal gases is justified even at pressures of 30-70 bar because of the high temperatures in the gasification process.

It should be noted that the model does not consider reaction kinetics and fluid dynamics. The assumption behind this simplification is that the gasification temperatures are high enough so that a thermodynamic equilibrium is likely, in which case, reaction kinetics become irrelevant. Higman and van der Burgt (2003) state that in the range between 800°C and 1800°C, the reaction rates are sufficiently high that such an assumption gives results that approach reality. Below 800°C, the rates of reaction are expected to be too low for a thermodynamic equilibrium to be reached. Other considerations that are not taken

into account within the model are the operating conditions below the softening and above the melting temperatures of the ash. However, these criteria may become important in some cases; e.g. fluid-bed gasifiers cannot operate above the softening temperature because the ash starts to agglomerate (Higman and van der Burgt, 2003). A further simplification in the model is the assumption that the system operates at a fixed temperature, which means that the ways in which energy is supplied or removed are not considered.

The model does not treat the ash as inert, but it predicts its composition with respect to the presence of chemical elements, oxides and/or chlorides. The model also helps to determine whether the components are stable in the reducing environment of the gasifier. This information is of great interest because metal oxides tend to stay in the ash as their boiling temperatures are high. However, if they are converted to chlorides, which have lower boiling temperatures, it is possible that the metal in question will end up in the synthesis gas. Metals also have lower boiling temperatures than their oxides, and may vaporise; this is particularly true for mercury, if present.

## 2.1 Equilibrium Reactions

Gasification of waste or indeed other carbon-based materials, such as coal and biomass, can be represented by the reactions with solid carbon, regardless of the hydrocarbons present in the feedstock. In gasification, there are many reactions producing and/or consuming the seven main substances: carbon, carbon monoxide, carbon dioxide, hydrogen, water, methane and oxygen. These reactions have been described in detail elsewhere, e.g. by Higman and van der Burgt (2003) or Rezaiyan and Cheremisinoff (2005). However, in order to determine the equilibrium concentrations of these seven substances, only four independent chemical reactions and the elemental mass-balance equations for carbon, oxygen and hydrogen are necessary. In this work, the reactions selected are the complete combustion of carbon,



the Boudouard reaction,



the water-gas shift reaction,



and the methanation reaction,



The other sets of reactions are those for hydrogenation, oxidation and chlorination of impurities in the waste feedstock. In the case of hydrogenation, only the formation of HCl, HBr, HF, H<sub>2</sub>S and NH<sub>3</sub>, have been considered. The general chemical reaction for hydrogenation is:



The oxidation reactions have the general form:



As for the chlorination reactions, their general form is:



where  $A$  represents the metals present in the waste stream. In total, there are 30 elements and 59 equilibrium reactions. With the 89 species being considered, the resulting system of equations consists of 89 unknowns and 89 equations.

## 2.2 Thermodynamic Properties of the Species

The general form of the reactions (1)-(7) is:



The equilibrium constant  $K$  for each reaction can be determined from the equation:

$$K_j = \exp \left[ -\frac{\Delta G_{rxn,j}^\circ}{RT} \right] \quad (9)$$

where  $\Delta G_{rxn}^\circ$  is the Gibbs free energy of reaction.  $\Delta G_{rxn}^\circ$  can be calculated as:

$$\Delta G_{rxn,j}^\circ = \sum_{i=1}^N \nu_{ij} \Delta g_{f,i}^\circ \quad (10)$$

where  $\Delta g_{f,i}^\circ$  is the Gibbs free energy of formation of species  $i$ . Most chemistry and thermodynamics books have tabulated values for the heat of formation of species  $i$ ,  $\Delta h_{f,i}^\circ$ , and either the entropy,  $s_i^\circ$ , or the Gibbs free energy of formation,  $\Delta g_{f,i}^\circ$ , at 25 °C and 1.013 bar.

For ideal substances at constant pressure, the heat of formation can be calculated at any temperature using the following equation:

$$\Delta h_{f,i}^\circ(T) = \Delta h_{f,i}^\circ(T_0) + \int_{T_0}^T C_{P,i}^\circ(T) dT + \sum_{T_{pi} < T} \Delta h_{p,i}(T_{pi}) \quad (11)$$

where  $C_{P,i}^\circ(T)$  is the constant-pressure heat capacity of species  $i$  at temperature  $T$  and  $\Delta h_{p,i}(T_{pi})$  is the enthalpy of a phase change or magnetic transition of species  $i$  occurring at temperature  $T_{pi}$ . Similarly, the entropy of ideal species  $i$  for any temperature at constant pressure can be calculated as:

$$s_i^\circ(T) = s_i^\circ(T_0) + \int_{T_0}^T \frac{C_{P,i}^\circ(T)}{T} dT + \sum_{T_{pi} < T} \frac{\Delta h_{p,i}(T_{pi})}{T_{pi}} \quad (12)$$

The general form of the constant-pressure heat capacity is as follows:

$$C_{P,i}^\circ(T) = a_i + b_i T + \frac{c_i}{T^2} + d_i T^2 \quad (13)$$

Using this general form of the constant-pressure heat capacity allows analytical solution of the integrals in equations (11) and (12). The results are as follows:

$$\int_{T_0}^T C_{P,i}^\circ(T) dT = a_i(T - T_0) + \frac{b_i}{2}(T^2 - T_0^2) - c_i \left( \frac{1}{T} - \frac{1}{T_0} \right) + \frac{d_i}{3}(T^3 - T_0^3) \quad (14)$$



$$\int_{T_0}^T \frac{C_{P,i}^\circ(T)}{T} dT = a_i \ln \frac{T}{T_0} + b_i (T - T_0) - c_i \left( \frac{1}{T^2} - \frac{1}{T_0^2} \right) + \frac{d_i}{2} (T^2 - T_0^2) \quad (15)$$

Finally, the Gibbs free energy for species  $i$  can be calculated, for any temperature at constant pressure as:

$$\Delta g_{f,i}^\circ(T) = \Delta h_{f,i}^\circ(T) - T \cdot s_i^\circ(T) \quad (16)$$

### 2.3 Solving for Chemical Equilibrium of the System

The general condition for chemical equilibrium at constant mass, temperature and pressure is when the total Gibbs free energy of the system,  $G$ , is at a minimum. This can be written as:

$$G = \sum_{i=1}^N n_i \mu_i = \sum_{i=1}^N \left( n_{i,0} + \sum_{j=1}^M \nu_{ij} \xi_j \right) \mu_i \quad (17)$$

where  $N$  is the total number of species present and  $M$  the total number of independent reactions in the system;  $n_{i,0}$ ,  $\nu_i$  and  $\mu_i$  are the initial number of moles in the system, the stoichiometric coefficient and the chemical potential of species  $i$ , respectively.  $\xi_j$  is the molar extent of reaction  $j$ . This minimum is achieved when all the partial derivatives of the total Gibbs free energy are equal to zero, i.e.:

$$\left( \frac{\partial G}{\partial \xi_j} \right)_{T,P,\xi_k \neq \xi_j} = 0 \quad j = 1, 2, \dots, M \quad (18)$$

As described in detail by e.g. Sandler (1989), equations (17) and (18) lead to the following conditions for equilibrium:

$$\sum_{i=1}^N \nu_{ij} \mu_i = 0 \quad j = 1, 2, \dots, M \quad (19)$$

Many of the chemical reactions occurring in the gasification of waste are heterogeneous. For instance, oxygen reacts with solid carbon to form carbon dioxide. If the gas and solid phases are assumed to be mutually insoluble, then the problem becomes one of calculation of chemical equilibrium, and not also of

phase equilibrium. This assumption certainly simplifies the problem. However, the condition described by equation (19) may not (and likely will not) hold for all the reactions in the system. If that is the case, then solving for the system of equations described by equation (19) will not be possible because some reactions will not reach the equilibrium.

Alternatively, one can identify the equations that either cannot achieve equilibrium or proceed to completion, and solve the system of equilibrium equations for the remaining reactions. For this, based on the chemical reaction described by equation (8), the quotient  $Q$  can be defined as:

$$Q = \frac{a_P^{v_P} \cdot a_Q^{v_Q}}{a_A^{v_A} \cdot a_B^{v_B}} \quad (20)$$

where  $a_i$  is the activity of species  $i$ .

For ideal systems, the activity of gases can be expressed as:

$$a_i \approx \frac{n_i P}{n_{\text{gas}} P_0} \quad (21)$$

In the case of pure unmixed liquids and unmixed solids, their activity is unity, i.e.  $a_i \approx 1$ . A particular reaction achieves equilibrium when equation (9) equals (20), i.e.:

$$K = Q \Rightarrow \exp\left[-\frac{\Delta G_{\text{rxn}}^\circ}{RT}\right] = \frac{a_P^{v_P} \cdot a_Q^{v_Q}}{a_A^{v_A} \cdot a_B^{v_B}} \quad (22)$$

If  $K$  is larger than  $Q$ , then the system cannot achieve equilibrium and the reaction proceeds to completion, i.e. until one of the reactants is fully spent. If  $K$  is smaller than  $Q$ , then the system does not achieve equilibrium and the reverse reaction proceeds to completion, i.e. until one of the products is entirely consumed.

### 3. CASE STUDY: APPLICATION OF THE GASIFICATION MODEL TO THE THERMOSELECT PROCESS

The Thermoselect process is one of the few MSW gasification technologies operating at large scale. The development of this process started in 1989 (Malkow, 2004) and a demonstration plant was in operation in Italy from 1992 to 1998 (Kaiser and Shimizu, 2004). Since then, three large-scale plants came into operation in Germany and Japan; the plants in Karlsruhe in Germany and Chiba in

Japan started in 1999 and the one at Mutsu in Japan started in 2003 (Kaiser and Shimizu, 2004).

As shown in Figure 1, the Thermoselect process can be divided into four stages: waste feed system, gasification reactor, synthesis gas cleaning and process water treatment.

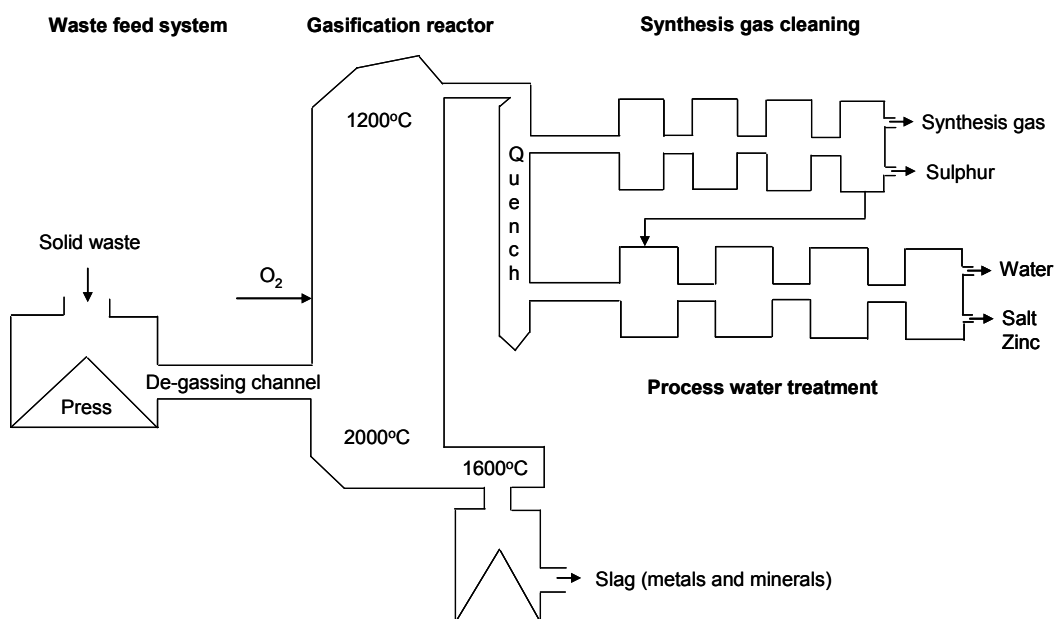


Figure 1 Schematic representation of the Thermoselect gasification process

In the waste feed system, the waste is processed in a press into dense plugs or briquettes. The briquettes are then fed into the de-gassing channel (which acts as a pyrolysis section with no oxygen being present) where they are heated to 400°C for 1 hour from the heat radiated from the gasification reactor. The temperature at the point where the waste feedstock meets the reactor is 1600°C. Gasification of the waste stream is assisted by the steam formed from the water in the waste and by the controlled injection of pure oxygen. Other additives such as methane, NaOH and glycol are also added in smaller quantities to aid gasification. All organic material in the waste is transformed into a synthesis gas. The inorganic fraction (e.g. metal and minerals) melts in the lower section of the reactor, where temperatures can reach 2000°C. More volatile metals such as mercury and zinc etc. are extracted together with the synthesis gas. The remaining molten minerals and metals are collected in the lower homogenisation reactor.

After gasification, the raw synthesis gas typically consists on a volume bases of 25-42% H<sub>2</sub>, 25-42% CO, 10-25% CO<sub>2</sub>, with the rest being N<sub>2</sub> and impurities. It leaves the gasification reactor at 1200°C and is then passed in the synthesis gas cleaning section through a water quench, acid scrubber, alkaline scrubber, water scrubber (for fine dust removal), de-sulphurisation and gas-drying stages.

The condensed water vapour is treated in the process water treatment section to remove iron and aluminium as well as heavy metal hydroxides; salt is removed in a final evaporator stage. The purified water is reused internally for cooling purposes.

Further detail on the Thermoselect process can be found in Drost et al. (2004) and Drost and Kaiser (2004). For the purposes of this work, only the gasification reactor is of interest, because the aim is to test the outputs of the gasification model developed here against the real reactor operating data.

### 3.1 Problem Setup

The model has been tested assuming that gasification occurs at 1200°C and that the system achieves thermodynamic equilibrium. The composition of the slag coming from the bottom of the gasifier has been taken as that of the species that are in the liquid and solid states (glass and molten metals) at 1200°C. No second chamber or reaction at 2000°C for the metals and minerals has been considered in this case study.

The composition of the final products from the Thermoselect process is a mixture of metals and minerals from the homogenisation reactor and a raw synthesis gas from the gasifier. As already mentioned and shown in Figure 1, the latter is processed further in the synthesis gas cleaning system, resulting in cleaned synthesis gas, water, sulphur, zinc-concentrate and salts. Table 1 shows the composition of these streams when added together (Drost and Kaiser, 2004).

As mentioned earlier, the gasification model requires the composition of the waste to be specified as an ultimate analysis; the moisture content of the waste is also a required input datum. As the original composition of the waste used in the Thermoselect process was not known, it has been estimated by back-tracking the elements from the reported outputs (as given in Table 1) through mass balances and the known data about the inputs. For instance, iron is present as 24.3 kg of elemental iron and 39 kg of Fe<sub>2</sub>O<sub>3</sub>. Consequently, in order to satisfy the mass balance, there must be about 52 kg of iron in the incoming waste as calculated by:

$$Fe \text{ (in the waste)} = 24.3 \text{ (kg Fe)} + 39 \frac{2 \cdot 56}{160} \text{ (kg Fe}_2\text{O}_3\text{)} = 52 \text{ kg} \quad (23)$$

Table 1. Outputs from the Thermoselect process (Drost and Kaiser, 2004)

| Outputs                        | Amount (kg/tonne of waste) |
|--------------------------------|----------------------------|
| Synthesis gas                  | 890                        |
| H <sub>2</sub>                 | 27                         |
| CO                             | 370                        |
| CO <sub>2</sub>                | 452                        |
| N <sub>2</sub>                 | 41                         |
| Metals                         | 29                         |
| Fe                             | 24.3                       |
| Cu                             | 3.7                        |
| Ni                             | 0.11                       |
| Cr                             | 0.08                       |
| Zn                             | 0.017                      |
| Other                          | 0.8                        |
| Minerals                       | 230                        |
| SiO <sub>2</sub>               | 104                        |
| Fe <sub>2</sub> O <sub>3</sub> | 39                         |
| CaO                            | 32                         |
| Al <sub>2</sub> O <sub>3</sub> | 28                         |
| Na <sub>2</sub> O              | 13.1                       |
| MgO                            | 5.5                        |
| K <sub>2</sub> O               | 2.5                        |
| P <sub>2</sub> O <sub>5</sub>  | 1.8                        |
| TiO <sub>2</sub>               | 2.1                        |
| Other                          | 2.5                        |
| Sulphur                        | 2                          |
| Zinc-concentrate               | 3                          |
| Salt (90% NaCl, 10% KCl)       | 10                         |
| Clean water                    | 350                        |

Drost and Kaiser (2004) report that 514 kg of oxygen, methane and other additives (H<sub>2</sub>O<sub>2</sub>, NaOH, CO<sub>2</sub>, triethylene glycol, and other non-specified substances) are used per tonne of waste gasified and that 55 kg of methane gas is typically added to the process. Since there was no available information on the mass values for these additives, they have not been taken into account in the model. In any case, the amount of the additives is expected to be much smaller than the amount of oxygen required by the process. Therefore, the amount of oxygen added to the process is taken to be the difference between 514 kg (the total amount) and 55 kg (amount of methane). Table 2 shows the estimated

composition of the waste and the amounts used to model the injections of methane and oxygen.

The gasification model was run for the composition shown in Table 2, at a temperature of 1200°C and an absolute pressure of 1.013 bar.

Table 2. Estimated composition of waste for gasification in the Thermoselect process

| Component                   | Mass (kg/tonne of waste) |
|-----------------------------|--------------------------|
| Waste                       | 1000                     |
| Moisture (H <sub>2</sub> O) | 226                      |
| C                           | 242                      |
| H                           | 27                       |
| O                           | 289                      |
| Cl                          | 5.96                     |
| Al                          | 14.67                    |
| Ca                          | 23.11                    |
| Cr                          | 0.08                     |
| Cu                          | 3.70                     |
| Fe                          | 51.9                     |
| K                           | 2.64                     |
| Mg                          | 3.34                     |
| N                           | 41.31                    |
| Na                          | 13.32                    |
| Ni                          | 0.11                     |
| P                           | 0.81                     |
| S                           | 2.01                     |
| Si                          | 48.6                     |
| Ti                          | 1.25                     |
| Zn                          | 3.03                     |
| Injected O <sub>2</sub>     | 459                      |
| Injected CH <sub>4</sub>    | 55                       |

### 3.2 Results and Discussion

Tables 3 and 4 show the results obtained by running the model and the corresponding values reported by Drost and Kaiser (2004).

Table 3. Composition of the synthesis gas: calculated vs. real data

| Species in the synthesis gas  | Data obtained by the gasification model (kg/tonne of waste) | Thermoselect process [as reported in Drost & Keiser, 2004] (kg/tonne of waste) |
|-------------------------------|---|--|
| H <sub>2</sub>                | 25  | 27   |
| CO                            | 387   | 370  |
| CO <sub>2</sub>               | 430   | 452  |
| H <sub>2</sub> O              | 360   | 350  |
| N <sub>2</sub>                | 41  | 41   |
| HCl                           | 0.19  | 0  |
| K                             | 2.64  | 0.50   |
| NH <sub>3</sub>               | 0.001   | 0  |
| Na                            | 9.58  | 0  |
| P                             | 0.69  | 0  |
| P <sub>2</sub> O <sub>5</sub> | 0.26  | In the liquid phase of the slag  |
| S + H <sub>2</sub> S          | 0.27 + 1.84 = 2.11  | 2.00 (total S after clean-up reaction)   |
| SO <sub>2</sub>               | 0.01  | 0  |
| Zn                            | 3.03  | 3.00   |
| Total                         | 1262  | 1246   |

Comparing the results in Table 3, it can be observed that there is a close agreement between the calculated and real values for the main constituents of the synthesis gas, i.e. H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub>. Comparing the impurities in the synthesis gas is harder because the composition of the raw synthesis gas in the Thermoselect process is not known. However, it is worth noting that all sulphur comes out in the cleaned synthesis gas. It is known from literature (Higman and van der Burgt, 2003), that a large fraction of the sulphur comes out as H<sub>2</sub>S. The value tabulated by Drost and Kaiser (2004) for the Thermoselect process is for sulphur once it has been recovered; overall the calculated and reported values compare well (2.11 vs. 2.00 kg/tonne of waste). Furthermore, according to our model, both P<sub>2</sub>O<sub>5</sub> and Zn come out with the synthesis gas. This fact is consistent with their boiling temperatures. However, Drost and Kaiser (2004) report both phosphorus and a very small amount of zinc as part of the minerals and metals that come out from the homogenisation reactor.

Table 4. Composition of the bottom ash: calculated vs. real data

| Species in the bottom ash                                 | Data obtained by the gasification model (kg/tonne of waste) | Thermoselect process [as reported in Drost & Keiser, 2004] (kg/tonne of waste) |
|---|---|--|
| $\text{Al}_2\text{O}_3$                                   | 27.7  | 28.0   |
| $\text{CaO}$  | 32.3  | 32.0   |
| $\text{Cr}$   | 0.0   | 0.1  |
| $\text{Cr}_2\text{O}_3$                                   | 0.1   | 0.0  |
| $\text{Cu}$   | 3.7   | 3.7  |
| $\text{Fe}$   | 0.0   | 24.3   |
| $\text{Fe}_2\text{O}_3$                                   | 0.0   | 39.0   |
| $\text{FeO}$  | 66.7  | 0.0  |
| $\text{K}_2\text{O}$ (decomposes at $827^\circ\text{C}$ ) | 0.0   | 2.5  |
| $\text{MgO}$  | 5.5   | 5.5  |
| $\text{NaCl}$   | 9.5   | 9.0  |
| $\text{Na}_2\text{O}$                                     | 0.0   | 13.1   |
| $\text{Ni}$   | 0.1   | 0.1  |
| $\text{P}_2\text{O}_5$                                    | In the gas phase  | 1.8  |
| $\text{SiO}_2$  | 104.0   | 104  |
| $\text{TiO}_2$  | 2.1   | 2.1  |
| $\text{Zn}$   | In the gas phase  | 0.017  |
| Total   | 252.0   | 265.0  |

Table 4 also shows a reasonably good agreement of our model with the reported data. The amounts of  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Cu}$ ,  $\text{MgO}$ ,  $\text{NaCl}$ ,  $\text{Ni}$ ,  $\text{SiO}_2$  and  $\text{TiO}_2$  are predicted accurately by the model. However, this is not the case for all the oxides, for instance  $\text{Fe}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ . In the case of iron, the thermodynamic equilibrium at  $1200^\circ\text{C}$  favours the formation of  $\text{FeO}$ . According to the model, neither  $\text{Fe}$  nor  $\text{Fe}_2\text{O}_3$  are formed. In the case of sodium, thermodynamic equilibrium indicates that  $\text{Na}$  does not oxidise to  $\text{Na}_2\text{O}$ . In the case of  $\text{K}_2\text{O}$ , physical data indicate that  $\text{K}_2\text{O}$  decomposes at  $827^\circ\text{C}$ , thus it cannot exist at  $1200^\circ\text{C}$ . Another difference is that the model predicts that chromium will be present as  $\text{Cr}_2\text{O}_3$ , while the values reported show that it is present as  $\text{Cr}$ .

One of the reasons for these discrepancies may be due to the fact that the model considers a uniform temperature profile throughout the gasifier ( $1200^\circ\text{C}$ ). However, in real situation, as the gasification process involves several steps, namely pyrolysis, combustion and gasification, the temperature varies along the longitudinal length of the gasifier. From literature (Ray et al., 2003), it is evident



that temperature shoots up due to very high exothermicity of the oxidation reaction in the combustion zone whereas in the gasification zone, due to the endothermicity of the series of gasification reactions, temperature sharply falls to create thermally stable condition of the reactor system. As the temperature varies, the nature of the thermodynamic equilibrium reactions are expected to vary as well, which has not been considered in the gasification model. A separate study would be necessary to identify the temperature distribution throughout the gasifier which would depend on the mode of gasification, type of gasifier and the characteristics of the waste material used.

In the Thermoselect process, metals and minerals at the bottom of the gasifier are melted in the homogenisation reactor at 2000°C and recovered as two separate streams. In our model, the bottom products are assumed as coming out at 1200°C. Some discrepancies might be solved in the future by calculating the equilibrium of the bottom ash at 2000°C, but it seems unlikely that all the discrepancies will be resolved in this way. In the present study, we have not considered any metal-metal interactions in the equilibrium calculation or any possibility of metal dissolution, for instance Na or K with Cu. If in the real situation, highly reactive Na or K are dissolved in the bottom product, they may at lower temperatures (e.g. 800°C) reduce oxides to a metal, for instance FeO to Fe, themselves being oxidised to Na<sub>2</sub>O or K<sub>2</sub>O. This may explain why our model is not showing Fe, Na<sub>2</sub>O or K<sub>2</sub>O in the bottom ash.

Table 5. Elemental composition of the bottom ash: calculated vs. real data

| Elements in the bottom ash | Data obtained by the gasification model (kg/tonne of waste) | Thermoselect process [as reported in Drost & Keiser, 2004] (kg/tonne of waste) |
|----------------------------|---|--|
| Al                         | 14.67   | 14.84  |
| Ca                         | 23.10   | 22.87  |
| Cr                         | 0.03  | 0.10   |
| Cu                         | 3.70  | 3.70   |
| Fe                         | 51.90   | 38.0   |
| K                          | 0.00  | 1.04   |
| Mg                         | 3.32  | 3.32   |
| Na                         | 3.74  | 8.40   |
| Ni                         | 0.10  | 0.10   |
| Si                         | 48.60   | 48.60  |
| Ti                         | 1.25  | 1.25   |

The presence of Fe<sub>2</sub>O<sub>3</sub> may be explained by the oxidation of FeO or Fe by air before the analysis of the slag took place. In fact, the best way to compare the

model with the experiment is to compare the elemental composition, which renders the subsequent chemical reactions irrelevant. This is illustrated in Table 5. Some of the discrepancies in Table 5 may be attributed to errors in the sampling or analysis of the bottom ash or in the analysis of the synthesis gas and other effluents. Given these facts, the agreement between the model presented here and the reported data is remarkably good.

### 3.3 Sensitivity Analysis

A sensitivity analysis was performed in order to evaluate how the production of the main components and impurities is affected by small variations in the temperature of the gasifier. The model was solved for a temperature 5% and 10% lower, and 5% and 10% higher than the operating temperature of 1200 °C (1473 K) assumed in the model.

Figure 2 shows the results for the main components of the synthesis gas. It can be observed that, at the higher temperatures, the equilibrium state of the system shifts towards the production of steam and carbon monoxide. This is in agreement with the known fact that gasification at the atmospheric pressure produces more CO<sub>2</sub> than CO at lower temperatures but more CO as the temperature increases.

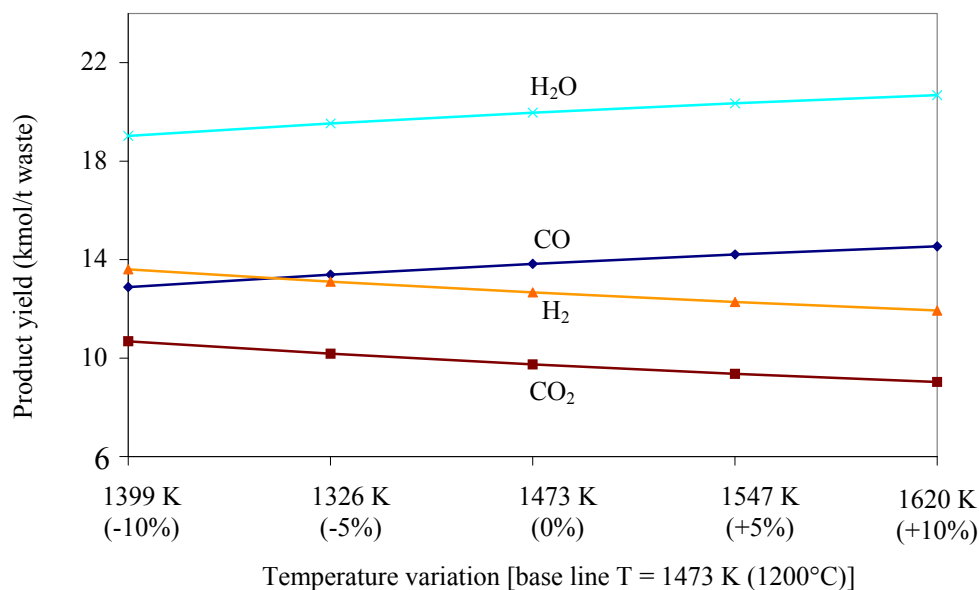


Figure 2. Yield of the main components of synthesis gas as a function of temperature

The sensitivity analysis showed no changes in the amount of oxides produced. However, interesting changes were observed in the equilibrium between HCl and NaCl, and H<sub>2</sub>S and S. Figure 3 shows the results for H<sub>2</sub>S, HCl and NaCl. The first observation is that amount of H<sub>2</sub>S formed is lower at higher temperatures. The formation of HCl was perhaps the most interesting result as it shows that in a narrow variation of temperature around the operating conditions of this process, HCl production can be very low or experience a sharp increase. For instance, with a 5% increase in temperature, formation of HCl quadrupled; with a 10% temperature increase, 13 times more HCl is produced. This behaviour is worth exploring further as production of HCl in the gasifier not only increases the risk of fouling and corrosion in the equipment but it can also increase the potential for the formation of dioxins and furans. Therefore, it may be desirable to operate the gasifier at a slightly lower temperature.

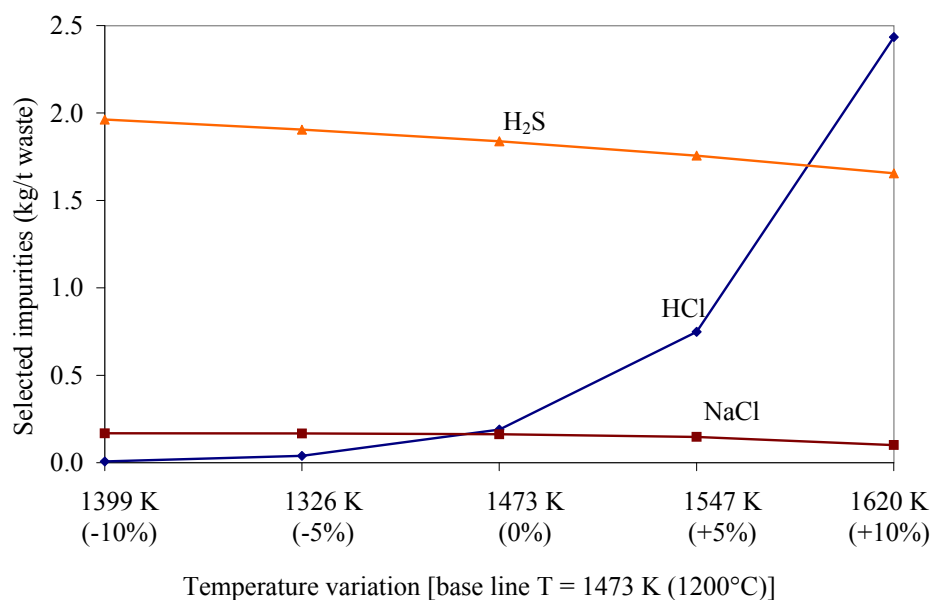


Figure 3 Variation of selected impurities with temperature

#### 4. CONCLUSIONS

This paper has presented a thermodynamic model developed for the estimation of impurities in the raw synthesis gas and in the slag resulting from gasification of solid waste. Thermoselect process has been chosen to test the model and compare the results with the experimental data available for this process. Both the compositions of the synthesis gas and the bottom slag have been compared.

The agreement between the results of the model and the reported experimental data is remarkably good, bearing in mind that the model is purely based on thermodynamic equilibrium of the reactions involved without considering reaction kinetics or fluid dynamics. The assumption behind this simplification is that the temperatures are high enough for the thermodynamic equilibrium to be likely. The good agreement of the results would suggest that this assumption is justified.

The sensitivity analysis with respect to temperature ( $\pm 10\%$  from the baseline temperature of  $1200^\circ\text{C}$ ) shows that the model is able to predict the main components of the raw synthesis gas ( $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) relatively accurately at different temperatures. However, some species appear to be quite sensitive to small temperature variations, particularly  $\text{HCl}$ . As no experimental data have been available to validate these results, it is not possible to comment on the reliability of the model with respect to these species at different temperatures.

Although most of the simulated values are in a good agreement with the experimental data, some discrepancies have been noted for both the synthesis gas and slag compositions. An improvement in the model could be achieved by:

- including a temperature variation along the longitudinal direction of gasifier;
- considering melting of the bottom slag at  $2000^\circ\text{C}$ ;
- incorporating metal-metal interaction in the equilibrium calculations;
- considering the occurrence of a chemical reaction as slag is cooled before discharge.

The gasification model can be used as a tool for predicting the impurities in synthesis gas and so serve as an aid in the design of a gas clean-up system. The slag composition can also be predicted using this model which would help to identify suitable options for the disposal of slag, particularly with respect to the content of toxic species. The model can be used for different waste materials, including municipal solid waste, mixed plastics waste, auto-shredder residue (ASR) and biomass.

## NOTATION

|                        |   |
|------------------------|---|
| $a_i$                  | activity of species $i$                             |
| $A$                    | metals present in the waste                         |
| $C_{P,i}^\circ$        | constant-pressure heat capacity of species $i$      |
| $G$                    | Gibbs free energy of the system                     |
| $\Delta g_{f,i}^\circ$ | molar Gibbs free energy of formation of species $i$ |
| $\Delta G_{rxn}^\circ$ | Gibbs free energy of reaction                       |
| $\Delta h_{f,i}^\circ$ | molar heat of formation of species $i$              |

|                  |   |
|------------------|---|
| $\Delta h_{p,i}$ | molar heat of phase change or magnetic transformation $p$ for species $i$ |
| $K_j$            | equilibrium constant of reaction $j$                                      |
| $M$              | total number of independent reactions                                     |
| $N$              | total number of species   |
| $n_i$            | number of moles of species $i$  |
| $n_{gas}$        | total number of moles in the gas phase                                    |
| $P$              | pressure of the system  |
| $R$              | universal gas constant  |
| $s_i^\circ$      | entropy of species $i$  |
| $T$              | temperature of the system   |
| $T_{pi}$         | Temperature of phase change or magnetic transition $p$ for species $i$    |

#### Greek symbols

|            |   |
|------------|---|
| $\mu_i$    | chemical potential of species $i$                         |
| $\nu_{ij}$ | stoichiometric coefficient of species $i$ in reaction $j$ |
| $\xi_j$    | extent of reaction $j$                                    |

#### Subscripts

|   |                |
|---|----------------|
| 0 | standard state |
|---|----------------|

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