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TECHNICAL ASPECTS AND THERMODYNAMIC EVALUATION OF A TWO STAGE FLUID BED-PLASMA PROCESS FOR SOLID WASTE GASIFICATION

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ABSTRACT

This study focused on the thermodynamic assets of using a two-stage process for solid waste gasification over the conventional single fluid bed approach. The study effectively demonstrated that the two-stage gasification system significantly improves the gas yield of the system and the carbon conversion efficiency, which are crucial in fluid bed systems, whilst maintaining high energy performances.

INTRODUCTION

Most of the gasification systems from waste are based on high-temperature techniques that use oxygen as a source of heat or as partial oxidation agent. Among all waste gasification technologies, fluidized bed reactors are the most promising, for a number of reasons (1). In particular, the enhanced flow mixing between reactants, the nearly constant temperature and the great operating flexibility of fluidized bed reactors make it possible to utilize different types of feedstock, including biomass and solid wastes. These gasifiers usually work as “partial combustors”, and a portion of the carbon present in the fuel is combusted to support pyrolysis and gasification reactions. Because of the relatively low temperature used to prevent agglomeration and sintering of bed material, the gas that is produced by a standard fluid bed gasifier (FBG) has tars and other condensable organic species that are technically difficult and costly to remove. Furthermore, the bottom ash/char that is generated in the gasifier or pyrolysis fluid bed reactor may contain high levels of carbon, heavy metals and organic pollutants which lower the conversion efficiency of the process and limit any secondary usage. Tar generation and ash disposal represent the strongest barrier for use of FBG for waste treatment, whereas sufficing for both is only possible with expensive cleaning systems and further processing.

The use of plasma systems has increasingly been applied with thermal waste treatment for its ability to completely decompose the input waste material into a tar-free synthetic gas and an inert, environmentally stable, vitreous material known as slag. The principal advantages that plasma offers to thermal conversion processes, besides the already mentioned tar/ash related issues absence, are a smaller installation size for a given waste throughput, and the use of electricity as energy source, characteristics which permit the technology to treat a wide range of low calorific value materials including various hazardous waste, such as PCBs, medical waste, and low-level radioactive wastes. Its efficient application in the treatment of general waste is still under debate though, due to the power required to convert the solid waste to a gas. Only additions of combustion heat supplied by the waste feedstock or a fuel additive make the process suited to large waste streams.

In applying the plasma technology to the gaseous products from a fluid bed gasifier, an advanced two-stage thermal process is able to achieve efficient cracking of the complex organics to the primary syngas constituents whilst limiting the electrical energy demand of the process.

The purpose of this work is to model a fluidized waste gasification system followed by a plasma converter in order to identify the relevant parameters in the design and operation of such an innovative technology and to compare single stage fluid beds with two-stage systems to determine if there are meaningful differences among them. The feedstock consists of different types of refuse derive fuel (RDF) produced from a combination of residual municipal, commercial and industrial wastes.

TWO STAGE GASIFICATION CONCEPTS

The physical and chemical processes which take place between the gasification agents and the fresh solid feed in the conversion route to synthesis gas are complex, influenced by varying feed, process design and operating conditions; nonetheless, the gasification chemistry may be considered as a two distinct conversion mechanisms. When biomass particles are rapidly heated at high temperature (above 600 °C) in the reactor, more than 80% of their (dry) mass is rapidly converted into permanent gases and organic vapours, leaving only a variable amount of char and few mineral ashes in the solid phase. This first step is usually referred to as pyrolysis, wherein water vapour, organic liquids and non-condensable gases, such as CO, H₂, CO₂, are separated from the solid carbon (i.e. char) and ash content of the fuel. The vapour/liquid product comprises mostly of polyaromatic hydrocarbons (PAHs) and tar (i.e. dark, oily, viscous material, consisting mainly of heavy organic and mixed oxygenates). Subsequently, the volatiles and char undergo a second gasification step and they modify their composition due to the occurrence of several reactions becoming the final syngas (see Table 1). Most of these reactions are endothermic and require a consistent amount of energy to proceed.

Reaction name	Biomass gasification	Energy (kJ/mol)
<i>Exothermic:</i>		
Combustion	(Char / Volatiles) $C + O_2 \rightarrow CO_2$	-398.3
Partial oxidation	(Char / Volatiles) $C + 1/2O_2 \rightarrow CO$	-123.1
Water gas shift	$CO + H_2O \leftrightarrow H_2 + CO_2$	-40.9
CO methanation (I)	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	-217.0
CO methanation (II)	$2CO + 2H_2 \leftrightarrow CH_4 + CO_2$	-257.0
<i>Endothermic:</i>		
Pyrolysis	$Biomass \rightarrow Char + Volatiles + CH_4 + CO + H_2 + N_2$	+200-400
Methane steam reforming	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	206.0
Water gas/steam carbon	(Char / Volatiles) $C + H_2O \rightarrow CO_2 + H_2$	118.4
Boudouard	(Char / Volatiles) $C + CO_2 \rightarrow 2CO$	159.9

Table 1. Typical gasification reactions (1)

The distinction between primary and secondary conversion is based on the different times of conversion of the various processes. Experimental studies have shown that as a result of the rapid heating of the fuel, 90% of devolatilization takes place in a matter of milliseconds, whereas the remainder of gasification processes (mainly heterogeneous reactions) take one or two orders of magnitude longer time (2).

From this general concept originates the idea of dividing the gasification process in two different reactor design arrangements, namely 'single-stage' and 'multi-stage' groups. The aim of a 'single-stage' fluid bed gasifier is to convert organic substances entirely in one reactor. Depending on the type of operation, the solid fuel is injected into the hot environment, together with oxygen and steam. As the fuel particles devolatilize, the hydrocarbons volatiles undergo gas-phase reaction with the most reactive species in the ambient gas, that is, oxygen. Thus, the oxygen supplies the required heat by reacting with the reactive volatiles (3).

The two-stage concept design physically separates the principal unit operations of pyrolysis-preliminary gasification zone from the final conversion zone, involving two different levels of heat intakes. Most of this type of advanced thermal processes eliminates char gasification as a limiting process step and, consequently, the efficiency of the process depends on how the conversion is organized. In a single stage process, the residual char reacts heterogeneously with the steam and CO_2 with a slow and highly endothermic process that is often accelerated to practical rates by the use of additional oxygen to keep the temperature high. The concept of two-stage gasification is based on providing longer residence time whilst making a more efficient use of the oxygen required to support the endothermic steam reactions. Figure 1 shows the effects of oxygen availability within the gasification reactions on the syngas calorific value, with a maximum achieved at a stoichiometric ratio (the ratio between the oxygen available and that required for complete combustion) of around 0.4, a value that depends on the composition of the RDF/waste being utilised as a feedstock.

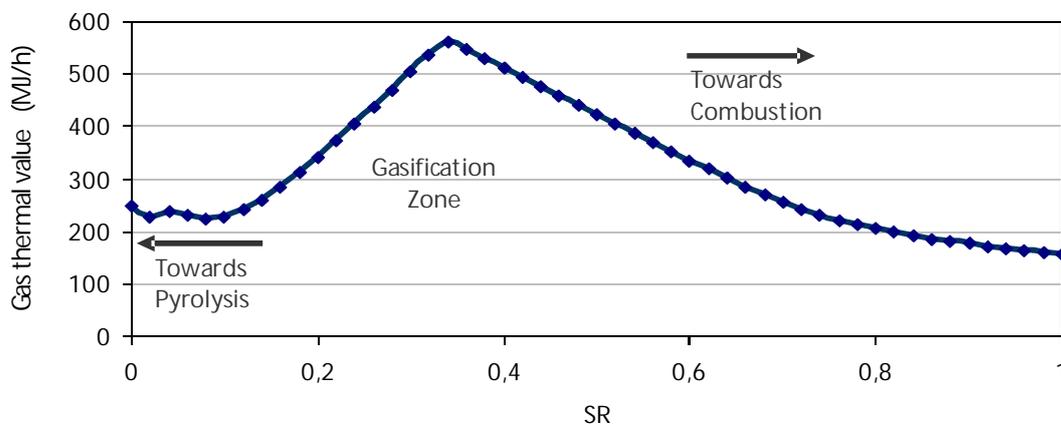


Figure 1: Influence of SR on gas thermal value from gasification of RDF in a FBG (30 kg/h of dry MSW)

The better use of oxygen results in higher yield of synthesis gas than is possible by single stage partial oxidation. Most such processes have been based on two sequential reactors where this can be achieved more easily. Furthermore, the separation and control of the unit operations provides the means for the independent optimization of each operation.

Advanced Plasma Power (UK) developed a two stage process (the Gasplasma process) which combines fluid bed gasification with plasma technology. The gasifier is a bubbling fluidized bed operated in temperature range between 650° and 800°C , with the actual operating conditions depending on fuel characteristics and desired reaction profiles. Fuel gas and carbonaceous particles, both produced in the gasifier,

are upgraded together in the second stage of the process: a single carbon electrode plasma furnace at temperatures between 1,100-1,200°C. Unlike some other gasification technologies, there is no need of intermediate fuel gas cleanup between the gasifier and the ash melting plasma converter. An addition of secondary oxygen feed assists in the break down of long chain hydrocarbons and ensures full conversion of carbonaceous residuals to a syngas virtually free of condensable liquids and tars. This crude syngas enters the side of the converter chamber above the slag level and circulates around the periphery of the chamber allowing the gas to increase in temperature while receiving maximum exposure to the intense ultra violet light within the converter, aiding cracking of tar substances, conversion of the residual char, and promoting the separation of particulates from the syngas. The converter is also designed to capture the particulate materials entrained in the gas flow from the gasifier and convert these into slag. The base of the converter chamber contains a layer of molten slag. The plasma power is controlled to provide a uniform syngas temperature and destruction of the residual tars and chars contained within the crude syngas. Downstream of the plasma converter, the syngas can be directed straight to a SOFC stack for power generation, or cooled to around 200°C in a steam boiler prior to cleaning treatment to remove any residual particulates and acid gas contaminants. The refined gas can be then used for power generation (gas engines or gas turbines), for conversion to a liquid fuel, or used as a chemical precursor.

PROCESS MODELLING AND VALIDATION

At this level of analysis, the gasification is treated from a purely thermodynamic point of view, and therefore the results are applicable to both stages, namely, single stage gasifier and plasma converter. For a given set of inlet conditions (feed composition and oxidant flowrates), the exit conditions are computed assuming thermodynamic equilibrium. A literature analysis has shown that, generally, equilibrium models fail in matching experimental results when the reactor temperature is below 800°C; particularly, these models are unsuccessful for methane and hydrogen estimated content in the gas (4). On the contrary, these models give good correlation at elevated temperatures (above 1000°C) that occur on advanced thermal processes, yielding predictions in close accord with experimental observation. A further assumption that is not always valid for practical gasifiers is that the residence time is sufficiently long to reach the equilibrium state (5). Although determining the intrinsic kinetics of all the reactions may be difficult, a multiple stage route sensibly enhances the residence time of the gas. Kinetic restrictions are then avoided by the synergy between high operating temperature and long residence time in the process, so the system closely approaches equilibrium.

In order to validate the simulation results, five different solid waste (described in Table 2) gasification experimental data were used. The tests were performed in the APP demonstration plant in Swindon (UK).

	Case 1	Case 2	Case 3	Case 4	Case 5
Description:					
O ₂ /fuel ratio (w/w)	0.51	0.59	0.59	0.79	0.50
Bed temperature (°C)	770	720	795	720	800
<i>Proximate analysis, % (w/w)</i>					
Fixed carbon	6.4	12.2	11.6	8.5	22.8
Volatile matter	59.6	50.2	64.8	47.6	68.0
Ash	19.1	23.2	12.1	8.9	0.5

Moisture	14.9	14.4	11.5	35.0	8.7
<i>Ultimate analysis, % (w/w)</i>					
C	41.0	47.0	43.0	31.5	45.2
H	5.7	6.3	5.6	4.1	6.46
O	17.5	6.9	26.6	19.7	45.38
N	1.2	1.74	0.61	0.4	0.26
S	0.2	0.15	0.25	0.17	0.01
Cl	0.4	0.31	0.34	0.23	0.25
GCV, MJ/kg (dry basis)	22.1	26.4	21.0	21.0	22.0

Table 2: Experimental parameters and characteristics of solid wastes (as received) (6)

RESULTS AND DISCUSSION

Figure 2 shows the comparison between experimental and model predicted gas compositions for a few gaseous species. The only components present at concentrations higher than 10^{-4} mol% at equilibrium beyond 700°C are CO , CO_2 , CH_4 , H_2 , N_2 , and H_2O . For the sake of simplicity, all the hydrocarbons measured data were enclosed in the label VOC (Volatile organic carbon). It is clearly evident that the gas stream exiting the single FBG shows a marked divergence from the predicted thermodynamic equilibrium conditions, whereas a very satisfactory agreement is found for the 2-stage process.

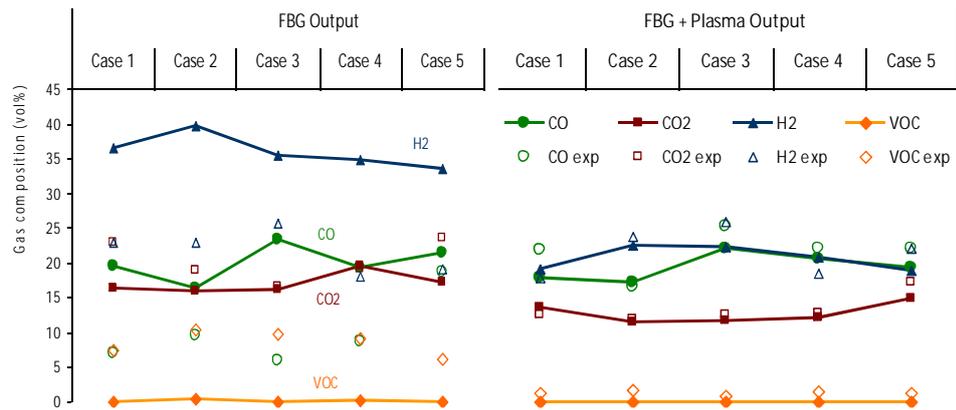


Figure 2: Comparison of gas composition predicted by the model with experiment data from (left) FBG gasifier; (right) FBG + Plasma converter.

Two possible reasons for the discrepancy between the observed and predicted gas composition results on the first stage were investigated.

As stated before, the solid carbon, which moves to the gas phase by the Boudouard and carbon-steam endothermic reactions after the supplied oxygen is completely consumed, barely reaches a 90% conversion in reality, as also supported by literature (7). Because the stoichiometry of the preliminary conversion process is usually beyond the carbon boundary point, which is obtained when exactly enough gasifying medium is added to avoid carbon formation and achieve complete gasification, its direct application to the gasifier stage implicitly considers a 100% complete carbon conversion. That results in some discrepancy in predicting gas composition and temperature in the gasifier. Furthermore, an examination of the gasifier exit gas composition (Figure 2) revealed that up to 10% methane and other

volatile organics were present in the measured data, while almost no methane formation was predicted by the model. VOC formation has a double effect on the exhaust temperature. First, its formation is exothermic, and second, for a given biomass carbon conversion, production of methane and other short-chain hydrocarbons decreases the production of CO and H₂, both of which are endothermic in nature. This also explains why the measured concentration of CO and H₂ is much lower than would be predicted from theory.

The actual conversion is also influenced to some extent by the effective CO/CO₂ ratio, with higher ratios leading to marginally higher conversions, hence approaching the thermodynamic equilibrium conditions. In the 2-stage process a complete conversion is achieved, and this is more evident from the comparison of process parameters in Figure 3, where CO/CO₂ and H₂/CO mole ratio data from experimental trial runs processing different wastes are normalised for direct comparison. On the plasma side, the comparison is good, showing that the carbon conversion efficiency and syngas quality achieved using a high-temperature 2-stage process tends to be higher than many other systems operating in a single stage.

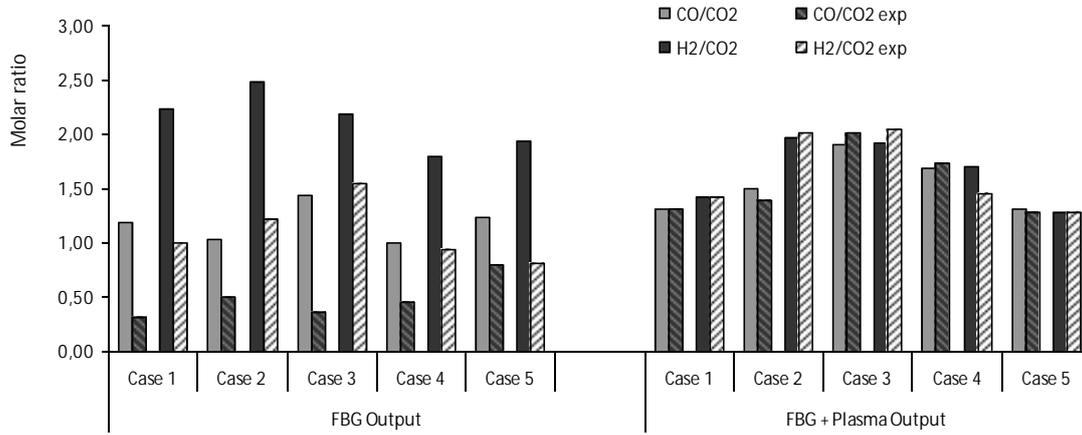


Figure 3. Comparison of model results with experiment data from the (left) FBG gasifier; (right) FBG + Plasma converter

Energy efficiency

Once it is established that for a thermal two-stage gasification process the product composition can be predicted from thermodynamics, one can proceed to impose process specific arrangements to optimize the performance of the process. The cold gas efficiency (CGE) is a standard criterion that is frequently quoted for traditional gasification process. This concept is modified and applied to a two-stage gasification process in this model:

$$CGE = \frac{\dot{m}_{syngas} GHV_{syngas}}{\dot{m}_{RDF} GHV_{RDF} + W_{power}} \quad (1)$$

Where \dot{m}_{syngas} and \dot{m}_{RDF} denote the mass flow rates of syngas and feedstock, while GHV_{syngas} and GHV_{RDF} mean the gross heating values of syngas and feedstock on mass basis. W_{power} denotes the power of plasma supplied in the arc electrode. By keeping constant the oxygen inlet at the first stage, figure 4 shows how the ratio

between the oxygen injected in stage-two and the total injected oxygen (oxygen partition ratio or OPR) affects the cold gas efficiency of the process.

An increase in secondary oxygen inlet flowrate is generally accompanied by reduced plasma power consumption, thus maintaining a constant high level of thermal energy to complete the gas reforming. In fact, keeping constant the temperature of the syngas exiting the plasma converter, the increase in this parameter involves a greater extent of the exothermic reactions, and, as a consequence, a lower electric power W_{power} is required by the plasma arch torch. With the increase of secondary oxygen intake (i.e. higher OPR), the change of CGE can be divided into two different parts. Initially, when OPR increases from 0 (i.e. no secondary oxygen inlet) to near 0.2, the CGE decreases slowly and approximately linearly from 0.83 to 0.80 (Case 2). If on the one hand, an increase in W_{power} should in fact lower the CGE, on the other hand plasma action plays a crucial role in the process of conversion of char to CO rather than CO₂, enhancing significantly the gas heating value, which is key in Eq1.

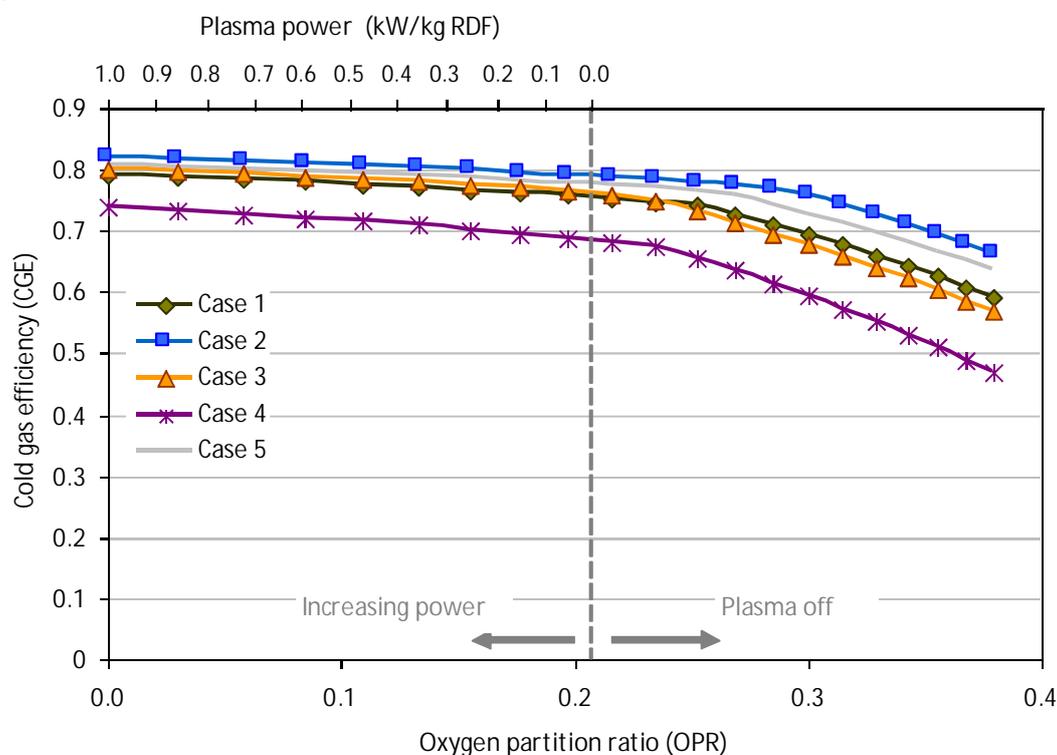


Figure 4. Effect of oxygen partition ratio and plasma power on overall process performance.

On this evidence, when reducing to zero the plasma input, whilst greatly enhancing the oxygen, the syngas quality is significantly diminished, leading to a more rapid decrease in CGE. The additional oxygen supplies the required heat by reacting with the reactive syngas, and hence, the ultimate CGE is drastically reduced by virtue of the low GHV having a predominant role; that is, by the time the system reaches the high temperature required for ash vitrification and tar reforming, more gas reacted to form H₂O and CO₂. Similar trends for syngas GHV and CGE are found for different feedstock cases.

Figure 4 showed the enormous benefit of working in combination with plasma and fuel oxidant streams. It is clear that the energy efficiency for the process sharply

decreases when plasma is switched off. Thus, it would not be profitable to alter the gasification extent only by increasing the oxidant inlet.

CONCLUSION

The known deficiencies of a single stage FBG process, have led to the theoretical prediction of the gas composition at the exit of the first stage deviating significantly from the values derived from the trials. It is evident that there are rate controlling mechanisms operating, including the rate of cracking of the organics and the rate of mass transport of the bulk oxidants to the surface of the fuel which make the equilibrium model unsuitable for the FBG, and in general for any single stage process operating with solid wastes. From a practical point of view, this is of no consequence, as the gasification reactions are completed in the plasma converter and it is the composition of the gas output from the second stage which is critical. The equilibrium condition is always attained for high temperatures and long residence time; thus, a thermodynamic model is suitable for predicting in a two-stage thermal conversion technology. The study effectively demonstrated that the two-stage gasification system significantly reduces the concentration of condensable tars in the syngas, improving the gas yield of the system and the carbon conversion efficiency which is crucial in other single stage systems. Furthermore, high GHV and CGE values are maintained for different power and oxygen conditions. The reason is that addition of plasma power into the converter decreases the amount of secondary oxygen required for complete gasification and produces larger amounts of CO and H₂ in the product gas. The optimizing direction for the two-stage process can only be determined after considering the detailed aim and situation on different projects.

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