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Synthesis Gas from Waste Plasma Gasification for Fueling Lime Kiln

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High fuel price coupled with the requirement to reduce the use of fossil fuels has created the interest to use low calorific value gases. Fuelling lime kilns with renewable fuels to displace fossil fuel is not a new idea and has been subject of many studies and projects. Various alternative renewable fuels have been introduced or studied for use in lime kiln including Wood pyrolysis oil, Waste Oil, Chipped tiers and Solid fuels (i.e. Residue Derived Fuel - RDF). A new idea is the application of synthesis gas in lime kilns where the gas originated from RDF feedstock. The synthesis gas, also known as "Syngas", is generated with a plasma gasifier fed with RDF. Raw Syngas resulted from a plasma gasifier is free from tar and has low dust load in comparison with the other gasifier types (circulated fluidized bed and bubbling fluidized bed), but still other contaminants (i.e. ammonia, chlorine, heavy metal and dust) in Syngas have to be polished out before introducing into the lime kiln. To launch renewable Syngas fuel, the raw Syngas generated from plasma gasifier must be cleaned from contaminants to meet process requirements and pollution control regulations.

This paper discusses about plasma gasification process simulation, cleaning scheme development to mitigate contaminants in raw Syngas to produce clean Syngas also technical issues due to change over from existing fuel gas to syngas fuel.

1. Introduction

Solid waste is generated in large volumes worldwide and it has significant impact on the environment. The impacts directly relate to atmospheric emissions and effluents from landfills. High fuel price along with the requirement to reduce the use of fossil fuels leads to find out opportunities for securing the cleaner supplies. The clear challenge is to achieve an economically viable solution to reduce fossil fuels consumption by substitution with green energy sources.

Many adverse impacts may occur from landfill operations (such as off gassing of methane generated by decaying organic waste, contamination of groundwater and/or aquifers and residual soil contamination during landfill) so it is expected that these landfills will become more and more restricted by the regulators.

Municipal solid waste thermal treatment (Thermochemical processes) has been subject of several studies in scientific literature which are based on the incineration (Lam et al., 2012), pyrolysis Bosmans et al., 2010), thermal treatment in general (Themelis, 2007) and gasification processes (Darley, 2004).

Gasification can be broadly defined as the thermochemical conversion of a solid or liquid carbon-based material into a combustible gaseous product (synthesis gas). This is accomplished by the supply of a gasification agent (steam, air, enriched air, oxygen) at a high temperature (Belgiorno et al., 2003). In the gasification process, the feedstock transforms into a synthesis gas composed primarily of H₂, CO, CO₂, H₂O, CH₄, N₂ and C₂⁺.

Among many types of gasification processes, recently plasma gasification drew many researchers and process developers' attention for waste conversion (Achinas et al., 2013). The plasma gasification is an interesting choice for waste conversion due to its flexibility (Arena, 2012), accepting different types of feed with wide range of composition and moistures (Fabry et al., 2013), no tar or very low tar containing synthesis gas (Minutillo et al., 2009), almost complete carbon conversion and non leachable bottom slag.

619

Because of the high temperatures involved, all the tars, char and dioxins are broken down. The exit gas from the reactor is cleaner, and there is no ash at the bottom of the reactor (Mountouris et al., 2005). The main disadvantage of plasma gasification is the high electric power consumption in the plasma torch and the low (atmospheric) operating pressure of the reactor.

2. Model Development

Waste gasification process modelling has been developed by different researchers. All the gasification reactions, with the exception of the oxidation ones (Molino et al., 2013), have been considered equilibrium reactions (Arena, 2012).

Based on experiments at high operating temperature, higher than 1200 °C, and enough residence time, i.e. for the solids it is about 1-2 h and for gas phase 2-4 s, are sufficient for chemical equilibrium to be attained (Mountouris et al., 2006).

A nonstoichiometric equilibrium model is consequently selected to model the plasma gasifier. In nonstoichiometric modelling, no knowledge of a particular reaction mechanism is required to describe the system. In a reacting system, a stable equilibrium condition is reached when the Gibbs free energy of the system is at the minimum. So, the method is based on minimizing the total Gibbs free energy. The method is particularly suitable for fuels like RDF, the exact chemical formula of which is not clearly known. The Gibbs free energy, G_{total} for the gasification product comprising N species (i = 1...N) is given by

$$G_{\text{total}} = \sum_{i=1}^{N} n_i \Delta G_{f,i}^o + \sum_{i=1}^{N} n_i \operatorname{RTln}\left(\frac{n_i}{\sum n_i}\right)$$
(1)

Eq(1) is to be solved for unknown values of n_i to minimize G_{total} , it is subject to the overall mass balance of individual elements. Irrespective of the reaction path, type, or chemical formula of the fuel, for each jth element we can write total mass balance and they should be solved simultaneously with Eq (1).

$$\sum_{i=1}^{N} a_{i,j} n_i = A_j \tag{2}$$

Where $a_{i,j}$ is the number of atoms of the jth element in the ith species, and A_j is the total number of atoms of element j entering the reactor. The value of n_i should be found such that G_{total} will be minimum.

2.1 Plasma Gasification Modelling

The plasma gasification process has been simulated in Aspen Plus V8.0. Figure 1 shows the unit operation model assembly to describe the plasma gasifier. Similar model configuration has been published for RDF (Minutillo et al., 2009) and Shredded tires, plywood and coal (Valmundsson et al., 2011). Main process blocks are described in Table 1.



Figure 1: Plasma gasification reactor model assembly

620

Table 1: Model main blocks description

Block Name	Block Type	Description
DECOMP WATDRYER SLAGSPLIT TORCH HTR LTR HEX1	RYIELD COMP SEPARATOR COMP SEPARATOR HEATER RGIBBS	Converts RDF into the constituent Separates water Separate ash To give electrical heat to plasma Gibbs reactors to calculate chemical equilibrium condition by
HEX2 HEX3 MELTER	HEATER	Heat exchanger
MIX MIX1	MIXER	Streams mixer
SPILWAT	SPLITTER	Stream splitter

The heat source for the whole process is an arc plasma torch which is modelled by "TORCH" heat exchanger. In order to validate gasification process model the refused derived fuel used by (Minutillo et al., 2009) is tested using pure air as the plasma gas. The reactor is operated at atmospheric pressure and the mass ratio of plasma gas to feedstock is 0.82. The composition of the feedstock is given in Table 2. A comparison between the model results and those obtained by Minutillo et al., 2009 are summarized in Table 3. The results show that the non-stoichiometric model gives a good match for plasma gasification reactor.

Table 2: RDF definition

Table 3: Plasma gasifier output

Proximate analysis (wt%)	Composition	Minutillo et al.	Simulation
Moisture	20.00	H ₂	0.2104	0.2168
Volatile matters (dry)	75.95	CO	0.3379	0.3333
Fixed carbon (dry)	10.23	CO ₂	0.0000	0.0000
Ash (dry)	13.82	N ₂	0.2697	0.2684
Ultimate analysis (wt	%)	CH ₄	0.0597	0.0502
С	48.23	H ₂ O	0.1168	0.1171
Н	6.37	HCI	0.0032	0.0031
Ν	1.22	H ₂ S	0.0022	0.0021
CI	1.13	COS	200 ppm	150 ppm
S	0.76	HCN		0.006
0	28.48	Ar		0.003
Ash	13.81	LHV	9.55	9.49

2.2 Raw Syngas Cleaning

Waste plasma gasification generates a raw gas that requires considerable cleaning, removing particulate and several vapour-phase contaminants to very low levels before the gas can be used in applications such as power generation, fuel/chemical synthesis and even burning in the furnace or kiln. The gas clean up process for a system is generally determined by the composition of the syngas exiting the plasma gasifier, the clean up requirement for the intended use and environmental considerations. One of the specific usages of syngas is burning in the lime kiln and phasing out for economic reasons the fossil fuels as shown in Figure 2. In this situation by providing syngas to the plant, the LPG fuel is phased out from plant fuelling and the produced COG (Coke Oven Gas) will be sufficient for other units in the plant. As a consequence the LPG is not required anymore.



Figure 2: Plant fuelling schemes

By using above gasification model and introducing a new RDF and pure oxygen as an oxidant instead of air into the plasma gasifier model, the resulted syngas will have less nitrogen percentage (compared to table 3). Table 4 shows the replaced COG and raw syngas (before cleaning) specifications.

Table 5: Clean Syngas Fuel

Composition (mol)	Existing COG to	Raw Syngas		Composition	Clean Syngas
	lime kiln plant	(Model)		(mol)	(Model)
H ₂	0.60	0.319		H ₂	0.421
CO	0.05	0.331		CO	0.440
CO_2	0.02	0.041		CO ₂	0.053
N_2	0.07	0.046		N ₂	0.062
Ar	N/A	0.006		Ar	0.008
CH₄	0.24	33		CH₄	45 ppmw
C_2H_4	0.02	N/A		C_2H_4	N/A
H ₂ O	Saturated	0.249		H ₂ O	0.016
HCI	N/A	0.006		► HCI	< 1 ppmw
H₂S	628	1319	After	H ₂ S	161 ppmw
COS	N/A	109	Cleaning	COS	91 ppmw
HCN	N/A	< 1	-	HCN	< 1 ppmw
NH ₃	42 ppmw	7		NH ₃	< 1 ppmw
Tar	1070	N/A		Tar	N/A
Dust	5 mg/m ³	18.6		Dust	< 5 mg/m ³
LHV (MJ/kg)	37.06	9.97		LHV (MJ/kg)	12.66
Temperature	18	850		Temperature	18
Pressure	1.3	1.01		Pressure (Bara)	1.3
Flow (kg/h)	3495	13696		Flow (kg/h)	10231

Table 4: COG and Raw Syngas fuel specification

A cold gas cleaning scheme is selected because there are mature technologies in this type of cleaning scheme. Also the syngas has a low pressure and the fuel gas pressure shall be increased by compressor before entering into the lime kiln plant. Therefore it needs to be cold syngas, so benefit of hot fuel gas production by hot / mild cleaning schemes are not anymore applicable.

According to Table 5, the following steps shall be carried out to prepare Syngas fuel for lime kiln plant:





An aspen model with electrolyte model was built to allow some of the molecular species dissociate partially or completely into ions in a liquid solvent, and/or some of the molecular species precipitate as salts. In this way halides and ammonia removal with caustic solutions and water are modelled more accurately than the conventional thermodynamic models like SRK, PR or activity models like NRTL, Wilson.

A combination of process gas boiler and venturi scrubber is used to cool down the hot syngas from plasma gasifier and produce plant's steam consumption and meanwhile part of the dust, ammonia and halides are also removed in the venturi scrubber. Main halides removal is accomplished in a caustic wash unit operation with pH between 9 and 10 equipped with solvent recirculation facilities and caustic injection package.

Stringent dust requirement (total dust load less than 5 mg/m³) is because of the compressor in the process scheme rather than the lime kiln itself therefore a wet electrostatic precipitator (WESP) is considered to clean up the small size dust and aerosols to meet the process requirement.

Raw syngas contains low amount of sulfur (less than 500 kg/d) however it is still needed to be reduced (less than 50 kg/d) to meet the original fuel's (COG) specification. Sulfur removal by SO₂ reagent as an oxidant or by aqueous-iron redox systems are proper options for small size sulfur recovery system (Dalrymple et al., 2004).

A centrifugal compressor is used for fuel gas pressurization to overcome the pressure drops and fuel to be mixed with combustion air for burning in the lime kiln. Table 5 shows the clean syngas fuel specification which meets the existing fuel (COG) requirements mentioned in Table 4.

622

3. Fuel Gas Combustion

To provide 120 GJ/h heat duty to lime kiln in new situation, it is needed to feed 10,231 kg/h clean syngas fuel in the kiln. In mass flow point of view it is about 3 times bigger flow than the COG fuel but in volumetric base it is about 1.6 times bigger, then the fuel distribution system including fuel burner lance shall be changed for new fuel gas.

Table 6 denotes the flue gas specifications for both COG and Syngas fuel gases.

Table 6: Flue gas specification

Composition (mol)	COG flue gas	Syngas flue	
	stream	gas stream	
CO ₂	0.057	0.154	
N ₂	0.721	0.680	
H ₂ O	0.194	0.137	
O ₂	0.022	0.021	
Ar	0.006	0.008	
Excess Air	15%	15%	
Flue Gas Temperature (°C)	180	180	
Flue Gas Flow (m3/h)	77174	68971	
Flow Gas Flow (kg/h)	56165	53644	
Adiabatic Flame Temp. (AFT)	1945	2063	



Figure 4: Lime kiln fueling scheme

Syngas flue gas stream has about 10 % lower volumetric flow than the COG flue gas (reversal trend compare to fuel flow due to higher oxygen content in the Syngas fuel) therefore the downstream facilities like bag filters for dust control, induced flue gas fan and stack not be affected.

4. Lime Calcination Reaction Rate

The main question is how the three times higher CO_2 concentration in the new flue gas will change the lime calcination reaction rate. Or in another word how reaction temperature should change in order to keep the chemical reaction rate R_{ch} constant (see Eq(4)) with the new flue gas composition.

The calcination process starts only if the partial pressure of carbon dioxide in the gas surrounding the limestone surface is less than the decomposition pressure of limestone (Stanmore et al., 2005). The decomposition pressure P_{eq} and the chemical reaction rate R_{ch} of the calcination process determined by (Silcox et al., 1989) are:

$$CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g) \tag{3}$$

$$R_{ch} = R_D (P_{eq} - P_{CO_2})$$
[mol m⁻ s⁻] (4)
$$P_{eq} = 4.137 \times 10^{12} \exp\left(-\frac{20474}{T}\right)$$
[Pa , K] (5)

$$k_D = 1.22 \times 10^{-5} \exp\left(-\frac{4026}{T}\right) \times f_m$$
 [mol m⁻² s⁻¹ Pa⁻¹] (6)

Substitution of Eq(5) and Eq(6) in Eq(4) will result in Eq(7):

$$R_{ch}/f_m = 5.0 \times 10^7 \exp\left(-\frac{24500}{T}\right) - 1.22 \times 10^{-5} \exp\left(-\frac{4026}{T}\right) P_{CO_2}$$
 [mol m⁻² s⁻¹]/[f_m]



Figure 5: Effect of CO₂ partial pressure [bar] and temperature on the reaction rate

Lime kiln with operating temperature of 900 °C and pressure mildly under atmospheric pressure (-1.35 kPag), in the new fuel condition (higher CO_2 content) the reaction temperature has to be increased from

(7)

900 °C to 905 °C in order to keep the calcination reaction rate unchanged. The calculated temperature increase is not a significant step and the new fuel gas is able to generate a higher adiabatic flame temperature and compensate the required increase in reactor temperature. Also this small temperature increase in reactor will not have major effect on reactor body material and downstream material integrity.

5. Conclusions

One of the major concerns of burning syngas in lime kilns is its lower heating value compared to existing fossil fuel. The low heating value implies that more fuel is required to achieve the heating rate, but not necessarily leading to higher amounts of exit flue gas going to the flue handling system. Main Conclusions from this study is listed hereafter:

- Non-stoichiometric equilibrium model is able to model plasma gasification reactor.
- Mature technologies are available to clean up the raw syngas fuel.
- Flue gas volumetric flowrate of Syngas fuel is about 10 % less than the COG fuel then no required to change lime kiln downstream facilities.
- Syngas has higher AFT (about 100 °C) than the COG fuel. Therefore will not impose any limitation to reach the required calcination temperature.
- Input syngas volumetric flowrate is about 1.6 times higher than the COG volumetric flow. Therefore the lime kiln input facilities including fuel piping, control valves, compressor, and burner lances shall be checked for the new fuel gas.
- Combustion air flow will be 82 % of the existing combustion air flowrate. The combustion air fan is expected to work without problem.

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624