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Aspen Simulation of Two-Stage Pyrolysis/Gasification of Carbon Based Solid Waste

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Thermo-catalytic cracking processes such as pyrolysis and gasification have great potential to convert carbon based solid waste to useful chemicals and energy. Although much attention has been devoted to gasification in recent years, there are still a number of challenges to full commercialisation of solid waste gasification. This work deals with two stage pyrolysis/gasification systems with great potential to produce tar free, high hydrogen content syngas from different types of heterogeneous solid waste. Advanced Aspen Plus simulation was employed in the modelling and optimization of a two-stage pyrolysis/gasification of lignocellulosic waste biomass (LWB) and refuse-derived fuel (RDF). Data required for process simulation, such as raw material elemental composition, heating value and particle size distribution, were determined by experimental measurements. Raw materials used in the process (RDF and LWB) were characterised by thermogravimetric (TGA) analysis, differential scanning calorimetry (DSC), elemental analysis and bomb calorimetry. The simulator process conditions were set based on experimental observations in laboratory scale pyrolysis and gasification experiments. Simulation of different scenarios and optimization of process parameters are presented. Based on the simulation results, under optimal conditions from each kg of RDF, 2.1 kg of gas with the heating value of 6.94 MJ/Nm^3, and from each kg of LWB, 1.78 kg of gas with the heating value of 7.27 MJ/Nm^3 can be obtained.

1. Introduction

The European Waste Framework Directive (Directive 2008/98 / EC) determines the rules and tasks related to solid waste disposal. Many tasks directly resulting from this directive predetermine the need of developing new technologies for waste processing and recovery.

Processes of thermochemical conversion such as pyrolysis and gasification have a great potential to transfer many types of solid waste to valuable chemicals and/or energy. By application of pyrolysis and gasification, biomass and solid waste can be used as a renewable source of hydrogen (Peres et al., 2013). Pyrolysis enables transformation of carbon based solid waste to solid, liquid and gas products, which can be used as feedstocks in other processes. Gasification of solid organic waste results in the production of combustible gas containing mainly H_2, CO, and CO_2. If air is used as the gasification agent, N_2 is also a significant component of the producer gas. Some methane, light hydrocarbons, H_2S, NH_3 and tar are also present (Higman and van der Burgt, 2008). As results from the review works on biomass gasification (Ruiz et al, 2013) and waste pyrolysis (Chen et al., 2014), thermochemical conversion of solid waste has been the subject of study in many research projects during last decades. However, both waste gasification and pyrolysis are process with very complex chemistry that requires high temperatures and can be carried out in a variety of reactor types and under different process conditions. Still some challenges, including technical, economic and social challenges in biomass and waste thermal processing are the subject of research. Some contemporary issues in thermal gasification of biomass and its application in electricity and fuel production were studied by Wang et al. (2008). Full commercialisation of these processes requires further investigation (Hellsmark and Jacobsson, 2012).

Nevertheless, a number of power generation plants based on gasification technology are in operation worldwide. A list of operating gasification plants has been provided by Higman and van der Burgt (2008). Modelling of gasification enables predicting optimal process conditions and reducing the number of experiments in the design and operation processes. A simple equilibrium mathematical model based on minimisation of the Gibbs free

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energy was used by many authors to model the gasification of waste and biomass. (Materazzi et al., 2013) used the equilibrium model to evaluate a two stage waste gasification system. Their results show that, except for H_2, the predicted composition of gas is in good coherence with the experimental data. However. Li et. al. (2008) applied an equilibrium model for coal gasification and declared that this model has some limitations in predicting gas composition. The equilibrium model was also applied by Barba et al. (2011) for RDF gasification and by Jarungthammachote and Dutta (2008) for the gasification of charcoal and coconut shell. The authors found that the model data are in good agreement with the experimentally measured ones. Generally, the equilibrium model provides good results at temperatures above 1,000 ºC and it fails at the reactor temperatures below 800 ºC (Materazzi et al., 2016).

In order to reduce the tar content in the product gas and increase the content of combustible components such as H_2 and CO, the so called two-stage pyrolysis/gasification has been developed, where the solid material is subjected to a pyrolysis process in the first step and the products of pyrolysis are subjected to a catalytic gasification process. The concept used in our previous works (Haydary et al., 2013) and also by other authors (Kosov and Zaichenko, 2016) deals only with cracking of the volatile fraction in the second stage. In a next work (Haydary, 2017), a concept where a pyrolysis reactor is combined with a char gasification reactor and a catalytic volatile gasification reactor was presented, and a concept of mathematical modelling of this system was introduced. Mathematical model presented for the pyrolysis step suggests a kinetic model of thermal decomposition combined with empirical models calculating product yields based on laboratory experiments. For the gasification stage, where temperature is above 800 °C, the equilibrium model based on the Gibbs free energy was applied.

In this work, the Aspen Plus environment was used to model two stage pyrolysis/gasification of waste biomass and refused derived fuel (RDF). Using input data obtained by laboratory experiments, empirical correlations derived from experimental data and the equilibrium model for both char and volatile fraction gasification enables prediction of carbon conversion, reactor temperature, gas composition and the gas heating value. Other advantages of Aspen modelling is the capability of case studies considering different process conditions, raw materials, oxidising agents and process material and energy integration.

2. Material and methods

2.1 Raw material characteristics

Two types of waste materials were the subjects of study in this work. The first type was RDF containing 63.2 mass % of paper, 15.8 mass % of polyethylene foil, 19.1 mass % of rigid plastics and 1.9 mass % of textiles. The second waste was a mixture of lignocellulosic-waste biomass containing 39.1 mass % of wooden chips, 22.5 mass % of sunflowers, 15.4 mass % of corn leaves and stalks 9.2 mass % of wheat straw and 13.8 mass % of barley straw. Table 1 shows the proximate and elemental composition and higher heating value (HHV) of used raw materials and products of their pyrolysis. Moisture (M), dry basis volatile matter (VM), fixed carbon (FC) and ash content of the samples were estimated by thermogravimetric measurements using the (Netzsch STA 409 PC Luxx, Germany) thermogravimeter. Elemental composition of waste samples was estimated by a (Vario Macro Cube ELEMENTAR, Italy) elemental analyser. The content of O_2 was calculated to match 100 % of the sample mass. Higher heating value (HHV) of the waste samples was measured using an FTT isoperibolic calorimetric bomb. In all material characteristics measurements, representative samples of waste were prepared by homogenisation, grounding, of a larger amount of material. The measurements were provided also for individual components of waste and the characteristics were also calculated additively.

Table 1: Proximate and elemental composition and HHV of waste and pyrolysis products

Waste	M	VM	FC	ASH	C	H	N	S	O	HHV (MJ/kg)
RDF	6.58	81.82	11.70	8.25	51.61	7.86	0.22	0.11	31.91	23.69
LWB	7.41	83.77	12.48	4.03	49.31	5.61	0.56	0.62	39.88	17.17
RDF-CHAR	0.5	17.2	39	40	51.1	3.8	0.9	0.34	3.86	14.0
WB-CHAR	0.4	13	73.36	13.64	75.8	2.43	0.68	0.3	7.15	29.8
RDF-TAR	8.9	97.8	ND	2.1	59.05	11.67	0.21	0.2	26.77	31.3
LWB-TAR	24	98.04	ND	1.96	45.82	4.92	1,15	0.2	45.95	21.0

Simulation of processes with non-conventional solids requires particle size distribution. The same particle size distribution for both RDF and LWB samples given in Table 2 was considered. Material characteristics were used as input data to the Aspen Plus process simulation model.

Table 2: Particle size distribution

Particle size (mm)	1	1.2	1.4	1.6	1.8	2
Mass %	10	20	30	30	20	10

2.2 Aspen Plus process flow diagram development

The process flow diagram developed in Aspen Plus V9 for the simulation of a two-stage pyrolysis/gasification of waste and biomass is shown in Figure 1. An industrial unit with the capacity of processing 17 t/h of solid waste working at a pressure slightly above the atmospheric one was considered. RDF, waste biomass and as well pyrolysis char and tar products were considered as nonconventional components characterised by proximate and elemental, HHV and density analysis. It was assumed that the raw material before entering the pyrolysis stage is dried and the moisture is reduced to a maximum value given in Table 1. The pyrolysis reactor (PYRO-R) works at 550 °C using the model described by (Haydary, 2017) and experimentally estimated composition of the pyrolysis gas product, the pyrolysis yields were calculated for each type of waste studied. A yield reactor model and a calculator block enabled the calculation of pyrolysis yields at a given reactor temperature. For the separation of pyrolysis products, a solid separator (G-SEP) model and a component separator (T-SEP) are used. A yield reactor model (CHAR-DEC), a Gibbs equilibrium reactor model (CHR-GASI) and a solid separator (ASH-SEP) simulate the solid gasification reactor. Primary enriched air (AIR-1) and preheated steam (STEAM) are added to the char (solid phase) gasification reactor. The secondary volatile fraction catalytic gasification reactor is modelled using a yield reactor model (TAR-DECO) for tar decomposition, and an equilibrium Gibbs reactor model (VOL-GASI) and a solid phase separator (FASH-SEP) for fly ash separation. As gasification agents in the secondary reactor, gas produced in the solid phase gasification reactor and additional secondary enriched air (AIR-2) are used.

The calculator tool of Aspen Plus is used to calculate the char and tar fractions decomposition yields. Heat needed for thermal decomposition of pyrolysis products and heat losses created 13 % of total feed calorific value, 4 % in the char gasification reactor and 9 % in the volatile gasification reactor.

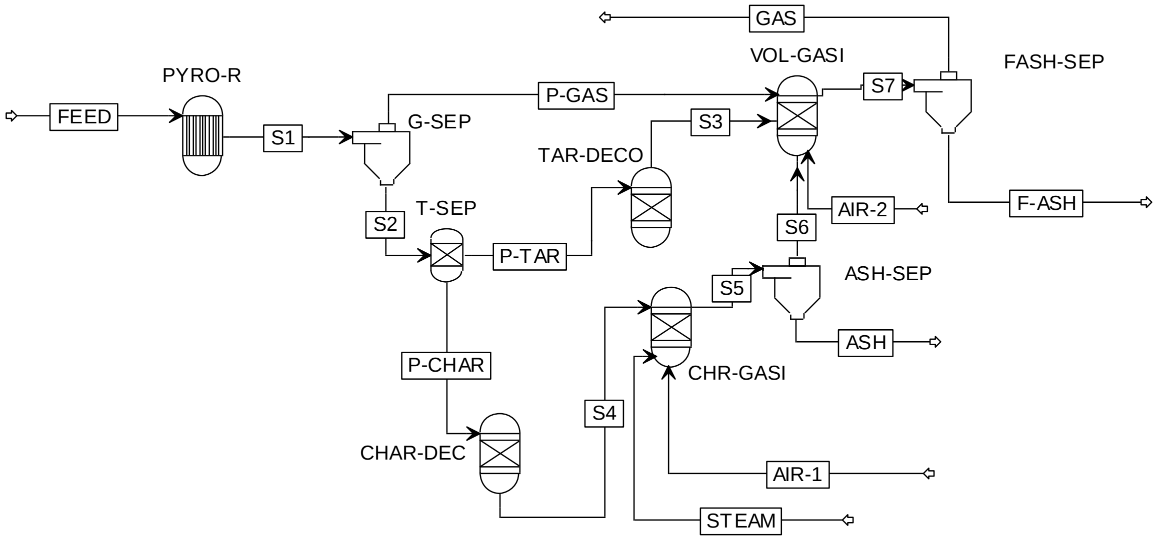

Figure 1: Aspen simulation process flow diagram of a two stage pyrolysis/gasification unit

Enriched air containing 40 mol % of O_2 and 60 mol % of N_2 was used as the oxidising agent. The same value of mass flow of primary enriched air (AIR-1) was used in all calculations. It was adjusted to keep the temperature of around 1,000 °C in the char gasification reactor (CHR-GASI). Preheated steam with the temperature of 250 °C at 500 kPa in the amount of 0.12 kg per kg of feed was also introduced to CHT-GASI. The ratio of secondary air mass flow to feed mass flow was selected as an independent variable and its effect on the reactor temperature, gas composition, carbon conversion and gas heating value was observed.

3. Results and discussions

Gasification of both types of waste (RDF and lignocellulosic waste biomass) with characteristics given in Table 1 in a two stage pyrolysis/gasification system was modelled. Gas composition, reactor temperature, carbon conversion in both gasification reactors and gas lower heating value were determined at different secondary enriched air to waste mass ratios (*R*). Composition of produced gas at different enriched air to waste biomass mass ratios is shown in Figure 2a. H_2 and CO are the most important components of the produced gas; the content of H_2 showed a maximum at minimum *R* and that of CO at *R*=0.46. At this value of *R,* the content of methane decreased to a value near zero. However, by increasing *R,* the content of N_2 increased together with the content of H_2O, which showed a minimum at *R*=0.4. The value of *R*=0.4 represents a point where the conversion of C is completed and, based on the equilibrium calculations, the products do not contain any unreacted C. As it results from Figure 3a, the producer gas at this value of *R* has the maximum heating value. However, as it is shown in the same Figure, the temperature of the second reactor (VOL-GASI) is only 721 °C under these conditions. Generally, equilibrium model based calculations provide good results at temperatures above 800 °C. In addition, gas produced at lower temperatures contains more tars. Therefore, as an optimal value of *R,* 0.52 kg of enriched air per kg of fed biomass was selected. At this vale of *R,* the second reactor temperature is 842 °C, the content of H_2 is 29.51 mole %, the content of CO is 32.51 mole % and the gas heating value is 7.27 MJ/Nm^3.

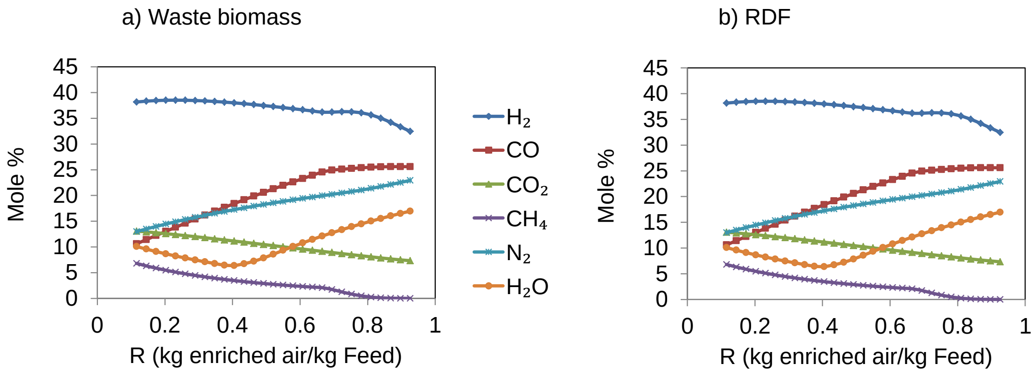

Figure 2: Produced gas composition versus secondary enriched air to feed mass ratio, (a) waste biomass (b)RDF

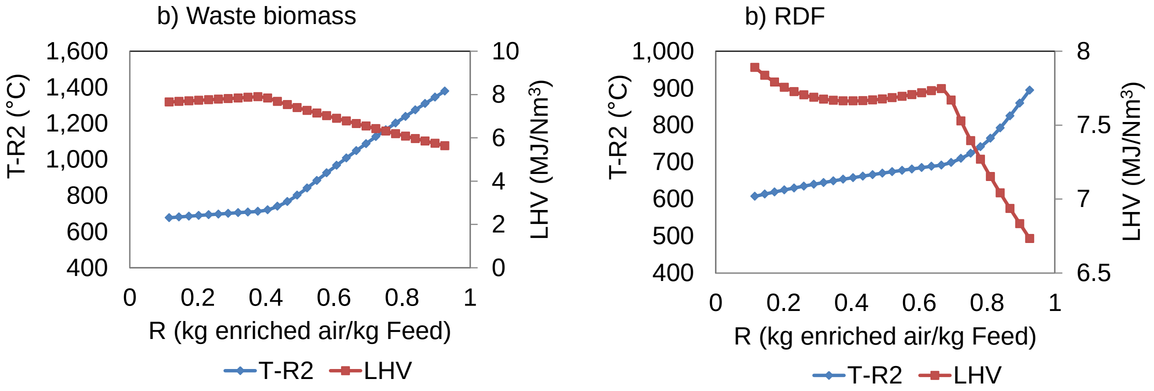

Figure 3: Secondary reactor temperature versus secondary enriched air to feed mass ratio (a) waste biomass, (b) RDF

Composition of gas produced by the RDF gasification at different values of *R* is shown in Figure 2b; compared with lignocellulosic waste biomass, the H_2 content is higher but the CO content is lower due to the higher H_2 content and lower O_2 content of RDF as it contains also polyolefins and other plastic materials. Another important difference between the gasification of lignocellulosic waste biomass and RDF is the requirement of oxidising agent (enriched air). For complete conversion of RDF, 0.694 kg of enriched air per kg of RDF was introduced to the secondary reactor. As it is shown in Figure 4, secondary enriched air requirement for RDF gasification is 1.73 times higher than in case of lignocellulosic waste biomass. However, to keep a temperature of around 1,000 °C in the char gasification reactor (CHR-GASI), in case of RDF, 0.314 kg of enriched air per kg of RDF was used compared to 0.347 kg in case of lignocellulosic waste biomass.

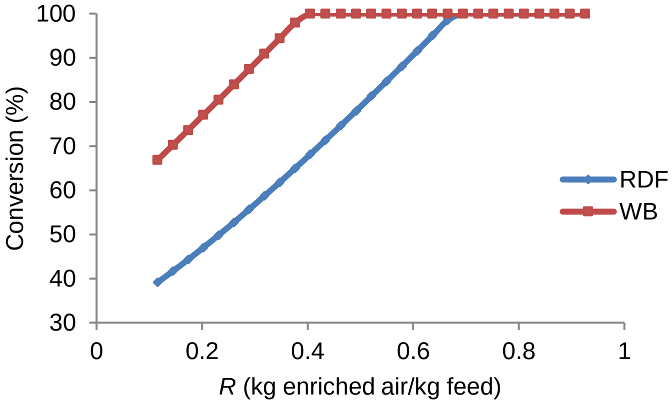

Figure 4: Total carbon conversion versus enriched air to feed mass ratio

At the point when complete conversion is reached (R=0.694), the gas heating value is 7.7 MJ/kg (Figure 3b). The gas heating value first decreased with the increasing *R,* then it increased from *R*=0.4 up to *R*=0.694, when it reached a maximum and then rapidly started to decrease because of the starting CO oxidation to CO_2. However, the secondary reactor temperature at maximum gas LHV is only 700 °C. Low reactor temperature can lead to high content of tar in the produced gas. But increasing the reactor temperature requires H_2 and CO oxidation resulting in the loss of the gas energy content. Based on this observation, optimal value of *R* of 0.868 kg enriched air per kg of RDF was selected. At this value of *R*, the temperature of the second reactor increased to 825 °C and gas LHV was 6.94 MJ/Nm^3. It was found that feed elemental composition and heating value can significantly affect the optimal value of *R*.

Table 3: Results of RDF and waste biomass gasification under optimal conditions

Parameter	RDF	Waste biomass
R (kg enriched Air/kg feed)	0.8680	0.5208
Conversion-R1-CHR-GASI (%)	100	100
T- R1- CHR-GASI (°C)	1,003	1,011
Conversion-R2- VOL-GASI (%)	100	100
T- R2 -VOL-GASI (°C)	825	842
H_2 (mole %)	34.22	29.51
CO (mole %)	25.6	32.31
CO_2 (mole %)	7.67	8.85
CH_4 (mole %)	0.05	0.03
N_2 (mole %)	22.13	20.67
H_2O (mole %)	10.3	8.59
LHV (MJ/Nm^3)	6.94	7.27
n (kg gas/kg feed)	2.1	1.78

Table 3 shows the summary of results of both RDF and waste biomass gasification in a two stage pyrolysis/gasification unit under optimal conditions. Comparing the RDF and lignocellulosic waste biomass, RDF gasification requires larger amount of oxidising agent. If both cases the same amount of the oxidising agent is used, in the case of RDF the reactor temperature is lower and the conversion can be incomplete; however, the content of H_2 is higher and those of CO and CO_2 are lower. The calculated produced gas to feed mass ratio is 2.1 kg of gas/ kg of feed for RDF and 1.78 kg of gas/kg of feed for waste biomass. However, LHV of gas from the RDF gasification is 6.94 MJ/Nm^3 and from the LWB gasification it was 7.27 MJ/Nm^3.

4. Conclusions

Using Aspen plus simulation, a model of a two-stage pyrolysis/gasification unit was developed. Gasification of two types of solid waste (lignocellulosic waste biomass and refuse-derived fuel) using enriched air as the main gasification agent was observed under different process conditions. Complete conversion of RDF was reached at the secondary enriched air to feed mass ratio of R=0.694, while for LWB this value was 0.4. However, because of the requirement for higher secondary reactor temperature and lower gas tar content than the optimal values of R, 0.868 was selected for RDF and 0.5208 for LWB. Under these conditions from each kg of RDF, 2.1 kg of gas with the heating value of 6.94 MJ/Nm^3, and from each kg of LWB, 1.78 kg of gas with the heating value of 7.27 MJ/Nm^3 were obtained. The H_2 content of gas was 34.22 mole % in case of RDF and 29.51 mole % in case of LWB. Gas CO and CO_2 content was 25.6 and 7.67 mole % in the gas from RDF gasification and 32.31 and 8.85 mole % in case of LWB. The Aspen simulation model developed in this work enabled parametric analysis of both pyrolysis and gasification stages, however it can be improved in the future by kinetic modelling of the gasification stage.

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