Performance Assessment of Waste and Biomass Two-stage Pyrolysis/Split Product Oxy-gasification (PSPOG) Using Aspen Simulation

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Abstract

Air blowing gasifiers produce syngas with low heating value, which can limit its application. The use of pure oxygen increases the gas heating value, however, in a single-stage gasification process, total carbon conversion is reached at relatively high equivalence ratio (ER), which results in high oxygen requirement. A two-stage pyrolysis/split product oxy-gasification (PSPOG) combined with steam reforming can reduce the required ER for complete carbon conversion at high cold gas efficiency (CGE) and high gas heating value. A laboratory scale PSPOG unit was used to determine suitable gasification conditions. In the next step, Aspen Plus simulation was employed to simulate an industrial scale PSPOG process. As a reference, a single-stage gasifier model was simulated. Carbon conversion in the PSPOG process was completed at ER of 0.11 which is almost 2.5 times lower than the value required in a single-stage gasifier for the same raw material. Theoretical CGE at this ER was 0.93, while for a single-stage gasifier it was 0.52 and reached the maximum value of 0.89 at ER of 0.25. Gas lower heating value (LHV) at complete carbon conversion was 15 MJ/Nm3 versus 12 MJ/Nm3 for a single-stage gasifier. Recycling of 22% of the produced raw gas back to the char gasification reactor helped to maintain the required reactor temperature.

**Keywords**: gasification, two-stage, oxy-gasification, equivalence ratio, Aspen Plus.

* 1. Introduction

Most solid waste streams are in form of mixed waste, the mechanical recycling of which is inconvenient. Based on OECD 2022 report, only 9% of plastic waste were recycled during the period of 2000–2019 (Zheng and Watanabe, 2022). Currently, most of this waste is disposed of in landfills or incinerators. Thermochemical methods like gasification and pyrolysis are considered as better alternatives as they enable energy recovery and recovery of valuable chemicals at the cost of much lower environmental side effects. Gasification can convert mixed plastic waste into syngas containing mainly CO, H2, CO2, H2O, and CH4. In addition to these major components, syngas can also contain impurities like solid particles, tars, compounds of sulfur, chlorine, etc. (Antoiou et.al, 2014). Syngas composition, heating value, and conversion efficiency depend on raw material composition, used gasification technology, process conditions, and on the type of gasification agent used (Ahmad, et.al, 2016). Air, pure oxygen, oxygen enriched air, and steam are the most often used gasification agents.

Air blowing gasifiers produce syngas with low heating value, which can significantly limit its application. The use of pure oxygen or oxygen enriched air increases the gas heating value. However, process operational cost also increases; therefore, the amount of oxygen required is very important. Syngas composition and overall performance of a gasifier are mainly affected by the equivalence ratio (ER) defined as the ratio of actual amount of oxygen used to the stoichiometric mount of oxygen needed for combustion (Jangsawang, et.al, 2015). Overall performance of the gasification process (Kuo et.al. 2014) is given by carbon conversion (CConv) and cold gas efficiency (CGE), which represent the yield of raw material energy content transferred to syngas and carbon conversion efficiency (CCE), which is defined as the ratio of carbon transferred to syngas to total carbon present in raw material.

Gasification technologies with fixed bed, fluidized bed, and entrained flow reactors commercialized in coal gasification use a single-stage process for the gasification of solid raw materials. In a single-stage gasification process, total carbon conversion is reached usually at ER above 0.3-0.5. At lower ER, the conversion is not complete, gasification temperature is low, and the gas tar content is high. However, at higher ER, the gas is diluted by CO2 and cold gas efficiency (CGE) is low as a large amount of combustible matter is used to ensure suitable conditions for the gasification process.

A two-stage gasification unit consisting of a pyrolysis stage and two gasification reactors for separate pyrolysis product gasification was developed and tested in a previous work (Šuhaj et.al, 2022). The unit is flexible for the use of different oxidizing agents and can work under any pyrolysis, gasification, or oxy-gasification conditions. By splitting the pyrolysis products and oxidizing agents, the system can work at significantly lower ER. In this work, gasification performance parameters (CConv, CGE, CCE), gas composition, and gas lower heating value (LHV) are investigated at different ER, oxygen split ratio (OSR), steam split ratio (SSR), and process gas recycling ratio (PGRR) in a two-stage pyrolysis/split product oxy-gasification (PSPOG) unit.

* 1. Materials and methods

A plastic mixture consisting of high-density polyethylene (HDPE, 7.95 wt. %), polypropylene (PP, 49.37 wt. %), and polyethylene terephthalate (PET, 42.68 wt. %) was considered in this work. Composition of the feed corresponded with average yields of individual plastic types in lithium-ion batteries (Dunn et.al, 2014). Each type of plastic material was characterized by thermogravimetric analysis (TG), elemental analysis (EA), and calorimetric analysis (CA). Using thermogravimetric data obtained by a STA 409 PC Luxx (NETZSCH, Germany) thermogravimeter, the content of moisture, volatile mater (VM), fixed carbon (FC), and ash was determined. The content of carbon, hydrogen, nitrogen, and sulfur was determined by a Vario Macro Cube® (Elementar, Germany) CHNS analyzer. Results of proximate and elemental analyses of all types of plastics present in the waste mixture, feed, and char from pyrolysis stage are shown in Table 1.

Table 1: Proximate and elemental analyses of individual plastics, waste mixture, and pyrolysis char

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Waste** | **Moisture** | **VM** | **FC** | **Ash** | **C** | **H** | **O\*** | **N** | **S** |
| HDPE | 0 | 96.5 | 0.76 | 2.74 | 85.3 | 13.8 | 0.72 | 0.12 | 0.06 |
| PP | 0 | 98.45 | 1.54 | 0.01 | 83.5 | 14 | 2.4 | 0.02 | 0.08 |
| PET | 0.75 | 88.21 | 11.79 | 0 | 62.9 | 4.27 | 32.79 | 0.04 | 0 |
| Feed | 0.32 | 93.92 | 5.85 | 0.22 | 74.85 | 9.83 | 15.24 | 0.04 | 0.04 |
| Pyrolysis char | 0 | 47.29 | 43.42 | 9.29 | 84.54 | 5.72 | 0 | 0.36 | 0.09 |

\* Wt% O = 100-(Wt % C + Wt % H + Wt %N + Wt % Cl + Wt % S + Wt % ASH)

Lower heating value of plastics was measured using a bomb calorimeter (Fire Testing Technology Ltd, United Kingdom). For LHV /values of 40.2 MJ/kg, 44.1 MJ/kg, and 24.4 MJ/kg were measured for HDPE, PP, and PET, respectively.

A two-stage laboratory scale pyrolysis/split product gasification (PSPG) unit, described in (Šuhaj et.al. 2022), was used to determine suitable gasification conditions, i.e., pyrolysis stage temperature, secondary catalytic reactor temperature, char gasification reactor temperature, product yield, and gas tar content.

In the next step, Aspen Plus simulation was employed using experimental data to simulate the industrial scale two-stage pyrolysis/split product oxy-gasification process shown in Figure 1. As a reference, a single-stage gasifier model was simulated. The feed of 10 t/h of feedstock into an industrial scale PSPOG unit was considered. The feedstock is pyrolyzed at 740 °C in the first stage. The yields of gas, liquid, and solid products obtained from the laboratory experiments were 49.7 %, 39.64%, and 10.66 %, respectively.

The composition of pyrolysis gases at 740 °C was derived from the composition of the pyrolysis gas of HDPE, PP, and PET obtained from literature (Jung et al. 2010). The liquid pyrolysis product was modeled according to four representative components (naphthalene, ethylbenzene, toluene, and benzenediol).

The thermodynamic equilibrium model for gasification was employed to analyze the performance of the PSPOG system. The solid pyrolysis product is gasified in a char gasification reactor (CHGR); produced gas from CHGR is used together with additional oxygen and steam as gasifying agents in the secondary catalytic reactor (SCR). A portion of raw syngas is recycled to CHGR to maintain the reactor temperature. Raw gas is cooled and cleaned in a gas cleaning unit. A fraction of clean gas is used to heat the pyrolysis reactor. The equivalence ratio (ER), oxygen split ratio (OSR), steam split ratio (SSR), carbon conversion (CConv), cold gas efficiency (CGE), and carbon conversion efficiency (CCE) are calculated by Eqs. 1-6.

$ER=\frac{\left(O\_{2}\right)\_{1}+\left(O\_{2}\right)\_{2}}{O\_{stechiometric}}$ (1)



Figure 1. Process flow diagram of two-stage pyrolysis/split product oxy-gasification

$OSR=\frac{\left(O\_{2}\right)\_{1}}{\left(O\_{2}\right)\_{1}+\left(O\_{2}\right)\_{2}}$ (2)

$SSR=\frac{SCR\_{steam}}{SCR\_{steam}+CHGS\_{steam}}$ (3)

$CConv=\frac{C\_{in}-C\_{out}}{C\_{in}}$ (4)

$CGE=\frac{m\_{syngas}HHV\_{syngas}}{m\_{feed}HHV\_{feed}}$ (5)

$CCE=\frac{C\_{syngas}}{C\_{feed}}$ (6)

Where (O2)1 and (O2)2 represent the oxygen flow to SCR and CHGR, respectively, *Cin* is flow of carbon entering the gasifier, *Cout* the flow of carbon in the remining solid residue, *msyngas* is the mas flow of syngas, *mfeed* the mass flow of feed, *HHVsyngs* is higher heating value of syngas, and *HHVfeed* is higher heating value of feed.

* 1. Results and discussion

The effect of ER on gasification performance parameters and gas composition is shown in Figure 2. Carbon conversion was completed at ER of 0.11. At this point, a theoretical CGE of 0.93 and CCE of 0.87 were reached, gas LHV was 14.8 MJ/Nm3, and the equilibrium content of H2, CO, and CH4 reached 43, 44, and 11 mole %, respectively.

Compared to one-stage gasification, ER for complete carbon conversion was almost 2.5 time lower. As it results from Figure 3a, carbon conversion was completed at ER of 0.25 in one stage gasification process. Theoretical CGE at this ER was 0.89 (Figure 3b), while at ER of 0.11 it was only 0.52. Gas LHV at complete carbon conversion was 11.8 MJ/Nm3 (Figure 3c) versus 14.8 MJ/Nm3 in the PSPOG process. However, in case of the PSPOG process, less gas is produced because lower amount of oxygen is used. The reason for high LHV of syngas at 100% carbon conversion in PSPOG is the much higher concentration of methane, 11 vol. %, compared to its practically zero content in case of one-stage gasification (Figure 3d). Carbon conversion efficiency in case of the one-stage gasification process is higher than in the PSPOG process. The reason is that in PSPOG, a portion of the gas is used to heat the pyrolysis reactor. Optimal value of gas fraction used to heat the pyrolysis reactor was found to be 0.11, at which the required temperatures of all three reactors are obtained.



Figure 2: Effect of ER on gasification performance parameters “a)” and syngas equilibrium composition “b)”



Figure 3: Comparison of PSPOG with one-stage gasification a) CConv, b) CGE, c) LHV d) CCE and methane concentration in syngas



Figure 4: a) Effect of OSR, b) Effect of RGR, c) and d) Effect of SCR steam mass flow on reactor temperatures and gas composition at CHGR reactor mass flow of 500 kg/h

PSPOG enables slitting oxygen and steam to SCR and CHGR, which can affect both gasification reactor’s temperature and gas composition and gasification performance parameters. It was found that maximum reactor temperature is reached at OSR of 0.6 (Figure 4a). At higher value of OSR, the SCR temperature decreases because of the decreasing CConv. Reactor temperature is maintained by the recycling gas ratio (RGR) (fraction of raw syngas returned to CHGR) and mass flow of steam used in SCR. The optimal RGR was found to be 0.22 (Figure 4b) and steam mass flow to SCR 2500 kg/h (Figure 4c) at the CHGR steam mass flow of 500 kg/h. At these conditions, carbon conversion was completed, CHGR was 890 °C, SCR temperature was 752 °C, and maximum CO/CO2 ratio was reached.

* 1. Conclusion

Pyrolysis/Split Product Oxy-gasification (PSPOG) process is efficient in increasing the gas LHV, CGE, and CCE at much lower ER than conventional one-stage gasification. Combination of a pyrolysis reactor with two gasification reactors for separate pyrolysis product gasification and their mutual integration has been proven as a convenient way to improve waste and biomass gasification performance. For a mixture of HDPE, PP, and PET plastics at ER of 0.11 and steam to feed ratio of 0.3, a gas with LHV of 14.8 MJ/Nm3 can be produced with the theoretical CGE of 93% and CCE of around 89%. This ER was almost 2.5 times lower than that for the one-stage gasification process. Combustion of around 11 % of produced gas covered the energy requirements of the pyrolysis stage. These results were achieved based on the thermodynamic equilibrium model and laboratory scale experiments, the effect of scale-up is not reflected.

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