Effect of Gasifying Agents on the Gasification of Plastic Waste

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Abstract. Gasification is an attractive valorization option because it can convert plastic waste into valuable products such as syngas. If the syngas meets certain specifications, it can be used to produce fuel, chemicals, and electricity. Additionally, plastic waste is rich in carbon and hydrogen, both essential for high-quality syngas production. This study examines how critical factors such as the equivalence ratio (ER) and the type of gasifying agents such as oxygen or a mixture of oxygen-carbon dioxide or oxygen-steam affect the composition of the syngas, particularly the composition of hydrogen (H_2) and carbon monoxide (CO), as well as the H_2/CO ratio and the Lower Heating Value (LHV) of the syngas. The findings reveal that lower equivalence ratios (ER) below 0.4 favor higher yields of hydrogen (H_2) and carbon monoxide (CO), with a maximum hydrogen content of 58% achieved at an ER of 0.22 without the presence of carbon dioxide (CO_2). Additionally, the highest CO composition of 51% was observed using an oxygen-carbon dioxide mixture at an ER of 0.36. The ideal H_2/CO ratio of 2, suitable for processes like Fischer-Tropsch or methanol synthesis, was obtained at ER values between 0.1 and 0.3. The study also identified that the highest Lower Heating Value (LHV) of 15.4 MJ/Nm^3 was recorded when using only oxygen as the gasifying agent at an ER of 0.1. Overall, this research highlights the potential of gasification to effectively address plastic waste management by optimizing syngas production through varying gasifying agents and operational conditions.

Keywords: Gasification, Equivalence ratio, Plastic waste.

1. Introduction

The increase in plastic waste, driven by factors like population growth, urbanization, and economic development, reached an estimated 400 million tons globally in 2022 [1]. Various methods to address this challenge include mechanical recycling, landfilling, incineration, and chemical recycling, with gasification being a preferred option due to its efficiency and ability to reduce greenhouse gases. The gasification process converts carbon-based materials, including plastic waste, into syngas using gasifying agents such as air, steam, and oxygen, in sub-stochiometric quantities, at temperatures between 550

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and 1000°C [2]. The choice of gasifying agents used in the gasification process plays a critical role in determining the energy efficiency, economic feasibility, and environmental sustainability of gasification systems. For example, oxygen gasification significantly increases the calorific value of syngas to 10 – 12 MJ/ Nm^3, enhancing energy efficiency and making it ideal to be utilized in power systems [3]. Oxygen can improve syngas quality and reduces downstream processing costs [3] However, the production of oxygen involves high operational costs, particularly through cryogenic air separation, making it a costly option. However, the use of oxygen may lead to higher NOx emissions, requiring additional environmental controls [4]. Steam gasification, on the other hand, enhances hydrogen production and syngas quality, which is advantageous for synthesis and clean energy applications. Although the generation of steam can be costly, especially in systems without waste heat recovery, the hydrogen -enriched syngas it produces is economically valuable in markets that demand clean hydrogen. From an environmental perspective, steam gasification is favourable, producing lower carbon emissions compared to traditional combustion [5]. Using carbon dioxide as a gasifying agent, enhances CO yield and, when integrated with carbon capture and storage technologies, offers a cost effective and environmentally sustainable pathway that can potentially achieve near-zero emissions [6]. Previous research [7, 8] has primarily concentrated on plastic waste gasification using single gasifying agents, without comparing oxygen to mixtures like oxygen-steam and oxygen-carbon dioxide. Furthermore, the choice of the gasifying agent impacts tar formation. The gasifiying agents influence the gasifier temperature. Elevated temperatures promote the breakdown of tar into lighter hydrocarbons, thereby lowering its concentration in the resulting syngas [9]. Additionally, studies have shown that introducing steam and carbon dioxide as a gasifying agent in air gasification of plastic waste can further encourage tar-cracking reactions [10], including the steam reforming and dry reforming of tars, methane, and light hydrocarbons [11].

This study seeks to explore the impacts of operating conditions—such as the equivalence ratio, steam-to-polyethylene ratio, and carbon dioxide-to-carbon ratio—while examining the effects of using single versus mixed gasifying agents. The focus is on evaluating the hydrogen composition in the product gas, the H_2/CO ratio, and the Lower Heating Value (LHV) of the syngas. Thermodynamic equilibrium models are used in this study to determine the outputs. These models are favoured for their simplicity and independence from gasifier design, making them valuable for assessing the impact of feedstock composition and process parameters on the output parameters. However, these equilibrium models have limitations as they do not account for reaction kinetics and are unable to predict the hydrodynamics aspects of the gasifier, which depend on the gasifier configuration [12].

2. Modelling Framework

A flowsheet for polyethylene gasification was designed using Aspen Plus process simulation software to investigate the effects of operating conditions and gasifying agents on syngas composition, particularly, hydrogen (H_2), quality (H_2/CO) ratio of the syngas, and Lower Heating Value (LHV) of the syngas. Low-Density Polyethylene (LDPE) was used as the feedstock in the model, and was included as a non-conventional component, with ultimate and proximate analysis data sourced from [13]. The thermodynamic calculations utilized the Peng-Robinson-Boston-Mathias (PR-BM) equation of state, chosen for its effectiveness in correlating low pressures with high temperatures (above 700°C) common in plastic waste gasification [14]. The process was modeled to operate at steady state, with the gasifier maintained at atmospheric pressure and minimal tar production. The gas composition was determined using the Gibbs free energy minimization approach.

The gasification process consists of three stages. In the initial stage, plastic waste is introduced into the RYield reactor, called DECOMP, where polyethylene is decomposed in an oxygen-free environment, transforming it into conventional elemental constituents. The second stage utilizes the RGibbs reactor, or GASIFER, to calculate the system's equilibrium composition based on Gibbs free energy minimization. Here, the elemental constituents from DECOMP are combined with gasifying agents such as oxygen, steam, and carbon dioxide, resulting in the production of syngas via various chemical reactions. In the final stage, a cyclone separates the solids from the gaseous products.

The selection of key operational parameters, such as the equivalence ratio (ER), steam-to-polyethylene ratio (SPR), and carbon dioxide-to-carbon (CO_2/C) ratio plays a pivotal role in determining the syngas composition, energy efficiency, and overall effectiveness of plastic waste gasification. In this study, these parameters were systematically varied to assess the impact on the process: the SPR was set at 0, 0.6, 1.5, and 4; the ER ranged from 0.1 to 1; and the CO_2/C ratio was adjusted to 0, 0.6, and 1.4.The ER represents the ratio of the actual air-to-fuel mixture to the stoichiometric ratio, influences the temperature profile and reaction pathways in the gasifier. As Khumalo et al. [15] noted, increasing ER from 0.1 to 1 significantly altered the syngas composition, including the hydrogen (H_2) and carbon monoxide (CO) concentration, the H_2/CO ratio, and the LHV. ER values between 0.1 and 0.3 favoured the production of high-quality syngas due to limited oxygen availability, which reduced complete oxidation. However, ER values up to 1 were also analysed to evaluate the shift toward complete combustion and its subsequent effect on syngas yield and quality. The steam-to-polyethylene ratio (SPR) is another critical variable. Steam not only supplies thermal energy but also drives endothermic reactions such as steam reforming and the water-gas shift reaction. Saebea et al. [16] observed that at a fixed temperature of 900°C and an SPR ratio of 1.5, results in the highest syngas yield and a H_2/CO of 2. However, a major limitation of increasing steam addition is the higher energy demands to drive the endothermic reactions. The CO_2/C ratio is also a significant parameter in altering the gasification environment. This ratio impacts key reactions such as the Boudouard reaction and dry reforming, which contribute to CO and H_2 production. Khumalo et al. [17] found that lower ratio of 0.6 resulted in superior syngas characteristics, including a higher hydrogen concentration, an optimal H_2/CO ratio of about 2, and increased LHV. These findings suggest that moderate CO_2 addition can improve syngas quality while facilitating effective carbon utilization.

The composition results of the products obtained from experimental work, conducted for the co-gasification of biomass and plastic waste [18] were compared with the values from the Aspen Plus model. In the experiment, raw straw and polyethylene were used as feedstock, and air served as the gasifying agent. The gasifier temperature was set at 1000°C with an equivalence ratio (ER) of 0.25. The operating conditions included a feed rate of 4 g/min, a primary gas flow rate of 2 L/min, and a secondary gas flow rate of 4 L/min. The incoming gas was preheated to 500°C. Yu. et al. [18]. The validation approach used in this study relied on calculating the relative error (ε_r), defined as the ratio of the absolute difference between the modeled values (from Aspen Plus), X_m, and the experimental values, X_e, to the experimental value. Moreover, the relative error analysis indicates that the modeled and experimental syngas composition values were found to be in good agreement and fall within an acceptable range—specifically, all relative errors were within ±15% [19]. The relative error values for each component are presented in Table 1 below. Aspen Plus predictions reveal that co-gasification of biomass with plastic waste produces a noticeable amount of methane, in contrast to the nearly negligible methane levels observed in polyethylene only gasification [20].

Table.1 Model validation: Comparison of the syngas composition obtained experimentally and from the model.

Parameter	Experimental (Xe)	Model (Aspen Plus)	Error, %
H_2	13	12.76	-1.846
CO	13.6	13.81	-1.471
CO_2	8.5	8.47	-0.353
CH_4	3.4	2.93	-13.82

3. Results and Discussion

3.1 Effect of gasifying agents and operating conditions on the hydrogen (H_2) composition of the product gas.

Figures 1 (a) and (b) illustrate the effects of various gasifying agents (oxygen, oxy-gen-steam mixture, and oxygen-carbon dioxide mixture) and operating parameters (equivalence ratio (ER), steam-to-polyethylene ratio (SPR), and carbon dioxide-to-car- bon (CO_2/C) ratio) on the hydrogen (H_2) composition of the product gas. Figure 1 (a) and (b) indicate that as the ER increases from 0.1 to 1, the H_2 composition initially rises, peaks, and then declines due to oxidation reactions that convert H_2 to water (H_2O) at higher oxygen flow rates. The highest H_2 composition occurs at ER values below 0.4, beyond which H_2 level declines due to complete combustion reactions being dominant at higher ER values. It is Furthermore, Figure 1 (a), illustrates that an increase in steam-to-polyethylene ratio from 0 to 4, results in decline in H_2 concentration from approximately 58.02% to 31%. This decrease occurs because excess steam increases the energy requirements in the gasifier, thus causing a decrease in the gasifier temperature, which is essential for maintaining optimal reaction conditions. Thus, highest hydrogen (H_2) composition of 57.8% at a steam-to-polyethylene ratio (SPR) of 0.6 and an equivalence ratio (ER) of 0.3. The highest H_2 is linked to steam reactions like the water gas shift reaction, water gas reaction, and steam reforming being promoted at low ER values.

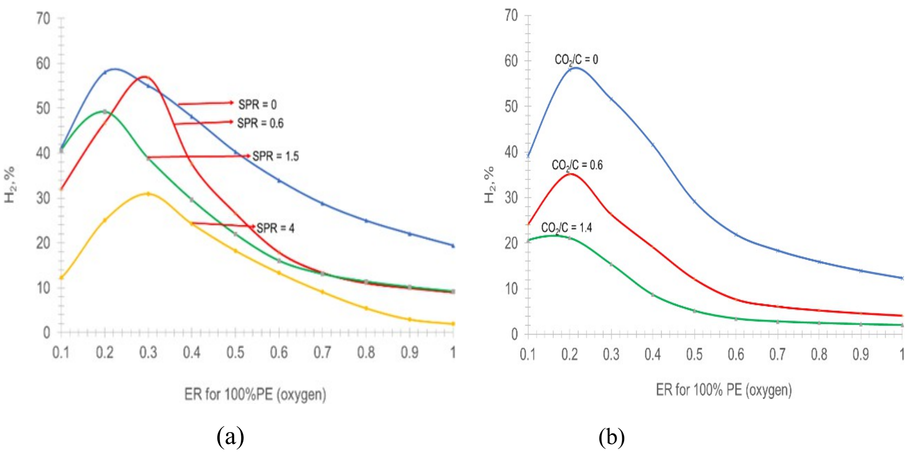


Fig. 1. Effect of operating conditions such as equivalence ratio (ER), steam-to-polyethylene ratio (SPR), and carbon dioxide-to-carbon ratio (CO_2/C) ratio on H_2 composition, when (a) oxy- gen and oxygen – steam and (b) oxygen and oxygen-carbon dioxide mixtures are used as gasifying agents.

Figure 1(b) shows that the hydrogen concentration significantly decreases from 58.02 % to 21% as the CO_2/C ratio increased from 0 to 1.4. This decline is mainly due to the reverse water-gas shift reaction, where CO_2 reacts with H_2 to produce CO. The maximum H_2 composition of 35% is achieved at CO_2/ C ratio equal to 0.6 and ER equal to 0.18. Importantly, using oxygen alone yields the highest H_2 value of 58.02% at an ER of 0.24, exceeding results from both oxygen-steam and oxygen-carbon dioxide mixtures. Additionally, comparing oxygen -steam and oxygen-CO_2 mixtures as gasifying agents, reveals that CO_2 has more negative effect on hydrogen production than steam, even at lower concentration. This indicates that CO_2 is less effective in promoting hydrogen generation during plastic waste gasification.

3.2 Effect of gasifying agents and operating conditions on the H_2/CO ratio of the syngas.

Figures 2 (a) and (b) demonstrate that the H_2/CO ratio of syngas decreases as the equivalence ratio (ER) increases from 0.1 to 1, primarily due to exothermic oxidation reactions that dominate at higher ER values. In Figure 2 (a), the recommended H_2/CO ratio of 2 is achieved within the ER range of 0.2 to 0.6 when using oxygen and oxygen-steam mixtures as gasifying agents. Additionally, increasing the steam-to-polyethylene ratio (SPR) from 0.6 to 4 enhances syngas quality, maintaining the recommended H_2/CO ratio of 2 through reactions like the water-gas shift and steam reforming.

Figure 2 (b) shows that the addition of carbon dioxide reduces the H_2/CO ratio due to the Boudouard reaction and reverse water-gas shift reaction, which increase CO composition. The recommended H_2/CO ratio of 2 is achievable within an ER range of 0.18 to 0.24 and a CO_2/C ratio of 0 to 0.6 using an oxygen-carbon dioxide mixture. However, increasing carbon dioxide flow rates beyond a CO_2/C ratio of 0.6 does not maintain this ratio. Both figures indicate that using oxygen, either alone or in combination with steam or carbon dioxide, can enhance the quality of syngas and achieve the desired H_2/CO ratio.

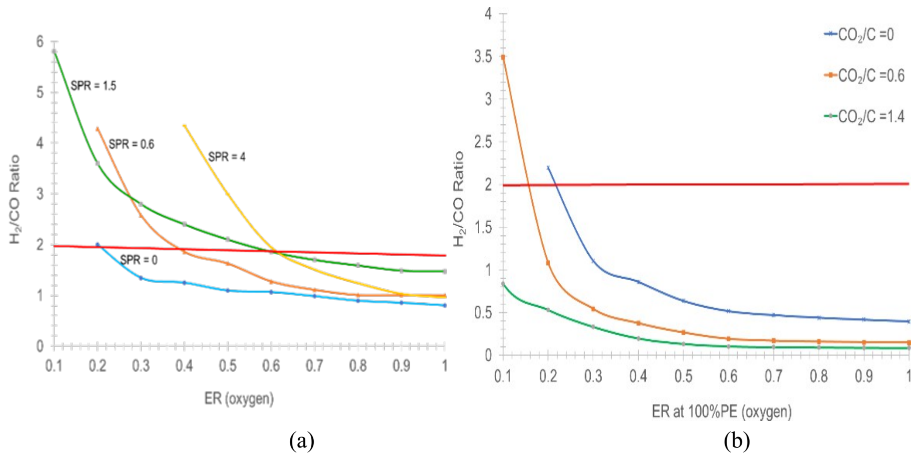
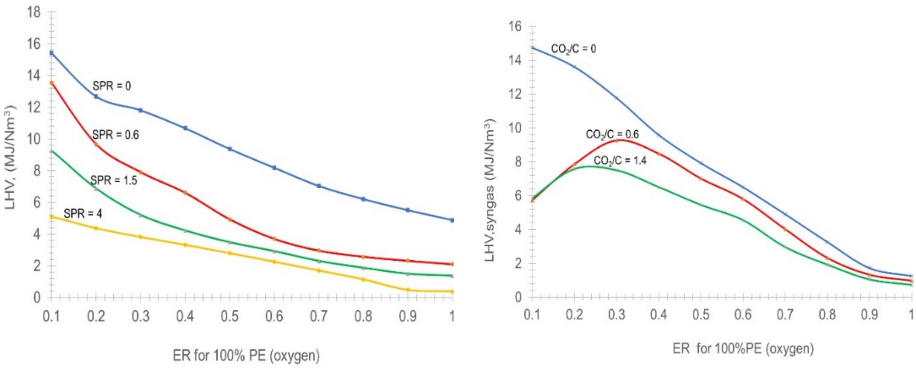


Fig. 2. Effect of operating conditions such as equivalence ratio (ER), steam-to-polyethylene ratio (SPR), and carbon dioxide-to-carbon ratio (CO_2/C) ratio on the H2/CO ratio of the syngas, when (a) oxygen and oxygen – steam and (b) oxygen and oxygen-carbon dioxide mixtures are used as gasifying agents.

3.3 Effect of gasifying agents and operating conditions on the Lower Heating Value (LHV) of the syngas.

Figure 3 (a) illustrates that the Lower Heating Value (LHV) of syngas consistently decreases as the equivalence ratio (ER) increases from 0.1 to 1, across all steam-to-polyethylene flow rates (i.e. SPR equal 0 to SPR equal to 4) when using an oxygen-steam mixture as the gasifying agent. At an ER value of 0.1, and SPR of 0, the highest LHV of approximately 16 MJ/Nm^3 is observed. However, as SPR increases to 0.6,1.5, and 4, the LHV decreases significantly to around 13.5,10 and 6 MJ/Nm^3 respectively, indicating a total drop of approximately 10 MJ/Nm^3 across the SPR range. This trend persists at higher ERs, although the rate of LHV decline becomes less steep. The reduction in LHV with increased ER is attributed to the higher availability of oxygen, which promotes complete combustion and reduces the formation of combustible gases. Similarly, increasing the SPR introduces more steam into the system, while encouraging reactions like steam reforming and water-gas shift, also absorbs thermal energy and dilutes the syngas, resulting in lower energy content.

In contrast, Figure 3 (b) shows that for CO_2/C ratios of 0.6 and 1.4, the LHV of syngas initially increases with rising ER, reaching a peak before declining with further increases in ER. When only oxygen is employed as the gasifying agent, with a CO_2/C ratio of 0, the LHV decreases with increasing ER. However, the overall trend shows that increasing CO_2/ C ratio from 0 to 0.6 and 1.4 decreases the LHV of the syngas. Thus, the highest LHV of 9.2 MJ/Nm³ is obtained at an ER of 0.32 and a CO_2/C ratio of 0.6. Overall, oxygen as a gasifying agent yields the highest LHV of 15.4 MJ/Nm³ at an ER of 0.1, surpassing values from oxygen-steam and oxygen- carbon dioxide mixtures. Figure 3 (a) and (b) shows that higher LHV are favoured at ER below 0.4. This is because at low ER values, partial oxidation is favoured, which promotes the formation of combustible gases, Additionally, the polymeric nature of polyethylene, which is rich in hydrogen, contributes to the higher values of LHV of the syngas.



(a) (b)

Fig. 3. Effect of operating conditions such as equivalence ratio (ER), steam-to-polyethylene ratio (SPR), and carbon dioxide-to-carbon ratio (CO_2/C) ratio on the Lower Heating Value (LHV) of the syngas when (a) oxygen and oxygen–steam and (b) oxygen and oxygen-carbon dioxide mixtures are used as gasifying agents.

4. Conclusion

The gasification of polyethylene with various gasifying agents specifically oxygen, an oxygen-steam mixture, and an oxygen-carbon dioxide mixture yielded notable results. Using oxygen alone at low equivalence ratios (ER) below 0.5 achieved a hydro- gen composition of 58.02% at an ER of 0.24 and a Lower Heating Value (LHV) of 15.4 MJ/Nm³ at an ER of 0.1, surpassing the performance of the other mixtures. The ideal hydrogen-to-carbon monoxide (H_2/CO) ratio of 2 was consistently reached with oxygen-steam mixtures across different steam-to-polyethylene ratios (SPR). However, the oxygen-carbon dioxide mixture achieved this ratio only at a CO_2/C ratio of 0.6, with higher carbon dioxide flow rates reducing the H_2/CO ratio. Additionally, the study found that increased steam and carbon dioxide flow rates negatively impacted the LHV of syngas, highlighting that lower flow rates resulted in higher LHV values. This research underscores the potential of polyethylene gasification using oxygen and its mixtures as a viable solution for plastic waste management.

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Disclosure of Interests. Authors declare no competing interests.

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