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Polyethylene terephthalate (PET) recycling via steam gasification – The effect of operating conditions on gas and tar composition



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ABSTRACT

Polyethylene terephthalate (PET) is widely used in textile fiber, film, and bottles. Although PET bottle recycling has made great progress, other PET waste is still not recycled. Gasification could be an option for recycling or recovering energy and chemicals from PET waste. However, single stream PET steam gasification in fluidized bed is seldom investigated. In this paper, individual PET gasification experiments were then conducted in a lab-scale bubbling fluidized bed to investigate how gasifying agents, temperature, residence time and steam/fuel ratio affect the product composition. The results showed that, in steam gasification, steam was the main source of H₂, but increasing the steam to fuel ratio cannot increase the H₂ yield remarkably. Temperature was an essential parameter. Increasing temperature from 750 to 800 °C improved the yields of H₂ (+87.7%), the dominant gas product CO₂ (+40.3%), and biphenyl (+123%) notably. In contrast to other common thermoplastics, high concentrations of CO₂ and biphenyl are the prominent characteristics of PET steam gasification. In addition, plastic steam gasification optimizations for syngas applications were discussed.

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1. Introduction

Plastics play a crucial role in the modern style of living because they are essential in many sectors, such as packaging, construction, agriculture, and households due to low density, corrosion resistance, and durability (Kunwar et al., 2016). Global plastic production increased from 322 Mt in 2015 to 368 Mt in 2019, a 3–4% annual growth (Plastics Europe, 2016; Plastics Europe, 2020). However, the significant surge of plastic production and utilization causes severe environment pollution. Plastic waste is mainly landfilled with other solid waste, but can remain in the soil semi-permanently, because of the low degradability, which can result in reduced landfill capacity and soil contamination. Some plastic waste is discarded in the ocean, threatening the marine creatures. Research reveals that 60% of plastic waste was landfilled or left in the environment between 1950 and 2015 (Geyer et al., 2017). Furthermore, plastics, derived from fossil fuels, are potential alternative raw materials for energy and chemicals production to lessen fossil fuel consumption. Thus, it is necessary and valuable to recycle plastics or recover energy from plastics.

Energy recovery through plastic waste incineration is a straightforward process for replacing fossil fuel in heat and power applications. Plastics are usually combusted with other municipal solid waste to produce heat and/or electricity. Numerous municipal waste power plants have been built to reduce solid waste. According to Geyer et al., 12% of all plastic solid waste was recovered as energy between 1950 and 2015 (Geyer et al., 2017). However, since plastics are of petrochemical origin, burning plastics contributes increasingly to net CO₂ emissions. The combustion of one tonne plastic waste and PET can release 950 kg and 2300 kg CO₂, respectively (Khoo, 2019; Chilton et al., 2010). Therefore, with the concern about global warming issues, it is inadvisable to recover energy from plastic incineration. An example of a response to this is the case of Denmark. The Danish government has initiated a reduction of waste incineration rate to improve the recycling quality and CO₂ emissions reduction (Rosendal, 2014).

Among the plastics, PET is the one of the most favorable food packaging materials, mainly for soft drinks and mineral water, because of its light weight and large containing capacity (Sharuddin et al., 2016). PET bottle recycling is universal worldwide, since PET bottles are easily separated and recollected (Welle, 2011). Many countries have established mature PET bottle recycling systems. Market data shows that PET accounted for 55% in global recycled plastics in 2017 (Locock et al., 2017). Although mechanical recycling is low cost, the products cannot be utilized

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for making high quality products due to the weakened thermal and mechanical resistance during the melting and remolding process (Park and Kim, 2014; Al-Sabagh et al., 2016). This fact explains why 72% of recycled PET was used in the form of fibers (Shen et al., 2010). In order to achieve sustainable PET recycling processes, chemical recycling should be considered.

Chemical recycling involves breaking the polymer chain, which can be carried out either by solvolysis or thermolysis. Solvolysis reactions include methanolysis, hydrolysis, glycolysis, aminolysis, and others, and have been shown to regenerate the monomers that produce PET. (Sinha et al., 2010; Nikles and Farahat, 2005). These regenerated monomers then reconstitute high-grade PET or other polymers (Jankauskaite et al., 2008). However, most of the research on the chemical recycling of PET was conducted on a small scale. There are still many barriers for large scale applications. For example, due to the complex reaction kinetics, depolymerization cannot complete as expected. Researchers make efforts to solve the problems of catalyst selectivity, solvent, reaction conditions, and final product separation (Al-Sabagh et al., 2016).

Both mechanical recycling and solvolysis require high plastic purity, which means that the plastics to be recycled must be sorted carefully. However, plastic wastes are collected as mixtures in most countries. Thermolysis is a possible solution to recycling mixed plastics instead of incineration. Pyrolysis and gasification are the two main thermolysis processes. Pyrolysis is the process that degrades the long chain polymer into smaller molecules with intense heat in the absence of oxygen (Sharuddin et al., 2016). The dominant mixed liquid products could be alternatives to crude oil-based fuels. For instance, the physical and chemical properties of polyethylene (PE) and polypropylene (PP) pyrolysis oil can be comparable to gasoline and diesel (Sharuddin et al., 2016). However, PET is not recommended for pyrolysis because gases dominate the product distribution. For instance, Çepeliogullar & Pütün (Çepeliogullar and Pütün, 2013) studied PET pyrolysis in a fixed bed at 500 °C and observed that 76.9% PET was converted into gaseous products. Furthermore, the condensed terephthalic acid and/or similar products can clog up pipes (Marco et al., 2002). The reactions of pyrolysis are complex, so it is difficult to predict the compositions of the products (Lopez et al., 2018).

Gasification could be another alternative. The objective of gasification is to convert carbonaceous materials into gaseous products (e.g., the mixture of H_2 , CO, CH_4 and CO_2). In contrast to incineration and pyrolysis, in the gasification process, the oxidizing agent (air, steam, and oxygen are commonly used) is introduced into the system in sub-stoichiometric quantities, and the fuel is decomposed into CO and H_2 at the temperature range of 550–1000 °C (Klinghoffer and Castaldi, 2013). In general, gasification processes comprise four steps: (1) drying; (2) pyrolysis (devolatilization); (3) tar cracking, combustion, and shifting, depending on the gasifying agent; and (4) char heterogeneous gasification reactions (Lopez et al., 2018). A remarkable advantage of gasification is that it is more flexible in treating various composites of feedstocks, because the intended products for different feedstocks are identical. Plus, gasification can be integrated into current energy systems and fuel production (Lopez et al., 2018; Pereira et al., 2012).

Some research related to PET gasification was carried out with other fuels in bubbling fluidized beds (BFB) (Pohořelý et al., 2006; Robinson et al., 2016; Brachi et al., 2014; Wilk and Hofbauer, 2013; Choi et al., 2021; Grause et al., 2011). PET was considered as a partial replacement for solid fossil fuels such as coal. Pohořelý et al. (Pohořelý et al., 2006) explored co-gasification of 23% PET and 77% brown coal in a fluidized bed in a medium of 10 vol% O_2 in a bulk of nitrogen. The TGA results showed that PET was more reactive and produced more volatiles than coal. Thus, free oxygen can immediately react with PET, and

much higher bottom char formation was obtained than observed in pure coal gasification. The tar content was more than three times higher in coal blending with PET than for coal alone. Increasing the bed temperature can increase the content of CO and hydrogen, whereas the freeboard temperature played a less important role since char gasification mainly took place in the bed.

PET was also selected to substitute biomass as the gasification fuel during the time that biomass supply is inadequate. Robinson et al. (Robinson et al., 2016) compared wood and wood-PET (mass ratio 50:50) pellet gasification in an air-blown bubbling fluidized bed. They observed that gases produced from wood-PET pellets tended to have higher concentrations of CO, CO_2 , C_2H_4 and C_3H_8 , but lower concentrations of hydrogen and methane, which led to a lower heating value than gas produced from the wood pellet. Tar formation also enhanced in wood-PET pellet gasification. Brachi et al. (Brachi et al., 2014) reported the co-gasification of the olive husk (75% wt) with PET (25% wt) pellets, where a mixture of steam and air was used as the gasifying agent, and found that high-yield H_2 can be obtained from sufficient steam, and that part of required heat for endothermic steam gasification can be provided by air gasification. They found that higher temperature and steam/fuel ratios can increase hydrogen and CO_2 yield, while reducing CO and methane. They also examined some molar ratios, including H_2/CO , $H_2/(2CO + 3CO_2)$, and $(H_2 - CO_2)/(CO + CO_2)$, used for methanol production to evaluate the feasibility of the application of their products to bio-methanol production.

PET with other plastic waste pyrolysis at 600 and 700 °C in fluidized bed was studied by Grause et al. (2011). Some experiments were conducted with the presence of steam, which is also steam gasification process defined in this paper. They observed that CO_2 concentration was tripled when temperature rose from 600 to 700 °C and silica sand as bed material. This enhancement could be due to PET decarboxylation reactions.

Recently, a gasification process using a dual fluidized bed (DFB) was developed and successfully applied on a large scale in Austria, Germany, and Sweden (Wilk and Hofbauer, 2013). The basic idea is that ungasified char in the BFB was transported to the interconnected circulating fluidized bed (CFB) combustor, where char was combusted with other fuels to supply heat for the BFB gasifier. Wilk & Hofbauer investigated PE, PP, and mixtures of PE + PS, PE + PET, and PE + PP in a DFB gasifier, in which the blending of PE + PET was 20%:80%. Steam was used as gasifying agent, and olive was the bed material. The results imply that the mixture of PE + PET produced more CO and CO_2 than the others due to the high oxygen content in PET, accounting for about 50% of gas products (Wilk and Hofbauer, 2013).

The above-cited research related to PET gasification only describes the experimental results of PET-mixed fuel gasification in fluidized bed. Choi et al. (2021) studied PET air gasification with active carbon in a two-stage fluidized bed gasifier to motivate tar cracking and hydrogen yields. Wang et al. (2020) and Bai et al. (2020) reported CO_2 and supercritical water assisted PET gasification in a fixed bed, respectively. Both of them concluded that increasing temperature promoted gas yields. However, so far, individual PET steam gasification in bubbling fluidized bed has been seldom investigated. This work aims to study separated PET steam gasification in order to investigate how different conditions affect the product composition, as well as, give insight on what role PET could play in steam gasification for syngas production. This research started by exploring the influence of agents with batch experiments. Special focus was placed on PET steam gasification to examine the influence of operating conditions on gas and tar product composition with continuous feeding. The results could provide a reference for PET-mixed fuel gasification analysis, as well as improving gasification methods.

2. Experimental design and process

2.1. PET characterization and bed material

Virgin PET (approximate cube shape with 1 mm length) was the feedstock in this work. The ultimate and proximate analyses of fuels are essential to establish the mass balance of a process. For comparison, the ranges of PET ultimate analysis results (in wt%, both here and below in 2.1, dry basis) from other research were collected and are in the range of: C: 62.00–63.00, H: 4.06–5.20, O: 32.63–33.69 and others: 0.00–0.11 (Yang et al., 2015; Zhou et al., 2014; Pohořelý et al., 2006). Therefore, it is reasonable to assume that impurities can be negligible and ultimate analysis can be calculated based on elemental composition (C: 62.5, H: 4.2, O: 33.3). Proximate analysis is descriptive for the gasification process, so this analysis was conducted by thermogravimetric analysis (TGA) in a LECO TGA701, which comprises a sample furnace with 19 crucibles, in the present study.

After adding 1 g virgin PET sample in each crucible, 7.0 L/min nitrogen was introduced into the system, so this process can be viewed as pyrolysis, consisting of the first three conversion steps of gasification mentioned in Section 1. First, the temperature was increased to 110 °C to release all moisture. After that, the sample was heated up to 900 °C, so that volatiles were discharged entirely. This was followed by cooling down the system to 450 °C and switching the gas to O₂. The remaining residue was combusted, and the amount of fixed carbon (char) and ash were determined. Furthermore, 50 °C/min (maximum TGA701 ramping temperature) was employed, which can only be reached in fluidized bed (Brems et al., 2011b). PET TGA and DTG curves at 50 °C/min are illustrated in Fig. 1.

The TGA curve shows that there was a minor amount of moisture (0.15%) and ash (0.01%) in the PET, which suggested that water and ash can be neglected throughout the process. This being the case, the primary mass loss was due to the devolatilization process (88.39%), and, as the DTG curve illustrates, the mass dropped dramatically (53%/min). The main PET mass loss started at 463 °C and completed at 630 °C. This implies that the PET gasification temperature must be higher than this range in order to release the most volatiles.

The major function of the bed material is to transfer heat, and sometimes the bed material can have catalytic effects (Marinkovic, 2015). In this research, olivine (MgO: 49.6%, SiO₂: 41.7%, Fe₂O₃: 7.4%, Al₂O₃: 0.46%, Cr₂O₃: 0.31%, NiO: 0.32% (Berdugo Vilches, 2018)) was employed as fluidized bed material,

because it has satisfactory mechanical properties and modest activity for tar cracking (Wilk and Hofbauer, 2013). Mastellone and Arena even reported that olivine was effective for tar removal in plastic waste gasification, but that carbon could deposit on the surface of the olivine particles to deactivate their function as a catalyst (Mastellone and Arena, 2008).

2.2. Reactor system

The gasification experiment was carried out in a lab-scale 253 MA steel reactor with a height of 1.27 m and an inner diameter of 77.9 mm. A schematic illustration of the experimental devices is depicted in Fig. 2, and details about the BFB reactor can be seen in the paper by Stenberg et al. (2018).

The fluidization gas was fed (and mixed if required) into the wind box and blew through the distributor with 61 holes (diameter: 0.6 mm) to the bubbling fluidized bed. The distributor was designed to provide a uniform gas distribution in the bed via a suitable pressure drop, meaning that the quality of fluidization and the amount of bypassing gas can be influenced by the distributor. A ring above the distributor was used to evenly mix the tracing gas with the fluidized gas (Ouyang and Levenspiel, 1986). Along the reactor were 8 vertical measurement points for sampling or detecting product concentrations. The angled tubes at the same height opposite to the vertical measurement points were used to measure temperature (by thermocouples) and pressure. The fuel feeding system consisted of a vibrating dosing system, and the voltage input regulated the fuel feeding rate. The feeding system was installed at the top of the reactor that was heated by an electrical furnace.

2.3. Experimental conditions

To assess the effect of the gasifying agent, the system was operated with batch feeding. Air and steam are the common gasifying agents in most processes, in which air is more prevalent due to its low cost. Since pyrolysis is a crucial step of gasification process, N₂ pyrolysis was also conducted as a comparison with air and steam gasification. Olivine contains a considerable amount of transition metals, and their oxides, Fe₂O₃, Cr₂O₃, NiO, are potentially oxidizing the products. In order to confirm the amount of oxygen

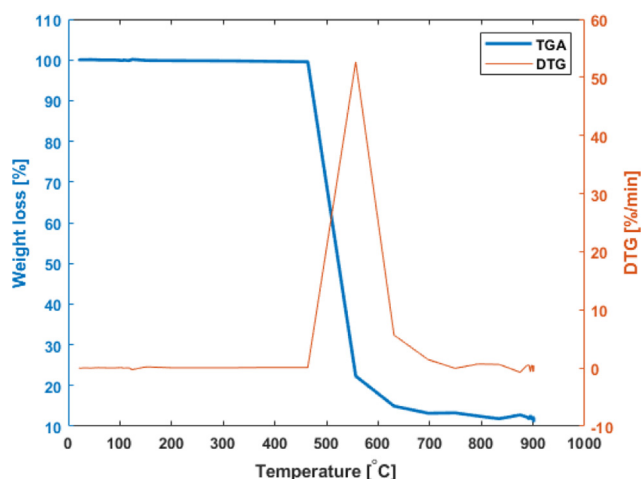


Fig. 1. PET TGA and DTG profiles at 50 °C/min.

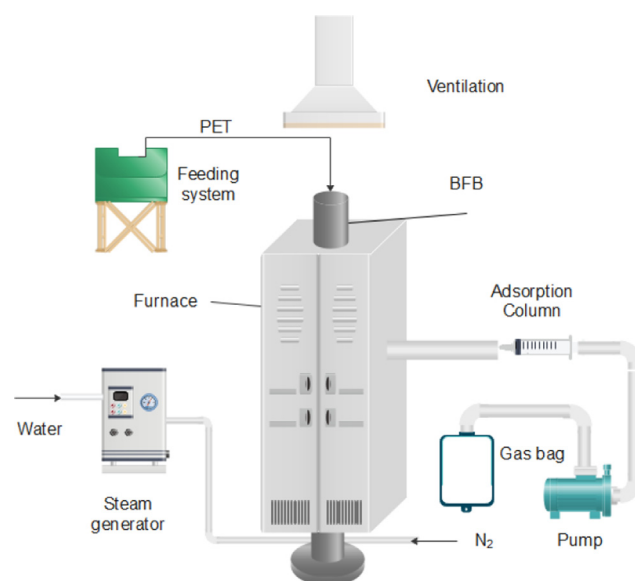


Fig. 2. Schematic illustration of the lab scale BFB and sampling system.

in the bed material involved in the reactions, PE plastic pyrolysis was carried out, thus avoiding interference from the oxygen in the PET molecules. PE was also gasified in steam so as to compare with PET steam gasification products. In each trial, 2 g fuel was fed into the reactor at 750 °C and the residence time was 3.23 s. The reasons for choosing these conditions are explained in the following paragraphs.

Regarding the continuous feeding experiments, steam was selected as the gasifying agent, and three operational parameters were investigated in this research: temperature, residence time, and the steam-to-fuel ratio. Temperature is an important parameter as it determines the thermal decomposition and affects the reaction kinetics. TGA results showed that the reaction temperature should be higher than 630 °C in order to guarantee the completed devolatilization process. For this reason, the temperature range of 700–800 °C was studied. In the residence time and steam-to-fuel ratio experiments, the temperatures were specified at 750 °C, i.e. the average of the 700–800 °C range.

Residence time is defined here as the quotient of the height of the sampling port above the surface of the bed and the gas feeding velocity. The minimum fluidization velocity U_{mf} was around 0.045 m/s in air, N₂ and steam, which could be computed according to the properties of olivine (particle density: 3300 kg/m³; average particle diameter: 288 µm). The range of bubbling fluidization gas velocity conducted by some researchers varied from 2 to 6 U_{mf} (Brems et al., 2011a; Berdugo Vilches, 2018; Robinson et al., 2016; Berdugo Vilches, 2018; Robinson et al., 2016). Given that the maximum gas flow rate was 10 L/min (at 20 °C) in the system, the gas feeding velocity was in the range of 4–5 U_{mf} . According to reactor performance in previous experiments, the measurement point at 31.65 cm above the distribution plate was a preferred position for collecting samples. Thus, taking gas inflation at high temperature into account, the residence time can be determined as 2.76–3.86 s, with error ± 0.1 s.

The amount of steam used could affect the hydrogen yield, and, therefore, the steam/fuel (S/F) mass ratio would be investigated. The PET feeding flow rate was controlled at 0.8 ± 0.2 g/min by setting the voltage at about 105 V because a high feeding rate induced a suitable combustion equivalence ratio at the reactor outlet when combined with a sufficiently high temperature (around 730 °C). Through testing the reliability of the steam generator, it was determined that a steam flow in the range of 1–3 g/min (S/F ratio: 1.25–3.75) was accurate. As this range of steam flow rate was not enough for particle fluidization, fluidization was assisted by addition of N₂. All experimental conditions are summarized in Table 1.

2.4. Product sampling and measurements

The raw products contain numerous components, ranging from inorganic gases to organic compounds, including steam, syngas

products, tars, undefined aromatic/tar species, and soot (Berdugo Vilches, 2018). In this experiment, syngas products (H₂, CO, CH₄, CO₂, C₂–C₃) and a portion of the tars were sampled and measured. The sampling process was conducted as follows: 0.05 L/min high-purity helium was exploited as the tracer gas to quantify the total dry gas flow per unit of fuel and calculate the product distribution. Gas bag (average volume: 1 L) and adsorption columns were used to collect gas and tar products, respectively. A needle connected to the adsorption columns was plugged into the measurement point. After 2 min of sampling, the gas bag and syringe were sealed and removed. 2 min was chosen as sampling time because devolatilization was finalized in under 2 min in previous tests. For continuous feeding experiments, sampling started 5 min after the feeding began to allow the system to stabilize. Between different conditions or agents, air was introduced into the reactor as a fluidization medium in order to burn the unreacted char, as well as the remaining syngas in the reactor, and to eject the gas product so as to avoid interfering with the next trial. Each case was repeated at least twice in continuous feeding experiment, and the average was employed as the estimation of product yield.

The cold gas distribution was analyzed by micro gas chromatography (µ-GC). µ-GC has two channels and two columns (Poraplot Q and MS5Å), with He and Ar as the carrier gases, respectively. The equipment took a sample for analysis every 3 min. Before each test, air was inserted to clean the columns. The gases which can be detected in this device are: CO, H₂, CH₄, CO₂, C₂H₆, C₂H₄, C₂H₂, C₃H_x, and N₂.

In addition, tar collection was carried out by a solid-phase adsorption (SPA) method, where the tar is absorbed onto a solid-phase extraction column with an amino phase and then desorbed by a solvent (Israelsson et al., 2013). In this case, Supelclean ENVI-Carb/NH₂ SPE columns were placed in the syringes, with higher efficiency of BTX (mixtures of benzene, toluene, and the three xylene isomers) adsorption (Berdugo Vilches, 2018). The tar sampling temperature should be retained around 350 °C to ensure that all the tars uncondensed before being absorbed by the column. Subsequently, the sample columns should be stored at –20 °C to avoid reactions between the different tars. Tars were analyzed by GC equipped with a flame ionization detector (FID), and 28 tar species which are commonly formed in the gasification process were detected. These 28 tar species can be classified into 8 groups, as Table 2 illustrates.

3. Results and discussion

3.1. Effect of gasifying agents on gas composition in batch feeding mode

The effect of gasifying agents is displayed in Fig. 3. For PE and PET, the presence of steam enhanced H₂ generation significantly

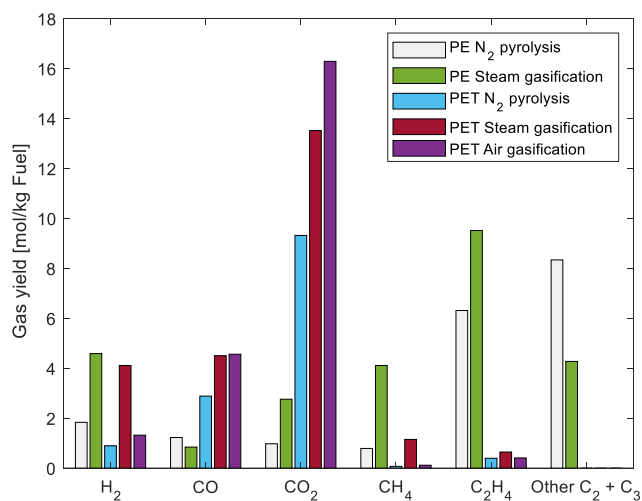
Table 1
Experimental conditions.

Feeding method	No.	Fuel	Mass[g] or mass flow rate [g/min] (±0.2 g/min)	Agent	Temperature [°C]	Residence time [s](±0.1 s)	Steam-to-fuel ratio [g/g]
Batch	1	PET	2	N ₂	750	3.23	–
	2	PE	2	N ₂	750	3.23	–
	3	PET	2	Steam	750	3.23	2
	4	PE	2	Steam	750	3.23	2
	5	PET	2	Air	750	3.23	Equivalence Ratio = 0.65
Continuous	6	PET	0.8	Steam	700	2.76	2.5
	7	PET	0.8	Steam	750	2.76	2.5
	8	PET	0.8	Steam	800	2.76	2.5
	9	PET	0.8	Steam	750	2.76	1.25
	10	PET	0.8	Steam	750	2.76	3.75
	11	PET	0.8	Steam	750	3.32	2.5
	12	PET	0.8	Steam	750	3.86	2.5

Table 2

Tar compounds groups.

Group	Tar substances
Benzene	Benzene
1-ring	Toluene, o/p-xylene, styrene, methyl-styrene
Biphenyl	Biphenyl
2 rings	Naphthalene, indene, 1,2-dihydronaphthalene, 1-methylnaphthalene, 2-methylnaphthalene
≥3-rings	Acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, xanthene, fluoranthene, pyrene, chrysene
Phenols	Phenol, o/p-cresol, 1-naphtol, 2-naphtol
Furans	Benzofuran, dibenzofuran
Unknowns	Species that can be found in the chromatograms but cannot be defined

**Fig. 3.** The effect of agents on gas product distribution in batch feeding method (experimental conditions given in Table 1).

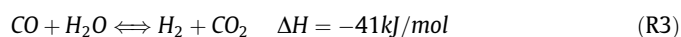
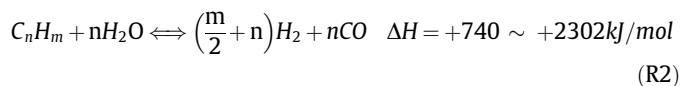
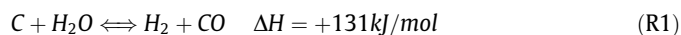
in comparison with pyrolysis, as indicated in those cases, steam is the primary source of hydrogen. The other main gaseous products of PET steam gasification, CO and CO₂, were mainly discharged from the pyrolysis steps. The yields of CO produced from steam and air gasification are almost equal, and steam gasification generated over 80% of the volume of air gasification when the equivalence ratio was 0.65. This fact suggests that, for PET gasification, steam cannot reduce CO₂ emissions significantly. For PET, C₁ ~ C₃ hydrocarbons are minor in both steam and air gasification.

The H₂/CO molar ratio is a crucial index for evaluating the fuel synthesis from syngas. The H₂/CO molar ratios of PET and PE steam gasification, shown in Fig. 3, were 1.02 and 5.45, respectively, indicating that PET blended with PE could elevate the H₂/CO molar ratio for methanol synthesis to 2. Nonetheless, Wilk & Hofbauer's (Wilk and Hofbauer, 2013) study results indicated that compared with individual PE and PP, PP + PE (50%:50% in wt%) steam gasification produced more H₂ as well as CO while H₂/CO molar ratio was decreased significantly due to the boost of CO. Therefore, there could be interaction effects when plastics are blended, meaning that products cannot be simply predicted from the weighted average of each component steam gasification product yields. Moreover, when the other two ratios, H₂/(2CO + 3CO₂) and (H₂ - CO₂)/(CO + CO₂), were applied to optimize the methanol production, PE steam gasification could not reach the recommended values 1.05 and 2, respectively (Brachi et al., 2014). The reason for this could be the high concentration of carbon in plastics. Therefore, when a plastic mixture is gasified for methanol production, CO shifting, and CO₂ removal are inevitable.

CO and CO₂ were detected in the PE pyrolysis products, which means that oxygen in the bed material involved in the pyrolysis process, since in olivine, MgO and other metal oxide components are active oxidants. Thus, in gasification, more oxygen in the bed material could participate in the reactions, and part of the CO₂ could be from bed material oxidation reactions. However, tar collections were challenging in the batch experiment due to the small quantity of fuel and short reaction time, and the effect of the gasifying agent on tars was not investigated in this research. Batch feeding mode mainly addresses the devolatilization, for a comprehensive analysis, continuous feeding experiments were performed.

3.2. The effect of temperature in continuous feeding mode.

Fig. 4 (A) depicts how the gas yield distribution altered with rising temperature. The dashed line represents the maximum CO₂ that PET pyrolysis can yield, which was computed as follows: the structure of the PET monomer (C₁₀H₈O₄, molecular weight: 192 g/mol) implies that each monomer can release up to 2CO₂ molecules, so the maximum CO₂ that 1 kg PET can form by pyrolysis is 10.24 mol. The curves in Fig. 4 (A) reflect the fact that nearly all gas products tended to escalate with increasing temperature. Among these curves, from 750 to 800 °C, the increase in H₂ was remarkable, whereas CO increased only slightly. This phenomenon could be explained by the chemical equilibrium. The char steam gasification (R1) and tar reforming reaction (R2) are both endothermic; therefore, enhancing temperature is likely to a shift of the reaction equilibrium towards the right side, which improves the yields of H₂ and CO. Even though a higher temperature caused the water-gas shift (WGS) reaction (R3) to move towards the left side, temperature did not affect the chemical equilibrium as much as the high S/F ratio in this case especially considering the catalytic function of olivine. Thus, H₂ had a faster growth rate than CO, and the CO₂ yield exceeded the maximum CO₂ generated from the pyrolysis process. The observed changes at 700 and 750 °C indicate only a moderate impact of R1 which is in line with the expected completion of the devolatilization step at that temperature as reflected in the TGA results. This is why the H₂ yields were lower than those of CO. Furthermore, no large impact of R2 and R3 is expected as catalytic properties of olivine are insufficient in the temperature interval. Moreover, high temperature also resulted in the breakage of more C–C bonds, so the yield of methane was more than that of C₂ + C₃.



Brem et al. (Brems et al., 2011a; Lopez et al., 2018) claimed that, in one of the most likely PET pyrolysis reactions, shown in reaction R4, CO₂ was discharged to form benzene and biphenyl with higher temperature. Thus, in Fig. 4 (A), CO₂ yields were very high, and in Fig. 4 (B), BTX was the dominant tar product at different temperatures. However, steam reforming (R2) is active, as mentioned, and the BTX consumption rate may have been faster than its generation; causing the BTX yield to decrease in this temperature range as well. For instance, toluene yields dropped from 81.03 g/kg PET at 700 °C to 48.98 g/kg PET at 800 °C. In contrast, biphenyl yield was small at 700 °C, but increased with the increasing temperature, which corresponds to the tar evolution pathway of PET. Phenols also decreased dramatically with increasing temperature and tended to disappear at 800 °C. According to Zhang and Pang (2019), toluene and phenols can be consumed as precursors for biphenyl

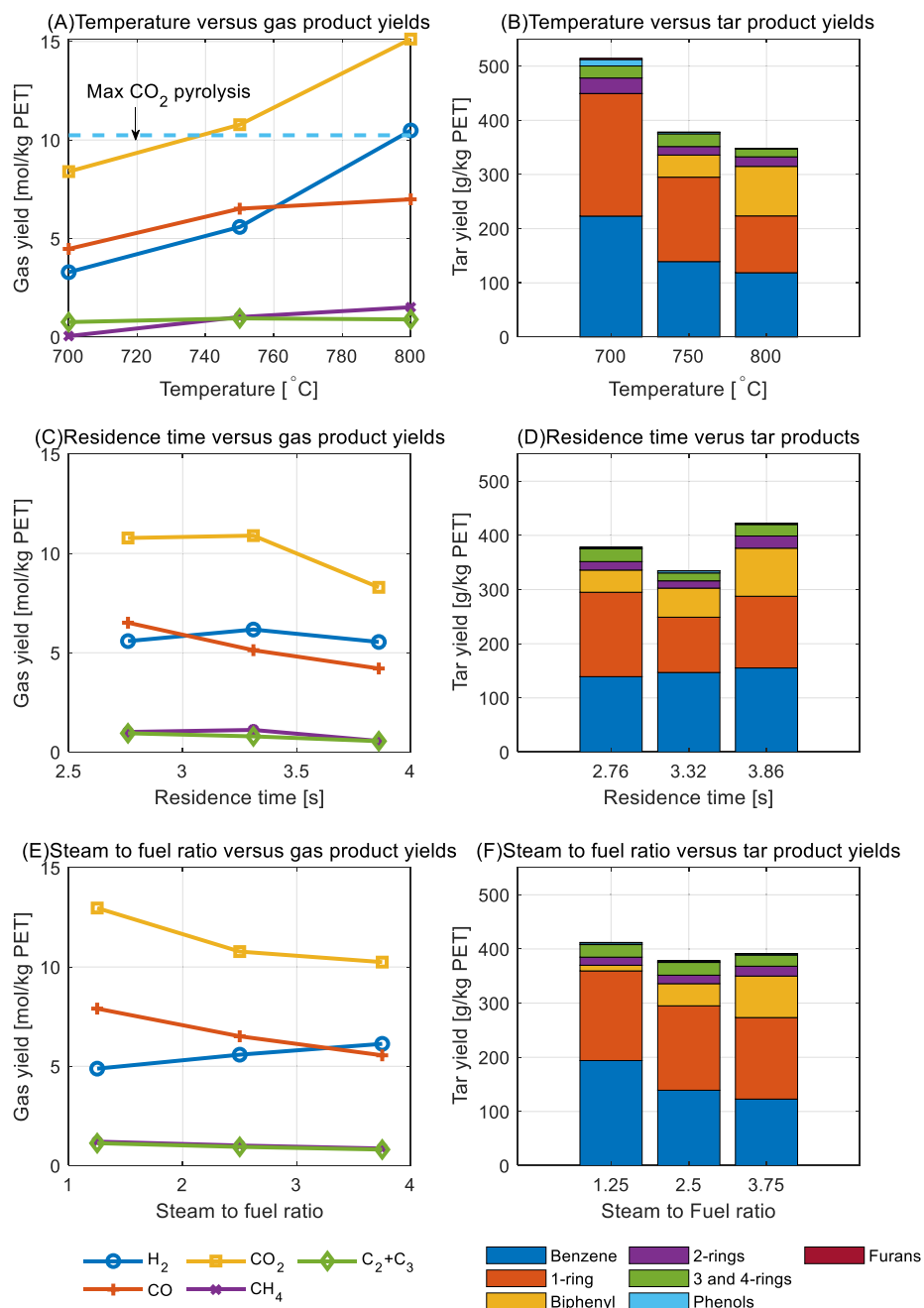
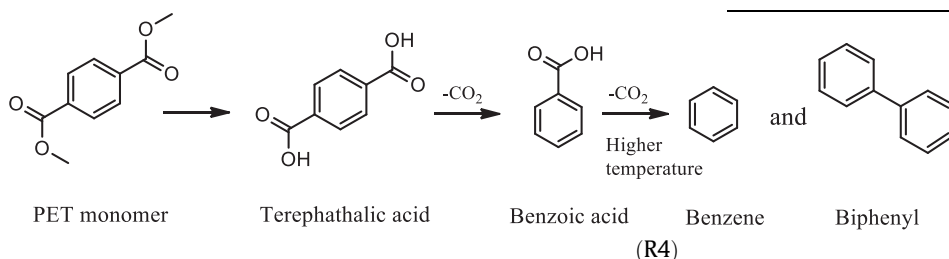


Fig. 4. The influence of operation conditions on gas and tar distribution of PET steam gasification.

formation, and they performed the mechanism of pathways. In Wilk and Hofbauer's (2013) research, only PET + PE mixtures produced significant amount of biphenyl and CO₂, indicating that PET is the main source of these two compounds when PET mixed with other plastics.



3.3. The effect of residence time and steam-to-fuel ratio in continuous feeding mode

As Fig. 4 (C) shows, CO decreased steadily with increasing gas residence time, while CO₂ dropped with longer residence time.

However, the other gas products did not alter significantly. The reason could be the prominent heat and mass transfer of the fluidized bed, preventing the residence time from affecting the extent of the reaction as it did in the fixed bed reactor. Furthermore, the residence time in the lab-scale BFB could be shorter and of less significance to the reaction than the large-scale production due to the reactor size. These could be the reasons why residence time was seldom investigated as an essential operational parameter in most research related to plastic gasification. The total tar yields were the lowest when the residence time was 3.32 s, but the prolonged residence time improved biphenyl and 2-ring tars. If we want to avoid tar formation, high temperature and long residence time should not be applicable for bubbling fluidized gasification.

As regards the influence of the steam-to-fuel ratio, an increased steam supply can increase H_2 yield via R2, WGS reaction R3, and char steam gasification R1. Fig. 4 (E) reveals that hydrogen yield rose slightly while CO formation decreased with higher S/F ratio, in which the WGS reaction could play an essential role. The same reaction also implies that CO_2 should increase, but, in fact, the opposite trend was observed. This phenomenon indicates that CO_2 generated from the WGS reaction did not dominate the CO_2 yield. CO_2 can be also released directly from PET pyrolysis processes, and the introduction of excess steam could prohibit pyrolysis reactions. This could explain why CO_2 dropped with the increasing steam-to-fuel ratio. The tar distribution in Fig. 4 (F) implies that a higher S/F ratio supported biphenyl formation, as did higher temperature and residence time. The condensed water could be collected when sampling the products in the case of an S/F ratio of 3.75. This fact implies that steam flow was excessive for PET gasification.

3.4. Sensitivity analysis of operational conditions

As shown, temperature, residence time, and S/F ratio affect gas and tar distributions. To identify the most relevant parameters and enhance performance, the trials were evaluated according to their coefficient of variation due to the scale of values and units. The averages and standard deviations alone cannot be used to compare the variation of each case. In statistics, a dimensionless constant, coefficient of variation C_v permits comparison free of scale effects, and it is defined as the ratio between the standard deviation (σ) and the mean ($\bar{\mu}$), expressing as

$$C_v = \sigma / \bar{\mu} \quad (1)$$

The higher value means that the operational condition is critical, which could be beneficial to optimize the process. The C_v values of each product and operating conditions (namely, temperatures between 700 and 800; residence times between 2.76 s and 3.86 s; and steam-to-fuel ratios between 1.25 and 3.75) were compared in radar charts in Fig. 5 (A) and (C).

The sensitivity analyses of operational conditions on gas are displayed in Fig. 5 (A). The extent of influence can be roughly sorted as **temperature** \gg **steam to fuel ratio** $>$ **residence time**, where temperature improved hydrogen and methane yields remarkably while CO and CO_2 were not enhanced so notably, as Fig. 4 (A) suggests. With respect to $C_2 + C_3$, the steam-to-fuel ratio can regulate the yield more than residence time and temperature. The reason for this could be that the temperature affected the distribution of C_2H_4 , C_2H_6 , C_2H_2 , and C_3H_x , while the total amount did not fluctuate as severely as the residence time and S/F ratio.

Nevertheless, the radar chart in Fig. 5 (A) only illustrates that gaseous products are sensitive to temperature change without knowing the extent of the increment or decrement. Thus, Fig. 5 (B) reveals the extent of each product range (δ) when the temperature varies within ± 50 °C, which is computed by Eq (2),

$$\delta = \frac{Y - Y_{ref}}{Y_{ref}} \times 100\% \quad (2)$$

where Y represents the yields, and the subscript ref means reference. In this case, the reference is the yields at 750 °C, and their δ values are zeros. For instance, Fig. 5 (B) shows that H_2 almost doubled, and CH_4 increased by around 40%, when the temperature increased from 750 °C to 800 °C, while CH_4 is more sensitive than H_2 when the temperature decreased from 750 to 700 °C. CO_2 has a similar increasing extent as methane, whereas CO was only improved by around 10% between 750 °C and 800 °C.

The sensitivity analysis of operational conditions on tar distribution is depicted in Fig. 5 (C). Temperature was still the essential parameter for the behaviors of tar species; especially furans, phenols, and biphenyl, whose σ values were over 1. This indicated that temperature could affect the formation or decomposition of biphenyl, furans, and phenols significantly. A remarkable dropping of furans and phenols can be observed from 700 to 750 °C in Fig. 5 (D), while biphenyl halved or doubled when the temperature increased or decreased by 50 °C, respectively. The impact of residence time ranked second except for benzene and biphenyl.

3.5. Carbon balance

The carbon (C) conversion ratio is a unique index for investigating PET conversion in this research since steam is involved in the reaction. Fig. 6 (A) illustrates the carbon conversion ratio of gas, tar, and char. In some cases, the overall conversion ratios are over 1, indicating that measurement errors should be considered, including fuel feeding errors, gas bag volume errors, and repetition errors. When calculating tar yields, all the gas bags were estimated as the averaged volume of 1 L because the gas bag volume varied from 0.8 L to 1.1 L in various cases. Since tars were measured based on the gas volume in the gas bag, errors from tars are more significant than those from gases. Considering all the errors, the standard deviations (SD) can be obtained by Eq. (3):

$$SD = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (x_i - \bar{x})^2} \quad (3)$$

The standard deviation results are displayed as error bars in Fig. 6 (A). Standard deviations of total carbon conversion varied $\pm 25\%$ in all cases. However, without considering the errors of fuel feeding and gas bag volumes, SD for each product (including H_2) changed around $\pm 10\%$ at most conditions, indicating that the repetitions in each case were stable. Less than half of the C in PET was converted to gaseous products via steam gasification. CO_2 was the dominant gas product that C was converted into. Moreover, increasing the temperature increased the carbon in gas significantly. Compared with the carbon conversion at 800 °C, only 30% of carbon was converted into gas at 700 °C, and the composition of the gas and tar products was prone to pyrolysis processes even though enough steam was injected into the reactor. This fact suggests that 700 °C is not a suitable temperature for PET steam gasification.

Syngas (mainly $H_2 + CO$), the desired product of gasification, can be applied to power generation and fuel synthesis. In the heat and power production sector, syngas is burnt as a combustible fuel directly in gas turbines, engines, or boilers. However, less than 30% of the C in PET was converted into combustible gas here, such as CO and $C_1 \sim C_3$ and the lower heating value (LHV) of syngas produced from PET at 800 °C was 8.66 MJ/N m³. Thus, PET should be avoided in the fuel for syngas aimed at heat production, because the low effective C conversion could reduce the syngas heat. For example, Wilk & Hofbauer observed that the LHV of syngas produced from PE was 25.8 MJ/N m³, while this decreased to

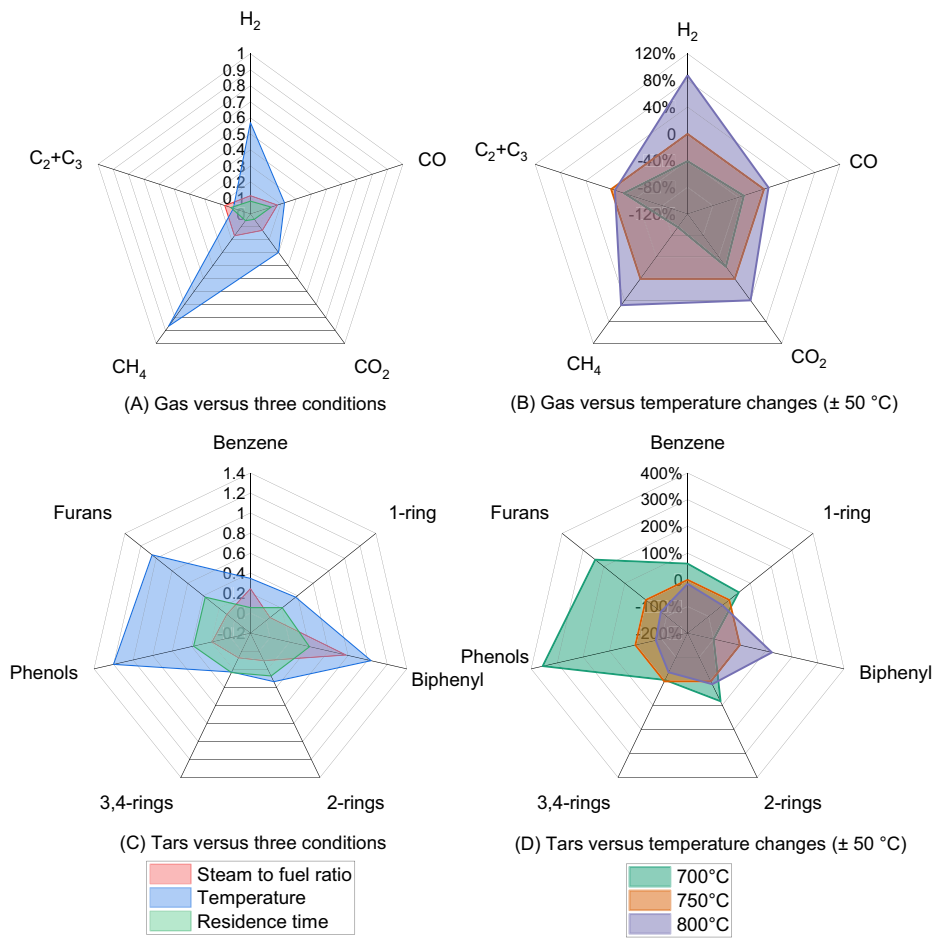


Fig. 5. The sensitivity analysis of operational conditions on gas and tar product yields.

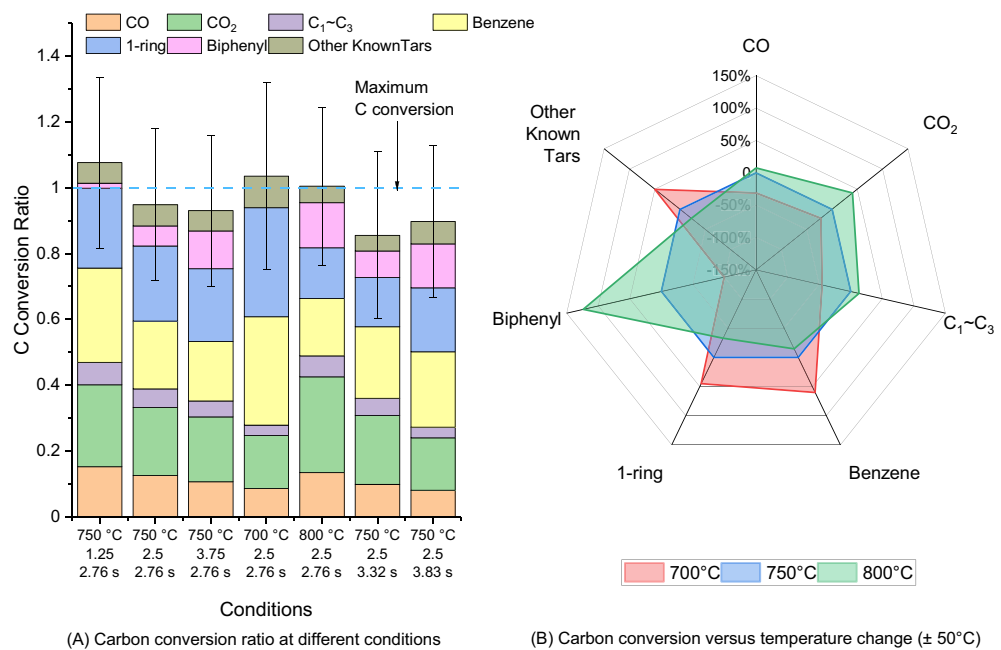


Fig. 6. Carbon balance of PET steam gasification experiments.

16.4 MJ/N m³ when the fuel was 80% PET blended with 20% PE (Wilk and Hofbauer, 2013).

In terms of tar yields, the total tar yield within the 750 to 800 °C range did not drop as significantly as between 700 and 750 °C, meaning that, although increasing the temperature above 800 °C can alter the distribution of tars, it is not an effective solution to reducing the total tars. However, more steam and longer residence time induced lower carbon conversion in gaseous products, in which a lower steam-to-fuel ratio (1.25) resulted in similar C conversion to that at high temperature (800 °C). A similar calculation of carbon balance was conducted with Eq. (2), and the results are depicted in Fig. 6 (B). Of all known carbon-related products, biphenyl is the most sensitive to temperature, and its amount increases with increasing temperature.

Since the PET molecule is built on an aromatic ring structure, aromatics were major tar products, especially benzene and biphenyl. Both of these are valuable chemical products; for instance, benzene is the precursor for many chemicals, such as polystyrene, phenol, nylon, and so on (Matar and Hatch, 2001). Biphenyl is also an important chemical raw material for polychlorinated biphenyls (PCBs), which are commonly used in the electrical industry, for capacitors, heat transfer, or hydraulic fluid, etc. (Moo-Young, 2019). The amount of benzene and biphenyl produced by PET steam gasification was also considerable (around 100 g/kg PET). Therefore, separating them from the tars could produce economic benefits.

In addition to the 28 tar species identified by GC, there are still at least 150 unknown tar species. It is not necessary to identify all of them, but some of them should be known. For instance, benzoic acid is a vital product of PET pyrolysis, which was not quantified in this research, but which is a possible source of benzene and CO₂ (Artetxe et al., 2010; Cit et al., 2010; Yoshioka et al., 2004). Through defining the amount of benzoic acid, reaction chain R4 could be confirmed.

The maximum amount of carbon in the form of char could be estimated by TGA results at 50 °C/min, where fixed carbon generated by pyrolysis accounted for 11.44% of PET. Therefore, if it is assumed that char is pure carbon, in BFB PET steam gasification, the carbon in char should be much lower than 18.3% (calculated by 11.44%/62.5%, where 62.5% is the C concentration in PET) of carbon in PET after R1 occurred. Nonetheless, it was not possible to conduct unconverted fuel sampling in the continuous feeding experiments, and the amount of unconverted char was not examined. Furthermore, black substance was observed in the feeding system, which attached on the surface of PET particles. This phenomenon indicates that some fine char particles were entrained.

4. Conclusions

This experimental work studied the influence of operating conditions on virgin PET gasification to investigate its product composition. On the one hand, batch experiments demonstrated that most of the H₂ was generated through reactions with steam, and the primary gas product, CO₂, was predominantly released during the pyrolysis step. Part of the products could be also oxidized by the bed material. On the other hand, continuous feeding experiments examined the influence of temperature, residence time, and steam/fuel ratio on PET steam gasification. In this work, among these three operational conditions, temperature affected the product distribution more significantly than gas residence time and steam/fuel ratio. Higher temperature can increase the H₂ yield and carbon conversion to gaseous products, with CO₂ as main product. According to the carbon balance, more than half of carbon was found in aromatic structures (tars). Among all the tars, the amount of biphenyl increased with the increasing temperature,

i.e. biphenyl yield doubled when the temperature was increased from 750 to 800 °C. Therefore, PET could contribute more CO₂ and biphenyl as products during PET steam gasification with other plastics such as PE.

High yields of CO₂ decreases the LHV of syngas, and lowers the value of the syngas in heat and power production, but PET mixed with PE could produce H₂/CO molar ratio of 2 to adjust for the synthesis of the most attractive fuel – methanol. Even though methanol production has a requirement of CO₂ concentration, the CO₂ removal process is unavoidable. However, PET gasification produces 3–4 times less CO₂ than PET combustion, which could reduce the extent of CO₂ removal process. Further, CO₂ and tar minimization strategies should be proposed and tested to decrease the amount of CO₂ and tars in the syngas product as much as possible. Alternatively, the utilization of tars/aromatics should be studied.

In future research, a particular proportion of plastic mixture could be studied for different fuel production, and the interaction effects should be observed. More accurate tar and char analysis, together with unreacted steam measurement and ultimate analysis of bed material before and after reactions could provide the mass balance of C, H, and O. Feeding issues and defluidization phenomenon can be studied and compared with computational fluid dynamics (CFD) simulation results. In addition, with these experimental results, plastic mixture steam gasification integrated with either heat production or fuel synthesis with the separation or cracking of tars can be modeled to analyze the technical and economic performance of the whole system, including the mass balance, energy and exergy balance, as well as the economic cost and benefit.

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CRedit authorship contribution statement

Shouzhuang Li: Writing-original draft, Investigation, Formal analysis, Visualization. **Isabel Cañete Vela:** Investigation, Supervision, Formal analysis, Writing-review & editing. **Mika Järvinen:** Supervision, Writing-review & editing. **Martin Seemann:** Conceptualization, Supervision, Project administration, Writing-review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Al-Sabagh, A.M., Yehia, F.Z., Eshaq, G., Rabie, A.M., ElMetwally, A.E., 2016. Greener routes for recycling of polyethylene terephthalate. *Egypt. J. Pet.* 25, 53–64.

- Artetxe, M., Lopez, G., Amutio, M., Elordi, G., Olazar, M., Bilbao, J., 2010. Operating conditions for the pyrolysis of poly-(ethylene terephthalate) in a conical spouted-bed reactor. *Ind. Eng. Chem. Res.* 49, 2064–2069.
- Bai, B., Liu, Y., Zhang, H., Zhou, F., Han, X., Wang, Q., Jin, H., 2020. Experimental investigation on gasification characteristics of polyethylene terephthalate (PET) microplastics in supercritical water. *Fuel* 262, 116630.
- Berdugo Vilches, T., 2018. Operational strategies to control the gas composition in dual fluidized bed biomass gasifiers.
- Brachi, P., Chirone, R., Miccio, F., Miccio, M., Picarelli, A., Ruoppolo, G., 2014. Fluidized bed co-gasification of biomass and polymeric wastes for a flexible end-use of the syngas: focus on bio-methanol. *Fuel* 128, 88–98.
- Brems, A., Baeyens, J., Beerlandt, J., Dewil, R., 2011a. Thermogravimetric pyrolysis of waste polyethylene-terephthalate and polystyrene: A critical assessment of kinetics modelling. *Resour. Conserv. Recycling* 55, 772–781.
- Brems, A., Baeyens, J., Vandecasteele, C., Dewil, R., 2011b. Polymeric cracking of waste polyethylene terephthalate to chemicals and energy. *J. Air Waste Manage. Assoc.* 61, 721–731.
- Çepeliogullar, Ö., Pütün, A.E., 2013. Utilization of two different types of plastic wastes from daily and industrial life. *J. Selcuk Univ. Nat. Appl. Sci.* 2, 694–706.
- Chilton, T., Burnley, S., Nesaratnam, S., 2010. A life cycle assessment of the closed-loop recycling and thermal recovery of post-consumer PET. *Resour. Conserv. Recycl.* 54, 1241–1249.
- Choi, M., Jeong, Y., Kim, J., 2021. Air gasification of polyethylene terephthalate using a two-stage gasifier with active carbon for the production of H₂ and CO. *Energy*, 120122.
- Cit, I., Sinağ, A., Yumak, T., Uçar, S., Sırsırloğlu, Z., Canel, M., 2010. Comparative pyrolysis of polyolefins (PP and LDPE) and PET. *Polym. Bull.* 64, 817–834.
- Geyer, R., Jambeck, J.R., Law, K.L., 2017. Production, use, and fate of all plastics ever made. *Sci. Adv.* 3, e1700782.
- Grause, G., Matsumoto, S., Kameda, T., Yoshioka, T., 2011. Pyrolysis of mixed plastics in a fluidized bed of hard burnt lime. *Ind. Eng. Chem. Res.* 50, 5459–5466.
- Israelsson, M., Seemann, M., Thunman, H., 2013. Assessment of the solid-phase adsorption method for sampling biomass-derived tar in industrial environments. *Energy Fuels* 27, 7569–7578.
- Jankauskaite, V., Macijauskas, G., Lygaitis, R., 2008. Polyethylene terephthalate waste recycling and application possibilities: a review. *Mater. Sci. (Medžiagotyra)* 14, 119–127.
- Kho, H.H., 2019. LCA of plastic waste recovery into recycled materials, energy and fuels in Singapore. *Resour. Conserv. Recycling* 145, 67–77.
- Klinghoffer, N.B., Castaldi, M.J., 2013. Gasification and pyrolysis of municipal solid waste (MSW), in *Anonymous Waste to Energy Conversion Technology*. Elsevier, 146–176.
- Kunwar, B., Cheng, H.N., Chandrashekar, S.R., Sharma, B.K., 2016. Plastics to fuel: a review. *Renew. Sustain. Energy Rev.* 54, 421–428.
- Locock, K.E., Deane, J., Kosior, E., Prabakaran, H., Skidmore, M., E Hutt, O., 2017. The Recycled Plastics Market: Global Analysis and Trends.
- Lopez, G., Artetxe, M., Amutio, M., Alvarez, J., Bilbao, J., Olazar, M., 2018. Recent advances in the gasification of waste plastics. A critical overview. *Renew. Sustain. Energy Rev.* 82, 576–596.
- Marco, I.d., Caballero, B., Torres, A., Laresgoiti, M.F., Chomon, M.J., Cabrero, M.A., 2002. Recycling polymeric wastes by means of pyrolysis. *J. Chem. Technol. Biotechnol. Int. Res. Process Environ. Clean Technol.* 77, 817–824.
- Marinkovic, J., 2015. Use of Bed Materials in Dual Fluidized Bed (DFB) Systems.
- Mastellone, M.L., Arena, U., 2008. Olivine as a tar removal catalyst during fluidized bed gasification of plastic waste. *AIChE J.* 54, 1656–1667.
- Matar, S., Hatch, L.F., 2001. *Chemistry of Petrochemical Processes*. Elsevier.
- Moo-Young, M., 2019. *Comprehensive Biotechnology*. Elsevier.
- Nikles, D.E., Farahat, M.S., 2005. New Motivation for the Depolymerization Products Derived from Poly(Ethylene Terephthalate) (PET) Waste: a Review. *Macromol. Mater. Eng.* 290, 13–30.
- Ouyang, F., Levenspiel, O., 1986. Spiral distributor for fluidized beds. *Ind. Eng. Chem. Process Des. Dev.* 25, 504–507.
- Park, S.H., Kim, S.H., 2014. Poly (ethylene terephthalate) recycling for high value added textiles. *Fashion Text.* 1, 1–17.
- Pereira, E.G., da Silva, J.N., de Oliveira, J.L., Machado, C.S., 2012. Sustainable energy: a review of gasification technologies. *Renew. Sustain. Energy Rev.* 16, 4753–4762.
- Plastics Europe, 2020. *Plastics—the facts 2020. An analysis of European plastics production, demand and waste data*. Plastics Europe.
- Plastics Europe, 2016. *Plastics—the facts 2016. An analysis of European plastics production, demand and waste data*. Plastics Europe.
- Pohořelý, M., Vosecký, M., Hejdová, P., Punčochář, M., Skobljá, S., Staf, M., Vošta, J., Koutský, B., Svoboda, K., 2006. Gasification of coal and PET in fluidized bed reactor. *Fuel* 85, 2458–2468.
- Robinson, T., Bronson, B., Gogolek, P., Mehrani, P., 2016. Comparison of the air-blown bubbling fluidized bed gasification of wood and wood–PET pellets. *Fuel* 178, 263–271.
- Rosendal, R.M., 2014. Danish policy on waste management - Denmark without waste. no.November 2015.
- Sharuddin, S.D.A., Abnisa, F., Daud, Wan Mohd, Wan, Ashri, Aroua, M.K., 2016. A review on pyrolysis of plastic wastes. *Energy Convers. Manage.* 115, 308–326.
- Shen, L., Worrell, E., Patel, M.K., 2010. Open-loop recycling: A LCA case study of PET bottle-to-fibre recycling. *Resour. Conserv. Recycl.* 55, 34–52.
- Sinha, V., Patel, M.R., Patel, J.V., 2010. *Pet Waste Management by Chemical Recycling: A Review*. *J. Polym. Environ.* 18, 8–25.
- Stenberg, V., Rydén, M., Mattisson, T., Lyngfelt, A., 2018. Combustion of methane in a bubbling fluidized bed with oxygen carrier aided combustion, 927–936.
- Wang, Z., Burra, K.G., Li, X., Zhang, M., He, X., Lei, T., Gupta, A.K., 2020. CO₂-assisted gasification of polyethylene terephthalate with focus on syngas evolution and solid yield. *Appl. Energy* 276, 115508.
- Welle, F., 2011. Twenty years of PET bottle to bottle recycling—An overview. *Resour. Conserv. Recycl.* 55, 865–875.
- Wilk, V., Hofbauer, H., 2013. Conversion of mixed plastic wastes in a dual fluidized bed steam gasifier. *Fuel* 107, 787–799.
- Yang, T., Hu, K., Li, R., Sun, Y., Kai, X., 2015. Cogasification of typical plastics and rice straw with carbon dioxide. *Environ. Prog. Sustain. Energy* 34, 789–794.
- Yoshioka, T., Grause, G., Eger, C., Kaminsky, W., Okuwaki, A., 2004. Pyrolysis of poly (ethylene terephthalate) in a fluidised bed plant. *Polym. Degrad. Stab.* 86, 499–504.
- Zhang, Z., Pang, S., 2019. Experimental investigation of tar formation and producer gas composition in biomass steam gasification in a 100 kW dual fluidised bed gasifier. *Renew. Energy* 132, 416–424.
- Zhou, H., Meng, A., Long, Y., Li, Q., Zhang, Y., 2014. Classification and comparison of municipal solid waste based on thermochemical characteristics. *J. Air Waste Manage. Assoc.* 64, 597–616.