

Effect of Spent Fluid Catalytic Cracking Catalysts on Syngas Yield during CO₂-Assisted Gasification of Solid Waste

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This research examines the synergistic effects of using CO₂, spent fluid cracking catalyst (sFCC), and municipal solid wastes (MSW) for energy and chemical production. The effect of utilizing sFCC catalysts on syngas yield and its quality and energy yield is examined during CO₂-assisted gasification of MSW components, pinewood, polyethylene terephthalate (PET), polystyrene, and waste tyres. The influence of catalyst position (in-situ and quasi-in-situ) and temperature were also investigated. In all cases, the sFCC catalyst resulted in doubling the yield of hydrogen and tripling methane which reveals that the spent FCC catalyst promoted the hydrocracking and CO₂ reforming of hydrocarbons in the gas phase. As such the presence of sFCC in-situ catalytic CO₂-assisted gasification increased the overall syngas yield by 62.5%, for PET, by 55% for waste tyres, 3.5 % for polystyrene and no change for wood when compared to their respective non-catalytic gasification cases. A comparison of quasi-in-situ gasification to in-situ catalytic gasification showed that quasi-in-situ gasification increased syngas yield and energy yields of pinewood by 21% and 22%, respectively. For PET, the quasi-in-situ catalytic gasification increased the syngas yield and energy by 27.5% and 23.8%, respectively. In the case of waste tyres, the syngas yield and energy yields increased by 24% and 23%, respectively. For polystyrene, the quasi-in-situ catalytic gasification increased the syngas yield and energy by 103.4% and 62.5% as compared to the in-situ catalytic gasification case. This implies that quasi-in-situ catalytic gasification is more efficient and effective at increasing the syngas yield. When comparing the carbonaceous sources, materials with higher volatile matter such as polystyrene had the highest overall syngas yield compared to other materials. Materials that have a higher tendency to form char had the least increase in syngas yield and energy due to soot and coke formation over the catalyst.

1. Introduction

In the USA, over 60% of the 292.8 million tons of municipal solid waste generated annually is biomass. Currently, only 34.6 million tons of MSW are processed through energy recovery in 75 facilities across the United States, which accounts for only about 12 % of available waste (EPA, 2020). The problem is that existing facilities are faced with severe pollutants emission challenges requiring energy-intensive flue gas cleaning, offering low energy recovery, and high investment costs which results in marginal to subpar economic viability, especially in competition with low-cost landfilling (Abubakar et al., 2022). Gasification is a good technology that can transform organic waste into useful energy and other chemical products (Peres et al., 2013). Synthetic gas which is a mixture of carbon monoxide and hydrogen is the most used raw material for the production of energy and many useful products. Converting biomass to synthetic gas seems a good practical method of making use of the large energy content available in the organic portion of waste in MSW (Figuerola et al., 2013). The predominant challenge with gasification is that there is a significant generation of tar and char, which significantly affects the gas yield and composition thus reducing the efficiency of the process (Ruoppolo et al., 2013). This work explores the effects of using the spent fluid cracking catalyst (sFCC) during the gasification of MSW, to increase the yield

of syngas through the thermal decomposition of tars. In the petroleum sector, the sFCC catalyst is utilized as a hydrocracking, hydro refining, and catalytic reforming catalyst to improve the output of gasoline and other hydrocarbons derived from crude oil (Wang *et al.*, 2019, 2021). The sFCC catalyst is discarded when it degrades so that it remains the largest source of solid waste in the petroleum industry. Owing to its substantial metal impurity level, sFCC is considered hazardous waste. This sFCC catalyst is still active (Bertero *et al.*, 2019) and the metallic oxides can function as reaction catalysts for pyrolysis and gasification (Mastry *et al.*, 2023). Pinewood, polyethylene terephthalate (PET), polystyrene, and waste tyres are used as representatives of the organic waste of MSW whereas CO₂ is used as a gasification agent. The MSW components are gasified under non-catalytic, in-situ, and quasi-in-situ catalytic configurations using a fixed-bed reactor in a carbon dioxide atmosphere at temperatures of 800 °C and 900 °C to study the effect of catalyst positioning on syngas yield. The distribution of gaseous products as well as the amount of energy produced by the various gasification configurations were analyzed and compared. There are many studies where sFCC is used to improve the yield of bio-oil during pyrolysis of different materials in pyrolysis (Heo *et al.*, 2023; Johansson *et al.*, 2023; Mendoza-Martinez *et al.*, 2023). However, to the best of the authors' knowledge, no study has been found that investigates the effect of sFCC catalyst on syngas yield during the CO₂-assist gasification of four different solid waste materials. This study aims to unravel the potential of using CO₂ greenhouse gas in gasification in an optimized catalytic route to enhance energy yield while also providing waste management.

2. Methodology

2.1 Materials

Pinewood pellets, waste tyres, recycled polyethylene terephthalate (PET), and polystyrene pellets were used as a representation of MSW. All the samples were ground down to a maximum size of 1000 µm with an industrial blender. The proximate and ultimate analyses of materials used in this test are shown in Table 1. The spent fluid cracking catalyst (sFCC) was a commercially available catalyst sourced from the largest chemicals manufacturer in the USA. The catalyst composition included zeolites, silicon dioxide, aluminium oxide, kaolin, calcined, magnesium oxide, aluminium calcium oxide, as well as small amounts of metal oxides and rare earth oxides. The study of catalytic and non-catalytic CO₂-assisted gasification of MSW was conducted at 800 °C and 900 °C. For all catalytic tests the organic MSW sample was kept constant at 10 g and the catalyst at 2 g. For the in-situ catalytic studies, 2 g of catalyst was uniformly distributed in 10 g of the MSW sample, while for the quasi-in-situ catalytic experiment, the catalyst bed was placed about 8 mm downstream of the feedstock.

2.2 Reactor Facility

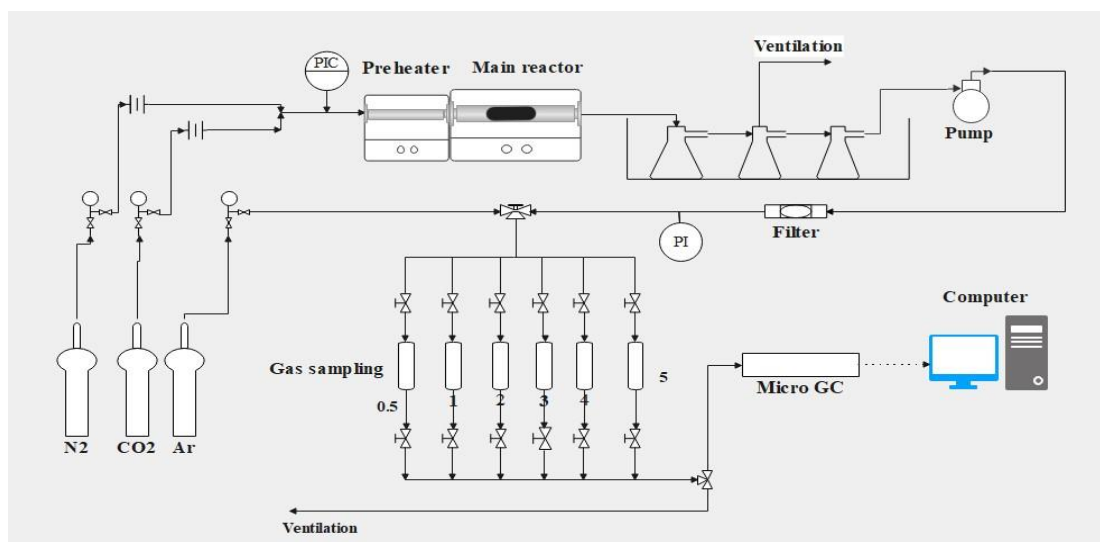


Figure 1. A schematic diagram of the reactor test facility

A lab-scale reactor facility was used for the gasification of all four types of samples, see Figure 1. The preheater and the fixed-bed reactor were both electrically heated. Before starting the experiment, Argon gas was used to flush the system from any residual gases present from the previous test run. Nitrogen (N₂) was used as the tracer gas due to its inert nature which assisted in analyzing the various gases produced during the reaction quantitatively. For gasification, a mixture of 75% CO₂ and 25% N₂ was used as the gasifying agent. The temperature was set at 800 or 900 °C for both the preheater and main reactor. The feedstock, mentioned in the

previous section, was only introduced into the reactor once the set temperature reached the desired value. The gases produced from the reactor were first passed through the condensers placed in an ice bath to remove tar, water, and other condensable vapours. The dry and tar-free gases were then passed through a filter to remove any particulates, such as soot or some other particulates. Finally, the gases were examined using a micro-GC to analyze the mole fractions of H_2 , CO , CO_2 , CH_4 , C_2H_4 , C_2H_6 , C_2H_2 , C_3H_8 , and N_2 . The gases were analyzed at 0.5, 1, 2, 3, and 4-minute time intervals from the start of the experiment, and then at 2.7-minute intervals from 5 minutes onwards up to 50 minutes. All the experiments were conducted three times to ensure the consistency of the results. The mean values from the 3 tests are reported here.

Table 1. Ultimate and Proximate analysis of carbon feedstocks (Liu et al., 2020).

Sample	Ultimate analysis (wt.%)						Proximate analysis (wt.%)				
	C	H	O	N	Cl	S	Moisture	VM	FC	ash	LHV (kJ/kg)
Pinewood	48.72	6.52	44.41	0.23	0	0.12	0	85.6	14.2	0.2	17.65
Waste tyre	81.85	6.66	8.42	1.7	0	1.37	0	62.5	27.9	8.9	33.33
PET	62.57	4.4	33.03	0	0	0	0	94.4	5.6	0	22.04
Polystyrene	92.8	7.2	0	0	0	0	0	99.9	0.1	0	11.022

3. Results and discussion

3.1 Temporal evolution of major syngas components

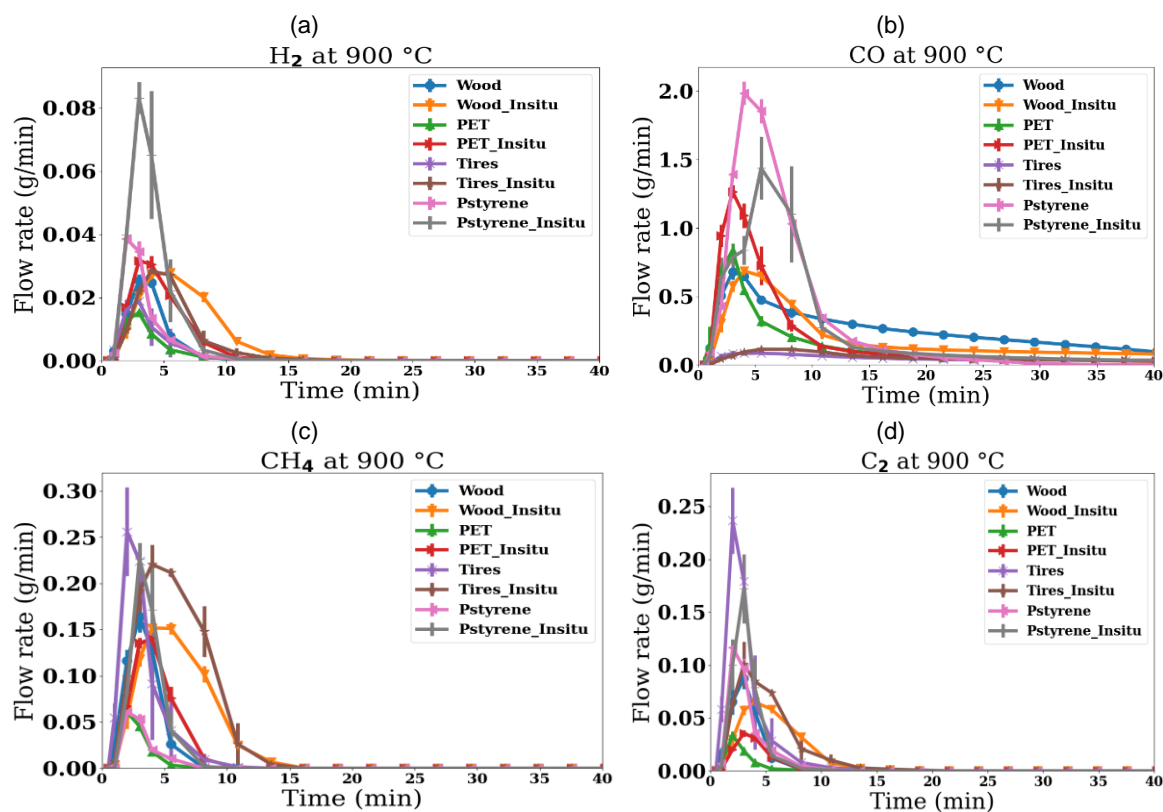


Figure 2. Temporal evolution of (a) H_2 , (b) CO , (c) CH_4 , and (d) C_2H_x flowrates during non-catalytic and catalytic-in-situ CO_2 -gasification of pinewood, waste tyres, PET, and polystyrene.

Figure 2 shows the transient behaviour of syngas during non-catalytic and in-situ catalytic gasification of pinewood, PET, waste tyres, and polystyrene. The characteristics of the thermal decomposition behaviour of the materials are compared at 900 °C temperature. It is evident from the results that direct in-situ gasification using the sFCC catalyst promoted the thermal cracking and dehydrogenation reactions of the larger hydrocarbons leading to increased H_2 yield for the materials studied. Polystyrene with nearly 100% volatile matter and the largest composition of H_2 , as shown in Table 1 produced the highest peak of H_2 followed by PET

and wood, and lastly the waste tyres. Figure 2(a) shows that the peak height of H₂ evolution doubled from 0.04 g/min to 0.08 g/min with sFCC addition for polystyrene. For PET, tyres, and wood, the H₂ peak height increased from 0.02 g/min to about 0.034 g/min, and the temporal evolution of H₂ terminated at about 15 minutes instead of 11 minutes observed during the non-catalytic case. The CO evolution peak is shown Figure 2(b). During PET gasification, adding sFCC increases the peak height CO evolution by nearly 56%, signifying an increase in CO yield. However, adding sFCC to polystyrene-CO₂-gasification there is a sharper decrease in CO peak compared to that of CO₂ gasification only. A similar behaviour is observed for wood, while sFCC didn't affect waste tyres by much. This means that sFCC inhibits the influence of the Boudouard reactions that produce CO. Figure 2(c) shows that the presence of sFCC catalyst increased the CH₄ production since larger hydrocarbons are reformed/cracked into smaller (light) hydrocarbons, including methane. CH₄ peak height tripled for PET and quadrupled for polystyrene when sFCC was added, whereas for tyres the CH₄ peak increased by 33.33%. For both wood and tyres in the absence of a catalyst, the CH₄ production terminated after 15 minutes but in the presence of sFCC the CH₄ production terminated after 15 minutes, meaning that the volatiles that would leave the reactor are cracked in the presence of sFCC. Hence CO₂ and sFCC catalysts aided the production of CH₄. However, the opposite was observed for C₂H_x (Figure 2(d)) wherein the sFCC catalyst significantly reduced the peak height of C₂H_x by nearly 50%. Thus, reveals that sFCC facilitated the reforming of C₂ and above hydrocarbons but not CH₄.

Figure 3 shows that the addition to sFCC improved the cumulative syngas yield and syngas energy for all materials with polystyrene and wood outperforming PET and waste tyres. This is because, under thermal treatment, PET and tyres will decompose into a series of heavy hydrocarbon compounds and some of those compounds form radicals that eventually form soot. These products are a result of complex reactive mechanisms of the volatile matter in PET and tyres, which include random chain scission, end-chain scission, chain-stripping, cross-linking, and coke formation. Therefore, tyres and PET are less reactive in the CO₂ atmosphere compared to wood and polystyrene.

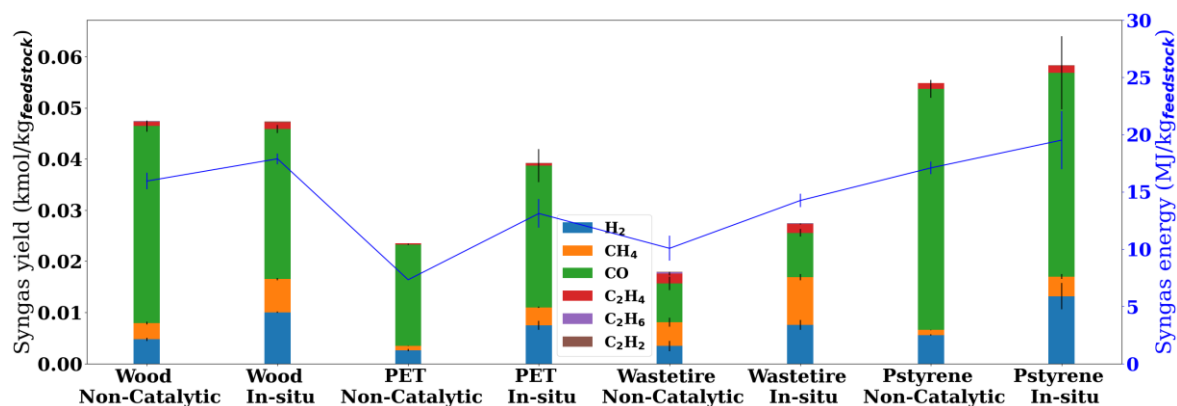


Figure 3. Syngas yield (bar plot) and energy yield (line plot) from CO₂-gasification of pinewood, PET, waste tyres, and polystyrene without and with catalyst.

3.2 Influence of catalytic position in CO₂-assisted gasification

In these tests, we placed the catalyst about 8 mm downstream of the test sample to facilitate thermal cracking without inhibition of CO₂ + char reactions as observed. This configuration is called quasi-in-situ. Figure 4 shows the accumulative yield of syngas major components for the in-situ, quasi-in-situ CO₂ gasification configurations. For all materials H₂, CO, and CH₄ yield increased when the catalyst was placed downstream of the feedstock revealing the sFCC catalyst to promote hydrocracking and reforming of hydrocarbons. For pinewood, the overall syngas yield increased by some 21.27% and the syngas energy increased by 22%, respectively, as compared to the in-situ case. For PET gasification, the overall syngas and energy yields increased by 27.5% and 23.8%, respectively in quasi-in-situ cases when compared to in-situ. Polystyrene provided the highest increase, with the quasi-in-situ catalytic gasification increasing the syngas yield and energy by 103.4% and 62.5% as compared to the in-situ catalytic gasification case, respectively. This, therefore, means that the quasi-in-situ catalytic gasification method is suitable for using sFCC catalyst in gasification. The spent FCC catalyst is a hydrocarbon cracking catalyst and does not participate in the solid reaction or the solid thermal decomposition of pinewood. It only participates during the thermal cracking of the volatiles that are evolved in the reactor. Therefore, this catalyst should be placed downstream of the reactor for secondary cracking.

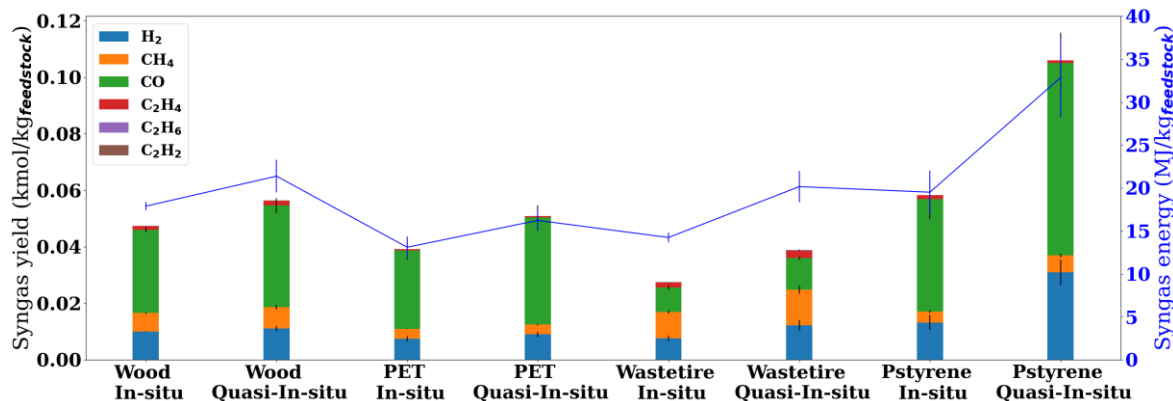


Figure 4. Syngas yield (bar plot) and energy yield (line plot) during in-situ, quasi-in-situ CO₂-assisted gasification of pinewood, waste tyres, PET, and polystyrene.

3.3 Influence of temperature

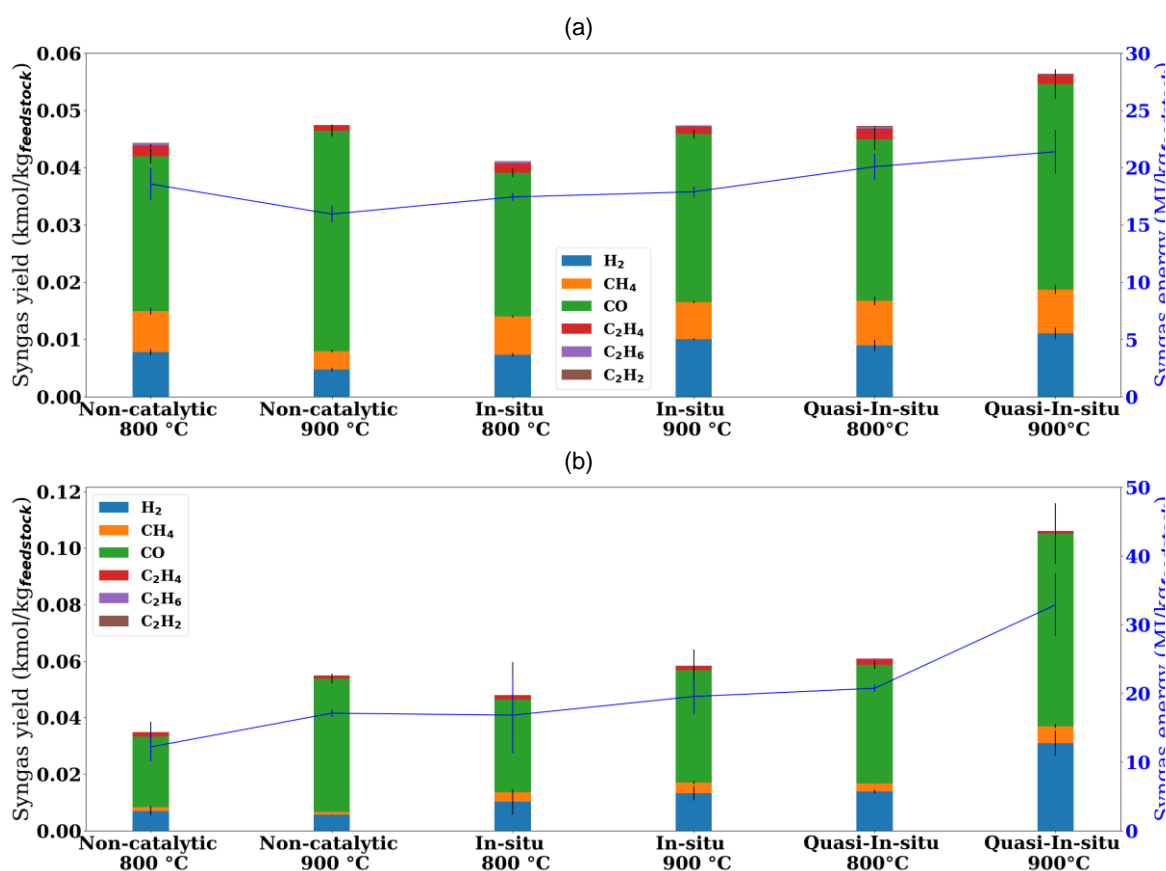


Figure 5. Effect of temperature on Syngas yield (bar plot) and energy yield (line plot) from catalytic CO₂-assisted gasification at 800 °C and 900 °C of Pinewood (a) and Polystyrene (b).

The effect of temperature was examined for pinewood and polystyrene. Figure 5 shows the influence of temperature during CO₂-assisted gasification. The results show that operating at a lower temperature of 800 °C has a negative impact on the CO yield because the Boudouard reaction responsible for carbon conversion to CO is favoured only at high temperatures. The other observation is that at lower temperatures there is a higher yield of C₂H_x hydrocarbons which suggests that CO₂-reforming of hydrocarbons is favoured at high temperatures which affects the overall yield of CO. For pinewood (Figure 5a) the yield of syngas energy decreased by 38.24% when the temperature was decreased from 900 to 800 °C. The in-situ catalytic case at 900 °C provided 42.42% higher energy yield compared to the in-situ case at 800 °C. Also, the quasi-in-situ case at 900 °C provided a 58.33% higher energy yield compared to the quasi-in-situ case at 800 °C. A similar behavior was observed for polystyrene, see Figure 5(b). At a higher temperature of 900 °C polystyrene provided a higher

yield of syngas compared to pinewood, PET, and waste tyres. This is because polystyrene is 100% volatile matter (Table 1) and has no tendency to form char.

4. Conclusions

The effect of adding spent FCC (sFCC) catalyst during CO₂-assisted gasification of MSW is explored to better understand the capabilities and potential of sFCC catalysts in assisting the thermal cracking of organic solid waste into syngas. Pinewood, waste tyres, PET, and polystyrene were evaluated as representative components in MSW. The results showed that the presence of sFCC increased the yields of total syngas and syngas energy compared to the non-catalytic cases. In-situ catalytic CO₂-assisted gasification increased the overall syngas yield by 81.25% for waste tyres, 62.5% for PET, 50% for pinewood, and 3.5 % for polystyrene when compared to respective non-catalytic gasification cases. For polystyrene, the quasi-in-situ catalytic gasification increased the syngas yield and energy by 103.4% and 62.5% as compared to the in-situ catalytic gasification case, respectively. However, for PET the syngas yield and energy increased by 27.5% and 23.8%. In the case of waste tyres, the syngas yield and energy yields increased by 24% and 23%, respectively. This suggests that quasi-in-situ catalytic gasification is more efficient and effective than in-situ catalytic gasification for increasing the syngas yield. High-temperature quasi-in-situ catalytic CO₂-assisted gasification is better suited to achieve high syngas energy yield. The findings presented here provide conclusive evidence of the synergistic potential of combining waste materials from FCC plants with those from MSW recovery facilities to recover valuable products while simultaneously reducing carbon footprint via catalytic CO₂-assisted gasification.

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