

Dry Reforming of Waste Polymers in Horizontal Reactor to Syngas Production

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The aim of the current study was the production of syngas and high value liquid by pyrolysis of waste plastic with various temperatures and catalyst type. Mixture of real waste polymers (LDPE, HDPE, PP and PET) were pyrolyzed under CO₂ atmosphere in horizontal reactor to obtain hydrogen rich/syngas. To increase the hydrogen yield, bimetallic synthetic zeolite catalysts were used. Firstly, the ZSM-5 catalyst supporter was impregnated with Ni and then other transition metals (Ca, Ce, La, Mg and Mn) were placed onto the Ni modified catalyst. It was found that the catalysts have a significant effect to the composition of gases and pyrolysis oil: e.g. increase the yields of gaseous product and syngas content of gases or occurring isomerization, cyclization and aromatization reactions. The results also showed that the increasing in the reaction temperature from 550 °C to 850 °C, more syngas was found. The maximum syngas yield was obtained over Ce/Ni/ZSM-5 catalyst.

1. Introduction

The global consumption of plastic has been increased due to its wide range applications (Park et al., 2018), which led to increasing in plastic waste. In one hand, different environmental problems have been reported as a result of high plastic waste accumulation in the landfills sites. On the other hand, choosing of unsuitable recycling technique could be contributing to atmosphere pollution (Özsin and Pütün, 2018). Therefore, many researches are focusing to alternative recycling methods to avoid such drawbacks of conventional recycling techniques (Anuar Sharuddin et al., 2016). Hence, waste to energy methods are considered as an attractive ways to reduce the plastic waste and save the environment. Different recycling techniques have been applied towards plastic waste management. Vast amount of plastics waste are treated by mechanical recycling, however, chemical recycling through thermal decomposition has gained the attention recently (Lopez et al., 2018). Pyrolysis and gasification processes are an example for chemical recycling, which can convert the plastic waste into valuable products in the absence and presence of catalyst (Adrados et al., 2012). The production of gases through pyrolysis process is affected by some factors such as atmosphere, temperature, feedstock and catalyst type. Gases from pyrolysis process can be improved by the addition of steam and catalyst (Garcia et al., 2002). Nowadays, most of researches are focusing on carbon capture processes due to the effects of carbon dioxide on climate change (Saad and Williams, 2017). Saad and Williams., (2017) have been used CO₂ atmosphere for the pyrolysis of waste LDPE, HDPE, PS, PET and PE. They found that the addition of carbon dioxide resulted in the increasing of syngas yields due to the dry reforming reaction. In other work, Zhang et al., (2015) have been studied the dry reforming of methane by using CO₂ atmosphere as alternative to steam (Zhang et al., 2015). However, thermal decomposition reaction is favourable at high temperature since most of the contaminants will be removed and more gases will be obtained. Various catalysts have been tested for the pyrolysis of waste plastics to enhance the process yields and improved the conversion rate. Nickel based catalysts are proved their efficiency in the decomposition reaction of waste plastics. While zeolite catalysts are considered as the best supporter due to their ability to promote the more cracking of waste polymers. Onwudili et al., (2018) investigated the effect of zeolite catalysts for the pyrolysis of waste of mixture (HDPE, LDPE, PP, PS and PET), they found that the addition of ZSM-5 and Y-zeolite to the process produced a significant increase in the gas yield (Onwudili et al., 2018). In other work, Yao et al., (2017) examined the bimetallic catalyst for the co-production of hydrogen and carbon nanotubes from catalytic pyrolysis of waste HDPE, LDPE, PP and PS.

They reported that the presence of Ni enhanced the thermal stability of produced carbons (Yao et al., 2017). However, it is uncertain whether second metal promoters would enhance the performance of the catalysts for waste plastic pyrolysis.

In the present study, the pyrolysis of waste plastics mixture (high and low density polyethylene, polypropylene and polyethylene terephthalate) was investigated at 550 °C and 850 °C using tubular furnace reactor. The influences of different modified catalysts and the different temperatures on the pyrolysis and syngas production were also investigated. The effect of CO₂ on the composition and pyrolysis product yields was also discussed.

2. Raw materials and methods

2.1 Raw materials

A mixture of waste low density polyethylene (14 %), high density polyethylene (17 %), poly propylene (19 %), polyethylene terephthalate (45 %) and polymers (5 %) were used as raw materials from municipal sources. They were shredded and milled into small particles by using laboratory grinder (Dipre GRS 183A9).

Various active metals (Ce, Ca, La, Mg and Mn) supported by synthetic Ni/ZSM-5 catalysts were used to enhance and improved the composition and product yields. The catalysts were prepared by wet impregnation method. Firstly, synthetic ZSM-5 supporters were added into 1M Ni(NO₃)₂·6H₂O, dissolution and continuously stirred for 2 h at 85 °C. Then catalysts were dried for 10 h at 110 °C, and conditioned at 650 °C for 5 h in air. Same procedure was used for placing the second metals using Ca(OH)₂, Ce(SO₄)₂·4H₂O, LaCl₃·7H₂O, MgSO₄·7H₂O and MnCl₂·4H₂O.

2.2 Raw materials

Raw materials were pyrolyzed in a tubular furnace at 550 °C and 850 °C using 0.5 dm³/h carbon dioxide flow (Figure 1). 5 g of raw materials and 2.5 g of the catalysts were placed in the quartz tube separated from each other by quartz wool. The reaction time was 20 minutes at the set temperature, then the reactor was disassembled, when the temperature reaches the 300 °C. Volatiles from reactor were cooled by cryostat using 10 °C, where the pyrolysis oil was condensed. Gaseous product was collected into a Tedlar bag. At the end of the reactions, products were weighted and their yields were calculated based on the weight balance.

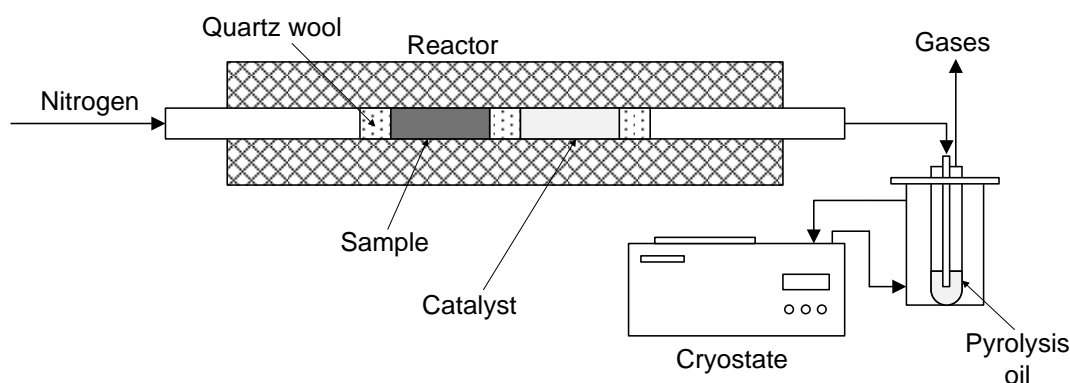


Figure 1: Horizontal tubular furnace for waste pyrolysis

2.3 Product analysis

Hydrocarbons in gases were investigated by a GC-FID (DANI GC) using Rtx PONA (100 m x 0.25 mm, surface thickness of 0.5 µm) and Rtx-5 PONA (100 m x 0.25 mm, surface thickness of 1 µm) columns. Sample analysis was taken using isotherm conditions (T=30 °C).

The hydrogen content in gases was measured by GC-TCD (Shimadzu GC-2010) using CarboxenTM 1006 PLOT column (30 m x 0.53 mm). The initial temperature was 35 °C (hold time 2 min), then it was elevated to 250 °C at 40 °C min⁻¹ heating rate and the final temperature maintained for 5 min.

Pyrolysis oil was analysed by GC-FID (DANI GC), using Rtx 1 dimetil-polysiloxan capillary column (30 m x 0.53 mm, thickness of 0.25 µm). Sample was dissolved in CS₂, and then injected to the instrument. The initial temperature was 40 °C for 5 min, then the temperature was elevated by 8 °C/min till 340 °C and it was kept at 340 °C till 20 min. Both the injector and detector temperature were 340 °C.

3. Results and discussion

3.1 Product yields

The product yields (gases, pyrolysis oil and char) obtained from the pyrolysis experiments with CO₂ atmosphere at temperature of 550 °C and 850 °C are shown in Figure 2. The data show that Ni/ ZSM-5 catalyst had the highest gas yields at 550 °C with yields of 42.4 %. While, La/Ni-ZSM-5 had the lowest gas yields (33.5 %). It can be also seen that clear increasing in the gas production was found with increasing the temperature to 850 °C for all catalysts type as well as for the experiment without catalyst. This was contributed to the more intensive cracking of C-C bond as a result of high temperature, leading to dominant formation of gases (Al-asadi et al., 2018). The maximum gas yield (79.3 %) was obtained also with Ni/ZSM-5 catalyst. On the other hand, catalyst of Mn/Ni/ZSM-5 had the lower effect on the decomposition reaction since lower gas yield was produced compared to the other used catalyst which is 68.8 %.

The yields of liquid for the experiments in the presence and absence of catalyst were higher at 550 °C in comparison to 850 °C. The liquid product was in the range of 32-57 %. The maximum liquid yield (57 %) was obtained in the decomposition reaction without catalyst. For the catalytic pyrolysis, Mg/Ni/ZSM-5 catalyst had the maximum yield of liquid 41.9 % among the other catalysts. However, clear decreasing in the liquid products was found with increasing temperature from 550 °C to 850 °C for both pyrolysis experiments (with and without catalyst). The obvious decreasing was attributed to the transformation of liquid into gases since higher temperature is responsible for more cracking of primary decomposition products. Therefore, it suggested that gasification was taken place. The yields of char for the various catalysts were relatively lower than gases and pyrolysis oil yields. This was corresponded to the gasification of char with carbon dioxide. Regarding to the carbon deposition on the catalyst surface, the result demonstrated that the temperature increasing to 850 °C resulted in decreasing of carbon deposited yields. This behavior was due to the ability of carbon dioxide for reducing carbon (CO₂+C=2CO).

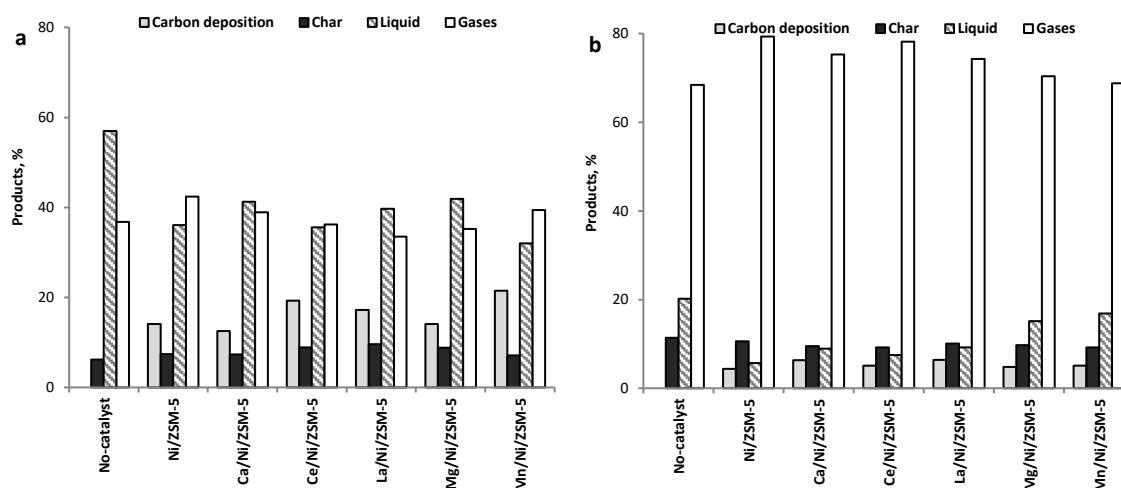
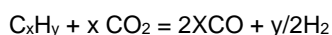


Figure 2: Product yields using different catalysts at (a) T= 550 °C; and (b) T= 850 °C

3.2 Gases

Figure 3 illustrate the compositions of gases, which shows the effect of temperature and catalyst type on the decomposition reaction. Gases contain H₂, CO, CO₂, CH₄, branched and non-branched hydrocarbons up to C₆. From Tables 1 and 2, it can be seen that the amount of hydrogen yield (H₂) over Ni/ZSM-5, Ce/Ni/ZSM-5 and La/Ni/ZSM-5 catalysts at 550 °C were almost same, which were in the range from 16.4 to 16.6 mmol/g. The Mg/Ni/ZSM-5 catalyst had the lowest H₂ yield (13.7 mmol/g). On the other hand, increasing the temperature to 850 °C had a positive effect on the syngas yields, because clear increasing in the syngas production was found for the different used catalysts as well as for the non-catalytic pyrolysis. Results show that Ce/Ni/ZSM-5 catalyst had the maximum hydrogen and carbon monoxide yields among the other catalyst which were 86.2 mmol/g and 45.8 mmol/g respectively. The marked increase in the syngas yields at 850 °C was attributed to the CO₂ dry reforming reaction (1) since the reaction require elevated temperature to occur as a result of low potential energy of methane and carbon dioxide (Saad et al., 2015)



This was further confirmed by the high reduction in hydrocarbons concentration (C₂-C₆) from 390.6 to 66.8 with increasing the temperature to 850 °C. No significant changing in the concentration of CO₂ yields was concluded for the different catalysts with changing the temperature from 550 °C to 850 °C, while slightly increasing in the concentration of methane (CH₄) was found with the temperature increasing. This is due to the methanization reaction (C+2H₂=CH₄).

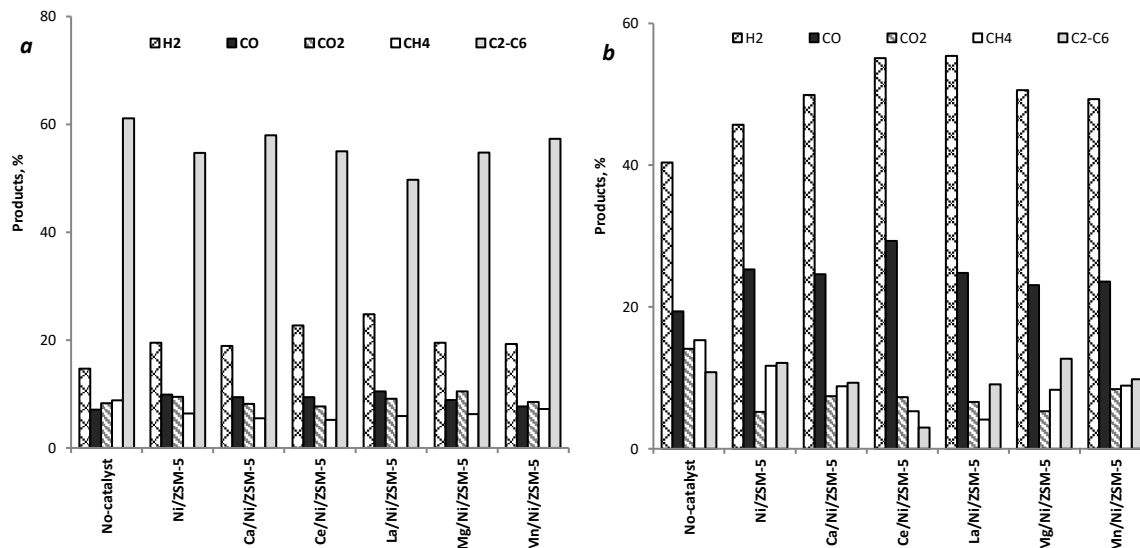


Figure 3: Gas composition by GC-FID and GC-TCD using different catalysts at (a) T= 550 °C; and (b) T= 850 °C

Table 1: Syngas yields (mmol/g) using different catalysts at 550 °C

| | No catalyst | Ni/ZSM-5 | Ca/Ni/ZSM-5 | Ce/Ni/ZSM-5 | La/Ni/ZSM-5 | Mg/Ni/ZSM-5 | Mn/Ni/ZSM-5 |
|----------------|-------------|----------|-------------|-------------|-------------|-------------|-------------|
| H ₂ | 29.7 | 38.8 | 38.8 | 39.9 | 37.1 | 35.6 | 38.8 |
| CO | 14.3 | 21.5 | 19.1 | 21.2 | 16.6 | 16.3 | 18.3 |
| Syngas yields | 44.0 | 60.2 | 58.0 | 61.1 | 53.7 | 51.9 | 57.4 |

Table 2: Syngas yields (mmol/g) using different catalysts at 850 °C

| | No catalyst | Ni/ZSM-5 | Ca/Ni/ZSM-5 | Ce/Ni/ZSM-5 | La/Ni/ZSM-5 | Mg/Ni/ZSM-5 | Mn/Ni/ZSM-5 |
|----------------|-------------|----------|-------------|-------------|-------------|-------------|-------------|
| H ₂ | 55.3 | 72.5 | 75.1 | 86.2 | 82.3 | 71.2 | 67.8 |
| CO | 26.5 | 40.1 | 37.0 | 45.8 | 36.9 | 32.5 | 32.5 |
| Syngas yields | 81.8 | 112.6 | 112.2 | 132.0 | 119.2 | 103.8 | 100.3 |

3.3 Pyrolysis oil

The compositions of pyrolysis oil analyzed by GC-FID are shown in Figure 4. Results indicate that the oil product contained n-olefins, n-paraffin, non-oxygenated aromatics, branched and oxygenated compounds. The concentration of n-paraffin and n-olefin were almost same for the various bimetallic catalysts. The maximum concentration of n-paraffin and n-olefin were achieved by Ca/Ni/ZSM-5 catalyst which were 19.6 % and 21.4 % respectively. Increasing the temperature to 850 °C resulted in lower concentration of n-paraffin and n-olefin compounds. The lowest amount was obtained by Mn/Ni/ZSM-5 catalyst. Regarding to the aromatic compounds in the oil, the results show different trends. At 550 °C, the maximum concentration of single ring aromatic (10.9 %) was obtained for Ca/Ni/ZSM-5 catalyst, while the maximum concentration of multi ring aromatic (6.4 %) was achieved over Mg/Ni/ZSM-5 catalyst. No marked changes in the concentration of single ring aromatic was concluded with increasing in temperature to 850 °C, while the concentration of multi ring aromatic is obviously increased. Ni/ZSM-5 catalyst had the maximum multi ring aromatic (13.0 %). This was attributed to the high activity of Ni/ZSM-5 catalyst in the aromatization reaction. Moreover, the presence of ZSM-5 led to more cracking of the heavy compounds and resulted in more aromatics in the pyrolysis oil products (Miskolczi et al., 2019). Regarding the oxygenated compounds in the pyrolysis oil, the maximum concentration of phenol and benzoic acid were obtained at 550 °C with catalyst of Ni/ZSM-5 and Mn/Ni/ZSM-5 catalyst respectively. The maximum concentration of terephthalic acid (12.0 %) was obtained in the absence of catalyst at 550 °C.

However, the concentration of oxygenated compounds was decreased with increasing the temperature to 850 °C. On the other hand, no significant difference was found in the concentration of other hydrocarbons by changing the catalyst type and temperature.

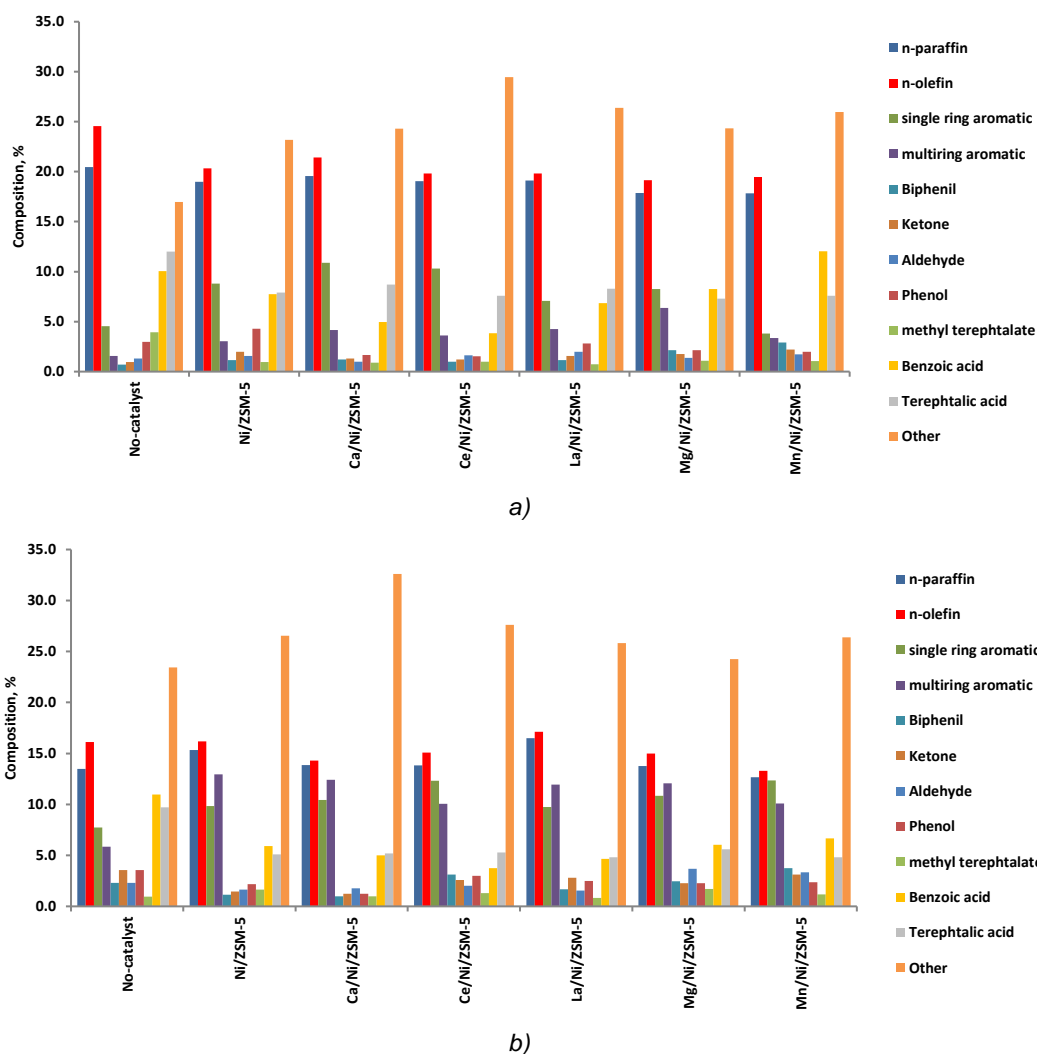


Figure 4: Pyrolysis oil composition using different catalysts by GC-FID at (a) $T= 550$ °C; and (b) $T= 850$ °C

4. Conclusions

Significant effect of temperature and catalyst type on syngas production from pyrolysis of waste mixture of (HDPE, LDPE, PP and PET) was demonstrated. The CO_2 atmosphere also influences the products yields by increasing the amount of hydrogen. The composition of gases in the product yields were mainly H_2 , CO_2 , CO , CH_4 , branched and non-branched hydrocarbons up to C_6 . Among the different used catalysts, Ni/ZSM-5 and Ce/Ni/ZSM-5 catalysts showed higher efficiency in syngas production at 550 °C and 850 °C. The maximum hydrogen yield was achieved over Ce/Ni/ZSM-5 at temperature of 850 °C. On the other hand, the maximum liquid products (57 %) were obtained in the absence of catalyst at 550 °C. The syngas yields were improved by the using of carbon dioxide as a carrier gas, furthermore, the carbon deposition on the catalyst surface was reduced for the same reason. According to the results, it can be seen that high temperature pyrolysis of waste plastic mixtures using different active metal catalysts showed great potential towards the syngas production. The present results will contribute to energy recovery from waste plastic and creating of renewable resources. Regarding to future work, two stage systems and finding new promoters would be effective for the syngas production from pyrolysis of waste plastic.

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