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Fuels by Chemical Recycling of Waste Plastic and Biomass Mixture and Utilization of the Products

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Plastics are key tools in many sectors in our everyday life. In 2016, 320 Mt of plastic waste was generated worldwide and the volume is growing rapidly. In Europe, plastic production increases by 3 % - 5 % a year. Plastics appear in mixed form with other constituents of the waste bins. In one hand, many processes are available for the selection of the pieces by type; on the other hand, these steps need additional cost. The amount of annual biomass waste is around $3.5x10^9$ t, which contain a huge amount of paper, cardboard, etc. Waste pyrolysis should be one possible option for high value-added, sustainable waste polymer and biomass recycling. During the pyrolysis valuable hydrocarbons could be obtained from waste streams. However, the long-term utilization of the products is an unsolved problem. This work is dedicated to the pyrolysis of plastic waste and biomass under mild conditions and investigation of the product properties by catalysts. For this purpose, synthetic zeolite catalysts were applied. It was concluded that the gas yields could be increased from 16.4 % to the range of 22.6 % - 32.2 % and to the range of 24.3 % - 29.4 % by using Ni/ZSM-5 and Ni/SAPO-11based catalyst mixture. The quality of oil produced by catalytic pyrolysis had favorable properties (lower C/H ratio, high mono-aromatic ration (13.9 % - 21.2 %); higher energy content, fewer contaminants or even better long-term properties) by the using of catalysts. Contaminants from raw materials move to gaseous and liquid fractions, and their level can decrease by catalysts.

1. Introduction

Plastics are important materials; e.g., cars, computers, bottles, phones, clothes, construction, agriculture and packaging need a vast amount of plastics. With the diversification of their uses and the lowering of their prices, plastics become the symbol of availability in consumerism; however, the long-term utilization of plastic wastes is an unsolved challenge (Fekhar et al., 2018a). Waste plastics cannot decompose; therefore, they cause significant environmental loading. On the other hand, some known solid waste treatments have high emission of greenhouse or harmful gases. The development of plastic and biomass valorization is one of the possible ways to offer a reasonable answer for waste utilization and solve the problem of climate change (Im-orb et al., 2018). Tsydenova et al. (2017) have summarized the chemical hazards related to the end-of-life treatment options and recycling of WEEE plastics waste and it was found that the incineration of waste that it contains flame-retardants (poly-brominated diphenyl ethers (PBDEs); pent bromophenol) can generate significant environmental and human health risks issues like air pollution and respiratory diseases.

In order to valorize polymeric wastes and reduce their negative effect on the environment, researchers have recommended many procedures to mitigate this problem. Among those procedures, the pyrolysis is considered as a most promising solution, produces carbonized organic materials, which are decomposed into gases (CO, CO_2, H_2, and CH_4), liquids (oils and heavy oils) and a carbon-rich solid phase (Roy et al., 2017).

Ji-lu (2007) has analyzed the energy performance of the pyrolysis of rice husk process, and the results were promising. For instance, the energy cascade was about 49 % for the produced pyrolysis oil and approximately 86 % for all products. The thermal energy contained in the liquid pyrolysis oil was 71.41 MJ/h and it was more than the energy consumed by electric heating (43.20 MJ/h) during the pyrolysis process.

Pyrolysis oils have significant potential as a substitution of fossil resources. The growing interest in these new resources comes from the fact that they can be considered carbon neutral. Indeed, the use of waste as raw

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material to produce potential value-added products would reduce the amount of carbon dioxide emission. The rapid and barely controlled breaking of molecules leads to a mixture of complex chemicals, which composition difficult to identify (Uddin et al., 2018). Rapid condensation of hot vapors freezes the unsaturated chains they led polymerization reactions and increases the yield of high molecular weight compounds during and their storage. The high oxygen content of the raw material (biomass and/or solid waste) will eventually appear in oil in various unwanted chemicals, like acids or molecules with duplicates carbon-oxygen bonds that tend to polymerize over time and increase the viscosity of the oil. In order to improve the quality of the oil, catalysts can be added (Papari et al., 2018).

Sajdak (2017) has studied the impact of plastic waste mixtures in different ratios with lignin-rich material in fixed bed pyrolysis. It was clearly showed that the combination of biomass with plastic materials had a positive effect on the liquid and gas yields. Franklin et al. (1981) used calcium carbonate and a mixture of calcite. They added 20.2 % $CaCO_3$ and 5.9 % of the calcite mixture (74 % $Ca(OH)_2$ and 26 % $CaCO_3$) as pyrolysis compartment. They concluded that calcium oxide (CaO) is the most active species because the other two compounds can decompose at high temperatures. The CO yields are tripled because calcium oxide (CaO) can catalyze the decomposition of phenolic compounds into CO, which reduces the tar. The reduction of methane yields from 4.5 % to 3 % suggests that secondary cracking due to CaO.

Fekhar et al. (2018b) investigated the co-pyrolysis of real waste high-density polyethylene and rice straw using different ratios of the raw materials. They have found that the activation energy of plastic decomposition could be significantly decreased by increasing the ratio of biomass. It was also demonstrated that the use of higher plastic ratio in raw material could remarkably decrease the yield of oxygenated compounds, for example, aldehydes, ketones, carboxylic acids or even phenol and its derivatives. Leclerc et al. (2018) have demonstrated the synergistic effect between the pyrolysis of cellulose and another type of plastic. They concluded that co-pyrolysis of plastic with cellulose can reduce the yield of styrene. This observation can explain by the hydrogenation of styrene. It was also found that the surplus of hydrogen needed to the hydrogenation was obtained by the pyrolysis of cellulose. Qiming et al. (2017) also investigated the co-pyrolysis of biomass and plastics in the temperature range of 800-1,100 °C. They concluded that the soot from plastic pyrolysis has higher yield and volume than that of from the biomass pyrolysis. Johansson et al. (2018) have highlighted the significance of co-pyrolysis to the product properties. The co-pyrolysis of different polymeric materials suppressed the formation of reactive oxygenated compounds and promoted the production of alcohols and esters. However, chlorinated compounds have appeared, therefore the acidity and the viscosity of liquid hydrocarbon are increased by the incorporation of plastic waste with biomass.

Catalysts can also affect the product yields, composition and long-term properties. Especially synthetic zeolite catalysts incorporated by different active metals are used for this purpose. The key issues are the reduction of acidic components, increasing in valuable products (both gases and pyrolysis oil), enhanced the long-term properties, e.g. storage, transportation, etc. Regarding the undesired components, especially the halogens, aldehydes, ketones, carboxylic acids, phenolic compounds have the most problems.

In our current work, the batch pyrolysis of waste plastic and biomass mixtures were investigated using different synthetic zeolite based catalysts to in-situ quality improving of the products.

The present paper aims is to investigate the effect of new and cost-effective catalysts mixture consist of different ration of Ni/ZSM-5; Ni/SAPO-11; $Ca(OH)_2$ and Red mud for the in-situ upgrading of pyrolysis oil quality produced by co-pyrolysis of biomass and plastic waste by the use of a batch reactor.

2. Raw materials and methods

2.1 Raw materials

A mixture of real municipal plastic waste and biomass was used as raw materials: 24 % LDPE, 22 % HDPE, and 16 % PP, 35 % biomass and 3 % of non-defined material.

Catalysts mixtures containing Ni/ZSM-5 or Ni/SAPO-11 catalysts, $Ca(OH)_2$ and red mud were used for in-situ products improving. Table 1 summarizes the composition of catalyst mixtures. Regarding the catalysts, their ration was in 5 % concentration. The Ni/ZSM-5 and Ni/SAPO-11 catalysts were synthesized by wet impregnation. The red mud has the following composition Fe_2O_3 (74.8 %), Al_2O_3 (9.8 %), CaO (4.6 %), TiO_2 (3.2 %), SiO_2 (2.2 %), MnO (1.2 %), Na_2O (0.9 %), V_2O_5 (0.4 %), SrO_2 (0.2 %) and 2.6 % others. The BET surface of the Ca $(OH)_2$ and red mud was 28.4 and 35.1 m^2/g, respectively. The ZSM-5 ($[Na_n (H_2O)_{16}] [AlnSi_{96-n}O_{192}]$) and (SAPO-11) ($[Na_n] [Al_{20}Si_nP_{20-n}O_{80}]$) catalyst has 5.3 x 5.6 Å and 6.3 x 3.9 Å pore size.

Table 1: The composition of the catalysts, %

	Ni/ZSM-5	Ni/SAPO-11	$Ca(OH)_2$	Red mud
111-Z	33.33	0.0	33.33	33.33
112-Z	50.0	0.0	25.0	25.0
121-Z	25.0	0.0	25.0	50.0
211-Z	25.0	0.0	50.0	25.0
111-S	0.0	33.3	33.3	33.3
112-S	0.0	50.0	25.0	25.0
121-S	0.0	25.0	25.0	50.0
211-S	0.0	25.0	50.0	25.0

2.2 Pyrolysis process

Biomass and plastics waste were pyrolyzed together in a one-stage stainless steel batch reactor at 510 - 520 °C in a nitrogen atmosphere (Figure 1). The heating rate was 15 °C/min. The volatiles from the reactor had been condensed, and then gases and liquid hydrocarbons were separated. The yields of different hydrocarbons were calculated in accordance with the mass balance Y (gas) = 100 - Y (pyrolysis oil) - Y (residue).

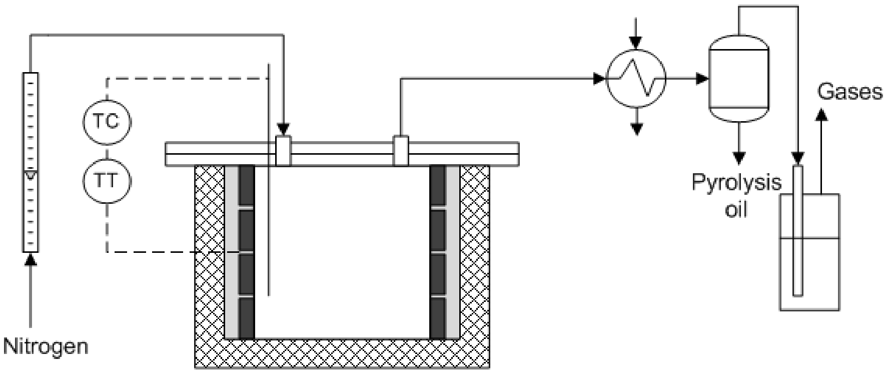

Figure 1: The batch process for pyrolysis

2.3 Product analysis

Gases were analyzed by DANI MASTER GC fitted with FID at 30 °C (Rtx PONA (100 m x 0.25 mm, using a surface thickness of 0.5 µm) and Rtx-5 PONA (100 m × 0.25 mm, using a surface thickness of 1 µm) columns). Hydrogen, CO, CO_2, and light hydrocarbons were measured using GC-TCD (Shimadzu GC-2010), with CarboxenTM 1006 PLOT column (30 m × 0.53 mm).

Pyrolysis oil was examined by GC-FID (DANI GC), using Rtx 1 dimethyl-polysiloxane capillary column (30 m x0.53 mm, thickens of 0.25 µm): 40 °C initial temperature for 5 min, then the temperature was raised by 8 °C/min till 350 °C and it was kept at 350 °C for 20 min. The temperatures of injector and detector have fixed at 350 °C. In order to investigate the yield of mono-aromatics and poly-aromatics a High-Performance Liquid Chromatography (HPLC) (Shimadzu Prominence UFLC fitted with polar amine-silica phase column and RI detector) were used according to EN 12916 standard. The column was tempered to 30 °C; the flow was isocratic with 1 mL/min. The acquisition time was 15 min and the effluent was HPLC grade n-heptane.

3. Result and discussion

3.1 Product yields

The yields of pyrolysis products are summarized in Figure 2. Pyrolysis was carried out until no volatiles could be produced from the reactor. In general, the yield of gaseous hydrocarbons was in the range of 32.2 % - 23.5 % and it was the highest produced overusing of Ni/ZSM-5 rich catalyst mixtures (112-Z and 112-S).

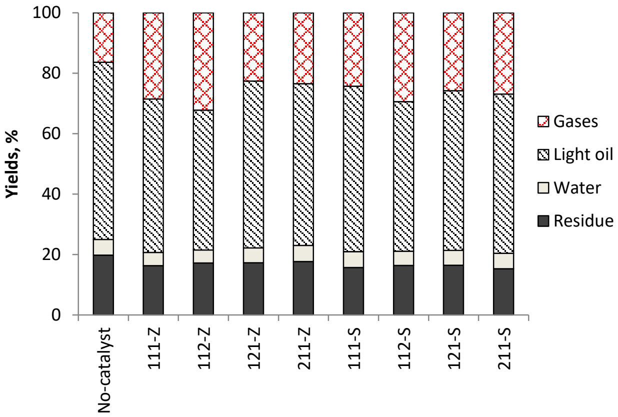

Figure 2: Yields of pyrolysis products obtained from the batch reactor

It is worth to mention that, the 112-Z catalyst has the highest Ni/ZSM-5 content, which due to the high BET surface area and higher micro-pore volume leads to C-C bond cracking. On the other hand, the yield of light oil was the predominant products in case of pyrolysis without catalyst with the yield of 58.6 %, which was slightly decreased to 46.3 % - 55.2 %, and 49.5 % - 54.7 % in case of the using of Ni/ZSM-5 and Ni/SAPO-11 based catalyst mixture.

Regarding the catalysts, there is a significant difference in the yield of gases and light oil. However, comparing the effect of the catalyst supporters (ZSM-5 and SAPO-11), no significant difference can be concluded. It is important to remark that the water in the products was the consequence of the biomass content of the raw materials. Biomass is built-in polysaccharides, which owing to the glycoside –OH groups results in water production. The amount of water was around 5 % and not affected by the presence of catalysts.

The presence of water in pyrolysis oil is considered as unfavourable properties since it can cause some complications like phase separation, and lead to the deterioration of pyrolysis oil properties during the long-term application (corrosion, storage or transportation problems). The yield of residue obtained by catalyst-free pyrolysis (19.8 %), can be reduced by catalysts, for instance, the yield of residue was in the range of 16.3 % - 17.7 % in the case of using Ni/ZSM-5 based catalyst mixture, and 15.3 % - 16.5 % in the case of Ni/SAPO-11 containing catalyst mixture.

3.2 Composition of gaseous products

Figure 3 summarizes the result of the analysis. Without a catalyst, the composition of gases was as follows: 7.2 %; 3.8 %; 5.6 %; 9.9 % and 73.5 % for hydrogen, CO, CO_2, CH_4, and C_2-C_5 hydrocarbons, respectively. As it is seen, the predominant product was the C_2-C_5 in both cases. For example, it was in the range of 64.2 % - 70.1 % in the case of using Ni/ZSM-5 based catalyst mixture, however using Ni/SAPO-11 based catalysts can slightly decrease the yield to the range of 55.1 % - 64.3 %. It is worth to mention that the increase in the ration of red mud in the catalyst can significantly decrease the yield of C_2-C_5. By way of illustration, it was 64.2 % and 55.1 % by using 121-Z and 121-S. On the contrary, the yield of methane was higher by using Ni/SAPO-11 based catalysts mixture comparing to Ni/ZSM-5 based catalysts.

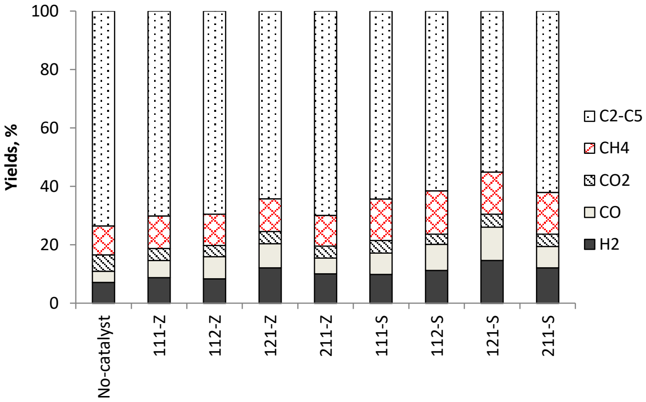

Figure 3: Composition of gases

From another point of view, there is no significant effect on the yield of carbon dioxide during the catalytic pyrolysis. For instance, it was in the range of 3.8 % - 4.2 % and 3.5 % to 4.4 % by using Ni/ZSM-5 and Ni/SAPO-11 based catalyst mixture, respectively. On the other hand, the yield of carbon monoxide has slightly increased by increasing the ration of red mud in the catalyst; it was 8.2 % and 11.4 % by the use of 121-Z and 121-S respectively. Furthermore, the yield of hydrogen has increased by introducing catalyst to the pyrolysis procedure and it was within the range of 8.8 % to 12.2 % by utilizing Ni/ZSM-5 based catalyst mixture, and in the range from 9.9 % to 14.7 % by applying Ni/SAPO-11 based catalysts mixture. The hydrogen content of the hydrocarbon gas products was 7.2 % without catalysts, which could be increased to 8.4 % - 12.2 % by utilizing Ni/ZSM-5 based catalyst and to 9.9 % - 14.7 % by using Ni/SAPO-11 based catalysts. Results also correspond to the synergistic effect of Ni and transition metals in red mud for hydrogen production.

3.3 Composition of liquid oil products

The pyrolysis oil was analyzed by GC-FID and HPLC. The results are summarized in Figure 4 and Table 2. According to the results, the pyrolysis oil was a combination of different hydrocarbon like n-paraffin; n-olefin; phenol and its derivate (e.g. m-cresol; 2-ethyl phenol; 2.4-dimethyl phenol); other oxygen-containing (aldehydes; ketones; carboxylic acid). Introducing the catalysts has a significant influence on the concentration of different composites in the produced pyrolysis oil. E.g., the yield of oxygenated compounds could decrease from 13.2 % (catalyst-free case) to the range of 10.5 % - 11.4 % by using of Ni/ZSM-5 based catalyst mixture, and to the range of 9.6 % - 11.4 % with Ni/SAPO-11 based catalyst mixtures. At the same time, it is also advantageous phenomena, which the concentration of phenol and its derivatives has also decreased with the applying of catalyst from 18.3 % (catalyst-free case) to the range of 11.0 % - 13.3 % (Ni/ZSM-5 based catalyst) and to the range of 9.5 % - 11.0 % (Ni/SAPO-11 based catalyst). On the other hand, the yield of n-olefins has increased, while less n-paraffin can be measured by the using of catalysts. Catalysts mostly can increase the amount of other hydrocarbons, which contained especially branched hydrocarbons. That result corresponded to the isomerization effect of the catalyst supporters.

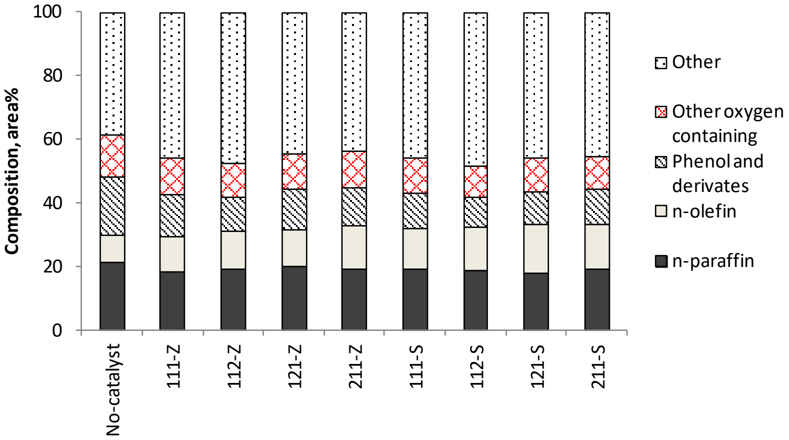

Figure 4: Composition of pyrolysis oil by GC-FID

The result of HPLC analysis is summarized in Table 2. Results well show that the used catalysts can drastically affect both the yield of mono-aromatic hydrocarbons and poly-aromatics. The yield of mono-aromatic hydrocarbons and poly-aromatics was 9.7 % and 6.8 % without catalysts, which can nearly double by Ni/ZSM-5 type catalyst mixtures (16.8 % - 21.2 %). Ni/SAPO-11 containing catalyst mixtures has less significant effect (13.9 % - 15.8 %). It is an important observation that opposite trend was found regarding the poly-aromatics, because catalysts synthesized by SAPO-11 supporter can increase the concentration of poly-aromatics hydrocarbons more significantly: to 9.2 % - 10.5 % and to 11.6% - 12.7 % by using Ni/ZSM-5 and Ni/SAPO-11 based catalysts mixture, respectively.

Table 2: the yield of mono and poly-aromatics by HPLC (vol %)

	No-catalyst	111-Z	112-Z	121-Z	211-Z	111-S	112-S	121-S	211-S
Mono-aromatic	9.7	17.4	21.2	16.8	17.1	14.7	15.8	13.9	14.2
Poly-aromatics	6.8	9.3	10.5	9.6	9.2	11.6	12.7	11.6	12.1

4. Conclusion

This paper has examined the pyrolysis of biomass and plastic waste under the mild condition and has investigated the influence of different catalysts mixture (Ni/ZSM-5, Ni/SAPO-11, $Ca(OH)_2$ and red mud) on the properties of the hydrocarbon products. Results have clearly shown that the introducing of catalysts has considerably increased the yield of gases due to its C-C bound cracking effect from 16.4 %to the range of 22.6 % - 32.2 % and to the range of 24.3 % - 29.4 % by using Ni/ZSM-5 and Ni/SAPO-11based catalyst mixture, respectively. The presence of biomass during the pyrolysis process leads to the appearance of water in the product, and it was in the range of 4.3 % - 5.2 %, which can reduce the quality of hydrocarbon liquid by causing many issues during the long-term application like corrosion, phase separation, etc. The amount of water was not affected by introducing different catalysts. On the other hand, the yield of residue has considerably reduced by the using of catalyst mixture, and it was in the range of 16.3 % to 17.7 % and in the range of 15.3 % to 16.4 % by using Ni/ZSM-5 and Ni/SAPO-11based catalyst mixture. The high ratio of red mud like 121-Z and 121-S has produced the littlest yield of residue. The increase in the ratio of red mud in the catalyst has affected the gas yield composition by decreasing the yield of C_2-C_5 hydrocarbon gas. However, those catalysts have promoted the yield of hydrogen. The yields of oxygenated compound (aldehydes, ketones, carboxylic acids, etc.) has significantly decreased via using the catalyst that can improve the quality of liquid hydrocarbons by increasing its energy density. The forthcoming investigation research should give emphasis to the examination of the effect of different catalyst mixture and combination on the pyrolysis oil de-contamination (the removal of different oxygenated compounds, phenol, aldehydes...etc.) for the purpose of enhancing the long-term pyrolysis product stability and applicability.

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