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Comparision of real waste (MSW and MPW) pyrolysis in batch reactor over different catalysts. Part I: Product yields, gas and pyrolysis oil properties

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HIGHLIGHTS

- Pyrolysis of MSW and MPW was investigated in absence and presence of catalysts.
- The *n*-olefin/*n*-paraffin ratio has decreased as function of temperature.
- Aromatic and cyclic compounds predominantly formed in the presence of catalysts.
- Aromatic carbon joined to hydroxyl and ether oxygen resonances both were not observed.
- The catalytic effect was more significant in case of MPW pyrolysis.

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ABSTRACT

Pyrolysis of municipal solid waste (MSW) and municipal plastic waste (MPW) have been investigated in batch reactor at 500, 550 and 600 °C both in absence and presence of catalysts (Y-zeolite, β-zeolite, equilibrium FCC, MoO_3, Ni–Mo-catalyst, HZSM-5 and $Al(OH)_3$). The effect of the parameters on the product properties was investigated. Products were characterized using gas-chromatography, GC/MS, ^{13}C NMR. Yields of volatile fractions increased, while reaction time necessity for the total cracking decreased in the presence of catalysts. Catalysts have productivity and selectivity in converting aliphatic hydrocarbons to aromatic and cyclic compounds in oil products. Gases from MSW consisted of hydrogen CO, CO_2, while exclusively hydrogen and hydrocarbons were detected from MPW. Catalyst efficiency was higher using MPW than MSW. Pyrolysis oils contained aliphatic hydrocarbons, aromatics, cyclic compounds and less ketones, alcohols, acids or esters depending on the raw materials.

1. Introduction

Pyrolysis is one of the mostly investigated ways for municipal waste (municipal solid waste (MSW) and municipal plastic waste (MPW)) recycling, which is suitable for production of gas, liquid and solid hydrocarbons or other valuable products. During the pyrolysis the large molecules of the raw material are degraded into smaller ones at temperatures of 350–1000 °C under atmospheric pressure using inert atmosphere. Basically polymers, like plastics or biomass could be processed by this way. The major area of the utilization of pyrolysis products is both the petroleum and petrochemical industry: they could be used as blending components for fuels or precursors of production of valuable chemicals. However the composition of products is strongly depending on the raw materials. Quite often plastics and organic wastes are impossible to collect separately therefore it is easy and more economical to dispose them together. That is why lot of co-pyrolysis studies were carried out, which were aimed to widen the possible range of raw materials. If biomass is pyrolized in itself, liquid products contain significant amount of water and other organic chemicals such as organic acids, alcohols, aldehydes, ketones, phenols and ethers that is unfavorable in terms of their utilization (Sharypov et al., 2002). Therefore most of the studies focus on biochar, the solid, residual product of biomass pyrolysis, which could be used for energy production like coal or for production of adsorbents (Bernardo et al., 2012). The predominant compounds in the pyrolysis-oils obtained from fluidized pyrolysis of waste square timber and waste ordinary plywood were methyl acetate, acids, hydroxyacetone, furfural, non-aromatic ketones, levoglucosan and phenolic compounds (Jung et al., 2012). The composition of the pyrolysis oils is depending on the raw materials and experimental parameters; higher plastic ratio in raw materials increases the oil yields and decreases the water content. Polymers that contain more hydrogen than bio-

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mass could provide hydrogen during co-processing (Miskolczi et al., 2011; Sharypov et al., 2002; Cornelissen et al., 2008). Sharypov et al. (2002) studied the co-pyrolysis of wood biomass and synthetic polymers. They found that 400 °C was the optimum temperature for biomass/plastic mixture degradation which corresponded to the maximum light liquid product yield. Congruent results were obtained by Cornelissen et al. (2008), who pyrolized biomass together with polylactic acid and investigated the bio-oil yield and heating values. Flash co-pyrolysis of willow and PLA resulted in an enhanced bio-oil yield with lower water content and a higher calorific value. Synergistic effects were observed to addition of PLA: an increase of 28% in bio-oil yield and a decrease of 37% in water content. The potential synergistic activities between tar sand and walnut shell during co-pyrolysis was also investigated and concluded that the bio-oil yield could be increased, it had more aliphatic and aromatic contents, and the alkane content was higher in the bio-oil from co-pyrolysis (Kar, 2011). On the other hand, the thermal decomposition of “model compounds” and not a real waste have been widely investigated. Product yields and compositions obtained from from co-prolysis were not comparable to the cases when the plastic and biomass were pyrolized separately. The products of the co-pyrolysis should be generally further upgraded to their utilization. In the literature no studies could be finding about catalysts during co-pyrolysis in order to improve the quality of the pyrolysis products.

In present study pyrolysis of real municipal solid waste (MSW) and municipal plastic waste (MPW) obtained from landfill, was carried out in a batch reactor at 500, 550 and 600 °C in absence and presence of catalysts (Y-zeolite, β-zeolite, equilibrium FCC, MoO_3, Ni–Mo-catalyst, HZSM-5 and $Al(OH)_3$). The effect of the pyrolysis parameters on the properties of products was investigated. Products were characterized using gas-chromatography, GC/MS, ^{13}C NMR.

2. Methods

2.1. Raw materials

In this work real municipal solid waste (MSW) has been used as raw material obtained from Hungarian waste recycling plant. Waste materials were collected mainly from households and it is consisted of plastics, paper, metals, textile, organic waste, etc. Then plastic particles were separated from the other constituents of MSW and called as municipal plastic waste (MPW). Before the pyrolysis experiments both MSW and MPW were shredded and scraped into particles with up to 10 mm size and then they were analyzed. Results are summarized in Table 1a. Based on visually observation and Fourier transformed infrared spectroscopy by particles to particles, MSW had 58.4% plastics, 27.5% papers, 8.1% other organic wastes (wood, thin foil, vegetable garbage, etc.), 4.8% textile/synthetic fibres and 0.9% metals, while MPW had polyethylene (59.1%), polypropylene (25.0%), polystyrene (7.2%) and others (PET, PVC, PA, ABS) (8.7%). In consequence of the high paper and organic waste content in MSW, its heating value was relatively low (27.1 MJ/kg), while MPW has considerable higher value (42.2 MJ/kg). The moisture and ash content was 5.2% and 4.7% in MSW, respectively, while MPW had 0.9% moisture and 1.4% ash. Ultimate analysis showed that MPW had higher carbon and lower hydrogen content than MSW. Oxygen was measured only in MSW (19.5%). Regarding other elements, MPW had less and significantly lower amount of contaminants. Based on 3 parallel measurements the deviation in reproducibility of the ultimate, proximate and contaminants analysis was 2.1%, 3.0%, and 2.2%, respectively.

Table 1a
Main properties of the raw materials (MSW and MPW).

Properties	MSW	MPW
Proximate analysis		
Moisture (%)	5.2	0.9
Ash (%)	4.7	1.4
Combustibles (%)	91.1	97.7
Ultimate analysis		
C (%)	59.3	85.9
H (%)	21.2	14.1
O (%)	19.5	0.0
S	648	135
Cl	11196	2689
Zn	4953	1310
Ca	6218	1504
Br	9105	2316
Sb	1299	749
K	226	
P	967	
Fe	8349	
Cr	2344	
Pb	992	
Heating value (MJ/kg)	27.1	42.2

Zeolite structures have efficient catalytic properties to cracking of the polymer skeletal and their activity is responsible for that via β-scission. Previous researchers found that metals (Ni, Mo, Fe, Al, etc.) exert a significant effect, especially to the product quality (Sharypov et al., 2002). E.g. the olefin and aromatic content or even hydrogen in gases could be changed in the presence of Ni or other noble metals catalysts and their small amount is sufficient to affect the product property to a large extent. In this work Y-zeolite, β-zeolite, equilibrium FCC, MoO_3, Ni–Mo-catalyst, HZSM-5, $Al(OH)_3$ were used in order to achieve more intensive degradation of raw materials and modification of pyrolysis product structure. Table 1b shows the main properties of the catalysts. The highest Si/Al ratio was found in case of FCC catalyst (23.2). Regarding BET surfaces the following order was found: Y-zeolite (379.5 m^2/g) > HZSM-5 (366.9 m^2/g) > β-zeolite (349.2 m^2/g) > Ni–Mo-catalyst (218.3 m^2/g) > FCC (192.2 m^2/g) > $Al(OH)_3$ (109.5 m^2/g) > MoO_3 (84.9 m^2/g). The microporous surface areas of catalysts were between 49.5 and 161.4 m^2/g, while the average pore size was in the range of 14.8 and 238.2 μm. Due to porous structure and cationic balance; Y-zeolite and HZSM-5 were the most acid catalysts.

2.2. Pyrolysis process

A small laboratory scale batch reactor was used for pyrolysis at 500, 550 and 600 °C under nitrogen blanket using atmospheric pressure. Fig. 1 demonstrates the layout of the process. In each case 50 g of raw materials were put into the reactor and 10% catalyst was used in thermo-catalytic pyrolysis. 500 °C temperature was used for thermo-catalytic experiments. Right before the experimental runs raw materials were crashed into particles with less than 10 mm in main dimension. The temperature of the reactor vessel has been measured by thermocouple and controlled by PID controller. Volatile products from the degraded polymer melts have been run via water cooled condenser, where pyrolytic oil and water were transformed to liquid phase. The condensed fraction (pyrolytic oil and water together) has been separated from gases and then it was further divided into pyrolytic oil and water based on their density difference in another separation unit. Pyrolytic oils have been collected in a sample holder and then analyzed by GC/MS, ^{13}C NMR. Residue oil and char was taken away from the reactor. Gas product was collected in a gas bag and analyzed by gas-chromatograph. Product yields were calculated based on their weight. The amount of pyrolytic oil, water and residue was measured by laboratory scale, while gas yield was calculated based