Fuels by Waste Plastics Using Activated Carbon, MCM-41, HZSM-5 and Their Mixture

Norbert Miskolczi [1], Chunfei Wu [2], Paul T. Williams [3]

[1] Chemical Engineering and Process Engineering Institute, MOL Department of Hydrocarbon and Coal Processing, University of Pannonia, Veszprém, 10 Egyetem u., 8200, Hungary
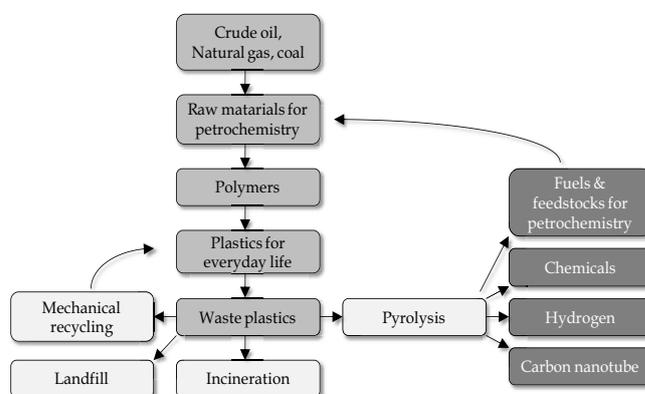[2] Energy Research Institute, University of Leeds, Leeds, LS2 9JT, UK
[3] School of Engineering, University of Hull, Hull, HU6 7RX, UK

Abstract. Waste material was pyrolyzed in a horizontal tubular reactor at 530-540°C using different catalysts, such as activated carbon, MCM-41, HZSM-5 and their mixtures. Products were investigated by gas-chromatography, EDXRFS and standardized methods. Catalysts significantly affected the yields of volatiles; e.g. HZSM-5 catalyst increased especially the yield of gaseous hydrocarbons, while MCM-41 catalyst was responsible for increasing the pyrolysis oil yield. Synergistic effects were found using mixtures of different catalysts. Furthermore the catalysts modified the main carbon frame of the products. Pyrolysis oil obtained over HZSM-5 catalyst contained large amounts of aromatics, while MCM-41 catalyst mainly isomerized the carbon frame. Regarding contaminants it was concluded, that the sulphur content could be significantly decreased by activated carbon, however it had only a slight effect to the other properties of the products.

1. Introduction

Pyrolysis has benefits not only by reducing the huge mass of polymer wastes, but also enormous energy could be saved by chemical recycling. During pyrolysis, the polymer macromolecules decompose into gaseous and liquid products, which have lots of similarities with commercial fuel gas, naphtha or even gas oil. In general, 400-1000 °C is used for waste depolymerization depending on the technologies (using batch reactor, tubular reactor, fluidized bed, rotary kiln, etc.) [1-5]. Higher temperature promotes the formation of gaseous hydrocarbons, coke deposits, and the products contain lots of cyclic hydrocarbons or aromatics. Aliphatic hydrocarbons (both saturated and unsaturated) are the main products using lower pyrolysis temperatures (<600°C) [4-9]. The product yields and composition are affected also by the application of catalysts, which could increase the yield of volatiles (both gases and pyrolysis oils) [10-14]. It was demonstrated, that the structure of zeolites had a key role in relation to the product properties. E.g. mainly alkanes are produced over y-zeolite, while unsaturated hydrocarbons and aromatics are the main fractions using ZSM-5 [4, 10, 11, 16].

Based on references, the energetic application of pyrolysis product is the mostly investigated way for their further utilization [15, 17]. However there are different alternatives for further product utilization, depending on the pyrolysis parameters (Figure 1).

Figure 1. Ways for utilizations of pyrolysis products obtained by waste plastic

Not only fuels, but also different other valuable products could be generated: chemicals, hydrogen, olefin rich fractions for petrochemical application, carbon nanotube, carbon black, etc. Hydrogen rich gas is the main product, using metal containing catalyst and high temperature, while olefin rich fraction and other chemicals are the main products using catalyst with high Si/Al ratio. Carbon nanotube production also requires special catalyst and elevated temperature. It is important to remark that corrosion and emission problems could occur when contaminated pyrolysis products are further used. Therefore the decreasing of contaminants in products is a real problem [9].

In this work thermo-catalytic pyrolysis of waste low density polyethylene and high density polyethylene was investigated in a horizontal tubular reactor at 530-540°C using activated carbon, MCM-41 and HZSM-5 catalysts and their mixtures. Especially the effect of catalysts and their mixtures to the product yield and composition was investigated.

2. Material and methods

2.1 Raw materials

Mixture of real waste high density polyethylene (HDPE) and low density polyethylene (LDPE) from packaging was used in this work. According to preliminary analysis, raw material contained 74.8% HDPE and 15.2% LDPE. The main properties of the raw materials are summarized in Table 1.

Table 1. The main properties of real waste plastics

Property	Value
Average particle size, mm	3-4
Proximate analysis	
Ash content, %	2.9
Volatile content, %	1.4
Combustible, %	95.7
Ultimate analysis	
C, %	85.71
H, %	14.21
Cl, %	0.05
S, %	0.02

Samples of average particle size of 3-4mm were used. Owing to the real waste source, raw material had contamination, in the form of chlorine (0.05%) and sulfur (0.02%), while the moisture and ash content were 1.4% and 2.9%, respectively.

In order to modify the yield and composition of products, different catalysts and their mixtures were tested: activated carbon, MCM-41 and HZSM-5. Table 2 demonstrates the composition of catalyst mixtures.

Table 2. The composition of catalysts (in%)

Catalyst	Activated carbon	MCM-41	HZSM-5
C-1	100	-	-
C-2	-	100	-
C-3	-	-	100
C-4	50	50	-
C-5	50	-	50
C-6	-	50	50
C-7	33.33	33.33	33.33

The main properties of catalysts are summarized in Table 3. Catalysts had similar grain size, in the range between 10 and 109 m. MCM-41 had higher Si/Al ratio than HZSM-5, while its acidity was lower. Activated carbon and MCM-41 catalyst had the highest BET surface area with 859m^2/g and 824m^2/g, respectively.

Table 3. The properties of catalysts

	Activated carbon	MCM-41	HZSM-5
Grain size, m	10-109	15-84	10-79
Si/Al ratio	-	40	25
Acidity, mequiv of NH$_3$/g	-	0.15	0.60
BET area, m^2/g	859	824	298

2.2 Apparatus for waste plastic pyrolysis

A horizontal tubular reactor was used for waste plastic pyrolysis. Waste plastics were ground to particles of 3-4mm before the pyrolysis. A hopper was filled with the plastic in the first section of the electrically heated extruder. The feed rate was 2 kg hourly. The molten waste raw material was directly fed into the reactor stage from the extruder end section, where it was suddenly heated to 530-540°C. Waste HDPE and LDPE were decomposed into smaller hydrocarbon molecules in the reactor. The mixtures of decomposed hydrocarbons were separated into gases, pyrolysis oil and heavy oil in a distillation column connected to the end section of reactor. Gases from the top section of the distillation column were condensed in a water cooled tubular heat exchanger, and then a given ratio of the condensed product (pyrolysis oil) was driven back to the distillation unit top section. Higher efficiency of distillation could be reached by this procedure. The bottom temperature of the separation unit was set 300-350°C. Temperatures were controlled by PID controllers in all of the technology. In case of thermo-catalytic pyrolysis 4 wt% of catalysts were added into the raw material. Products were collected and further analyzed.

2.3 Methods

Gases and pyrolysis oil were analyzed by DANI gas-chromatograph using FID. For gas analysis 50 m x 0.32 mm fused silica column with Al$_2$O$_3$/KCl coating was used and the temperature was constant 40°C during the analysis. In case of pyrolysis oil analysis, 30m x 0.32mm Rtx®-1 column was used. The temperature was elevated from 40°C to 330°C with 15°C/min ramp, and then the temperature was kept constant for 10 minutes.

The concentrations of sulphur and chlorine were measured by a PHILLIPS PW 4025/02 (MiniPal) EDXRF spectrometer, which was fitted with a rhodium-side window tube anode (power of 9W) and Si-PIN detector.

Volatile characteristic of pyrolysis oil was also determined by Engler distillation test to measure the volume of hydrocarbon distilled at given temperatures (ASTM-D 1078).

3. Results and discussion

3.1 Product yields

Product yields are summarized in Figure 2, which shows significant differences among quantities of gases, pyrolysis oil and heavy oil in the presence of catalysts and their mixtures.
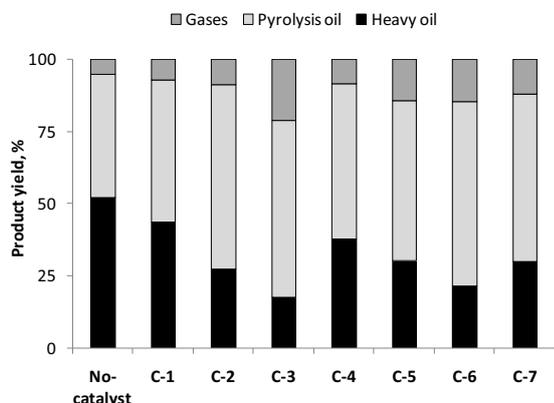

Figure 2. Product yields using different catalysts.

Pyrolysis of waste polymers resulted in 42.7% pyrolysis oil and 5.1% gases without catalyst, which did not change significantly using activated carbon, because the yields of gases and pyrolysis oil were only increased to 7.2% and 49.2%. Results demonstrated that the activated carbon had only a very slight catalytic effect. The increase in yields of volatiles rather could be attributed to the larger heat transmission area, which was due to the high BET surface area of activated carbon.

The increase in volatile yields was well shown using MCM-41 or HZSM-5 catalysts. HZSM-5 significantly increased the yields of gaseous product (21.1%), while 63.9% and 61.4% pyrolsis oil yield was observed using MCM-41 and HZSM-5 catalysts, respectively. Regarding the catalyst mixtures it could be concluded, that the adding of activated carbon only slightly deteriorated the advantageous properties of both MCM-41 and HZSM-5 to the pyrolysis oil yield increasing. Furthermore nearly the highest (63.7%) yield of pyrolysis oil was obtained from waste pyrolysis over 50%/50% MCM-41/HZSM-5 catalysts. MCM-41 catalyst had larger pore size than HZSM-5; therefore it has catalytic activity rather in pyrolysis oil increasing, while HZSM-5 catalyst with smaller pores efficiently could increase the yields of gaseous products.

3.2 Gases

The compositions of gaseous products are summarized in Tables 4/a and 4/b. Based on GC analysis, it is clear that the gaseous fraction contained methane, ethane and ethene, propene and propane, butane and butene, iso-C4, pentene and pentane, iso-C5 hydrocarbons. Without catalyst, the concentrations of before listed components were 13.5%, 29.9%, 22.8%, 28.6%, 3.4% and 0.9%, respectively. It means that mainly the C_2, C_3 and C_4 hydrocarbons represented the most dominant fractions in the gases. Similar result was found in case of catalysts; however notable isomerisation of the main carbon frame was also demonstrated. Especially the iso-C4

concentration could be increased; it was 11.7% and 16.6% using MCM-41 and HZSM-5 catalysts respectively. It is important to remark, that the application of activated carbon did not affect significantly the concentration of components in the gases.

Table 4/a. Composition of gases obtained by waste plastic pyrolysis at 530-540°C, in vol%.

Catalyst	No-catalyst	C-1	C-2	C-3
Methane	13.5	16.9	14.3	22.3
Ethene, Ethane	26.9	25.6	21.7	17.0
Propene, Propane	22.8	20.7	22.8	15.0
Butene, Butane	28.6	28.4	18.2	18.8
iso-C4	3.4	2.8	11.7	16.6
Pentene, Pentane	4.0	4.2	5.1	4.3
iso-C5	0.9	1.5	6.3	6.0

Regarding catalysts mixtures, it could be concluded, that only a slightly less effect of catalysts were found using 50% activated carbon and 50% MCM-41, or 50% activated carbon and 50% HZSM-5, than it was demonstrated in the case of MCM-41 and HZSM-5 catalysts. E.g. the iso-C4 content was 11.1% and 15.4% over 50% activated carbon and 50% MCM-41, or 50% activated carbon and 50% HZSM-5, respectively. Similar result was found regarding iso-C5 compounds, because it was increased from 0.9% (without catalyst) to 1.5% (activated carbon) – 6.3% (MCM-41). Regarding the gaseous fraction the HZSM-5 catalyst had a more significant isomerisation effect, than MCM-41 catalyst, which could be attributed to its BET area. The main frame of instable molecule fragments could be isomerized in the propagation reaction step resulting in high concentration of branched molecules.
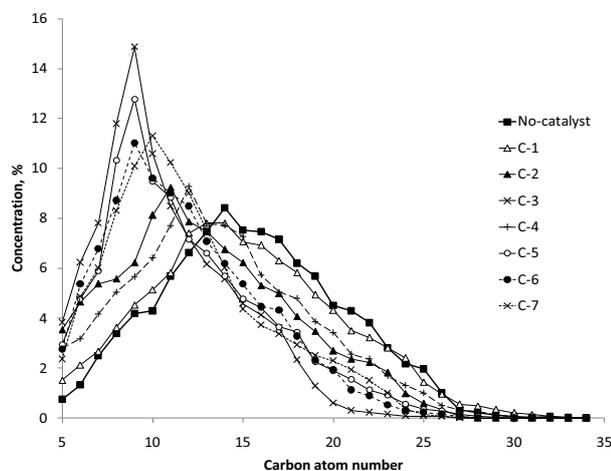
Table 4/b. Composition of gases obtained by waste plastic pyrolysis at 530-540°C, in vol%. (cont.)

Catalyst	C-4	C-5	C-6	C-7
Methane	13.6	19.8	16.1	13.7
Ethene, Ethane	20.8	21.0	19.6	23.1
Propene, Propane	19.6	16.4	20.6	21.3
Butene, Butane	25.6	21.0	18.8	17.0
iso-C4	11.1	15.4	13.8	13.0
Pentene, Pentane	3.8	3.7	4.9	6.3
iso-C5	5.5	2.7	6.2	5.6

3.3 Pyrolysis oil

Pyrolysis oils were analyzed by gas-chromatography to know more about their composition. Based on the results it was concluded, that C_5-C_{34} hydrocarbons were represented in the pyrolysis oils. The composition of pyrolysis oils as function of carbon atoms are shown in Figure 3. Owing to the structure of HDPE and LDPE, two well separated peaks were appeared in gas chromatograms belong to each carbon atoms. The statistical distribution of compounds concentration as function of carbon atoms is also characteristic of

polyethylene degradation. The structure of polyethylene is relative stable, because it contains mainly secondary carbon atoms, therefore the distortion of the electron cloud and the parts with structural faults are relatively low.
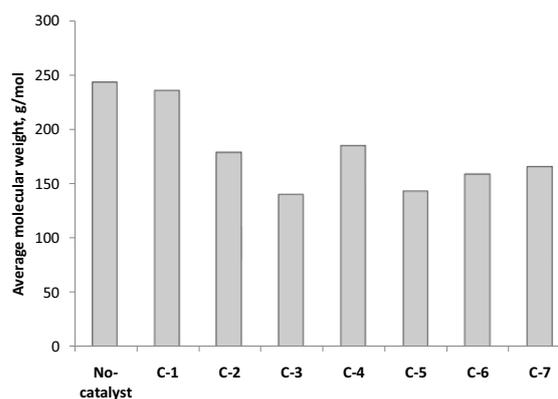

Figure 3. Distribution of compounds in pyrolysis oil as function of carbon atoms.

Regarding thermal pyrolysis without catalyst, compounds with carbon atoms of 14 had the highest concentration (8.43%). The application of activated carbon did not change notably the distribution curve, because e.g. the maximum point also belongs to carbon atoms of 14 (7.82%). However both MCM-41 and HZSM-5 catalysts had a significant effect on the product distribution: e.g. the maximum points were shifted to carbon atoms of 11 (9.02%) and 9 (14.88%) using MCM-41 and HZSM-5 catalysts, respectively. Regarding HZSM-5 catalyst, the high aromatic portion of pyrolysis oil was the cause for the high value of C_9 compounds.
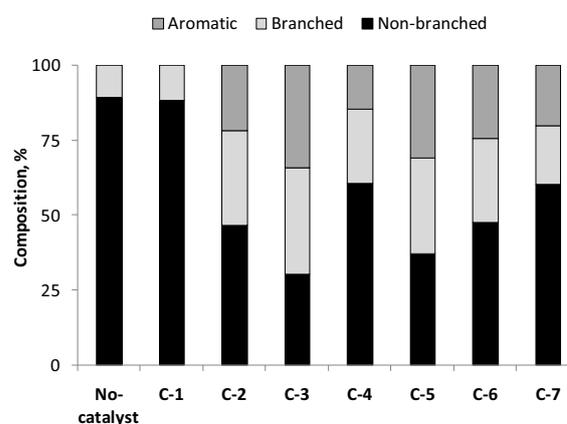
Significant increases in compounds with shorter chain ($<C_{14}$) was found using both MCM-41 and HZSM-5 catalysts, while the concentration of larger molecules ($>C_{14}$) decreased in those cases. That was the cause for the average molecular weight decreasing using both MCM-41 and HZSM-5 catalysts (Figure 4). As the data show the average molecular weight of pyrolysis oil was 242g/mol without catalyst, while it could be significantly decreased by both MCM-41 (178g/mol) and HZSM-5 (139g/mol) catalysts, while it could be only slightly decreased by activated carbon (235g/mol). Regarding the mixtures of catalysts, the 50%/50% HZSM-5 and activated carbon mixture have shown also a significant effect resulting in molecular weight decrease (142g/mol).

Figure 5 shows the composition of pyrolysis oils, which contain non-branched, branched alkanes and aromatic hydrocarbons. Results well demonstrate the isomerisation and aromatization effect of catalysts. E.g. pyrolysis oil contained 89.2% non-branched and 10.8% branched hydrocarbons without catalyst. The concentration of branched hydrocarbon increased to 31.9% and 35.5% by the using of MCM-41 and HZSM-5 catalysts.

Figure 4. Calculated average molecular weights of pyrolysis oil.

Regarding aromatics, the HZSM-5 catalyst showed the highest activity, because the concentration of aromatic hydrocarbons reached 34.1% using HZSM-5. This result was confirmed by earlier work, when the high activity of HZSM-5 catalyst to the aromatization reactions was concluded [4,10,11,16]. It is also clear, that activated carbon could not increase the aromatic content in pyrolysis oil. MCM-41 catalyst rather had an effect to the isomerisation reactions, which resulted in an elevated concentration of branched compounds. Regarding the application of catalyst mixtures, aromatization and isomerisation effect was found in the presence of HZSM-5 catalyst.

Figure 5. Composition of pyrolysis oils.

The composition of aromatics in pyrolysis oils are summarized in Figure 6. Pyrolysis oils contain benzene, toluene, ethyl-benzene, styrene, xylenes, isopropyl-benzene, a-methyl styrene, cumene and other aromatic hydrocarbons. According to the results, over HZSM-5 catalyst (C-3) significant values of ethyl-benzene, styrene and xylenes were measured; 17.12%, 19.67% and 16.33%, respectively. MCM-41 catalyst (C-2) has also aromatization function; because the total aromatic concentration was 21.6% using that catalyst.
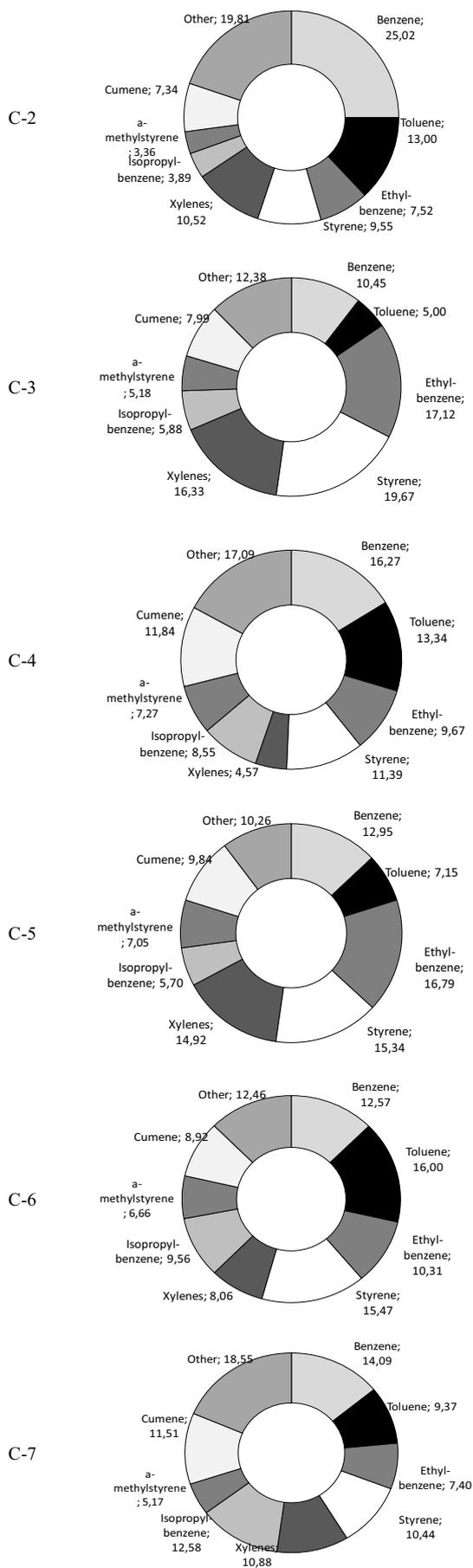
Figure 6. Composition of aromatics in pyrolysis oils.

It is an important observation, that the MCM-41 catalyst increases the concentration of benzene and toluene (25.05% and 13.00%), while that of ethyl-benzene, styrene and xylenes were lower (7.52%, 9.55% and 10.52%). This phenomenon could be attributed to the larger pore size and BET surface area of the MCM-41 catalyst, because those properties are favoured for the hydrogen transfer reactions and aromatization. That is why the aromatic side chain of aromatics could be further cracked which resulted in smaller molecules with shorter side chain. Furthermore also further decomposition of side chain if aromatics were found in the case of catalyst mixtures using MCM-41 catalyst (C-4, C-6).

As it was demonstrated in Table 1, the raw material contained 0.05% chlorine and 0.02% sulphur, which should be transformed into compounds, which appeared in the pyrolysis oil fractions. Figure 7 demonstrates the concentrations of chlorine and sulphur in the pyrolysis oils. Without catalysts 257ppm chlorine and 125ppm sulphur were measured, which could be decreased using catalysts. Regarding chlorine, the MCM-41 catalyst had the highest activity in decreasing, because the Cl concentration was122ppm. Activated carbon had shown only a slight effect to the volatile product increasing and modifying the pyrolysis oil composition; however it has a significant effect in the case of sulphur content. Pyrolysis oil obtained by the degradation over activated carbon contained only 31ppm sulphur, which is a dominant decrease. On the other hand the two other catalysts only slightly could decrease the S content; 79ppm and 81ppm using MCM-41 and HZSM-5 catalysts. Presumably the large BET surface area was the cause for both Cl and S decreasing in the case of MCM-41 and activated carbon. According to Table 1, activated carbon had $859m^2/g$, while MCM-41 catalyst $824m^2/g$ BET surface area. Therefore possibly physical sorption was the cause for both Cl and S decreasing.
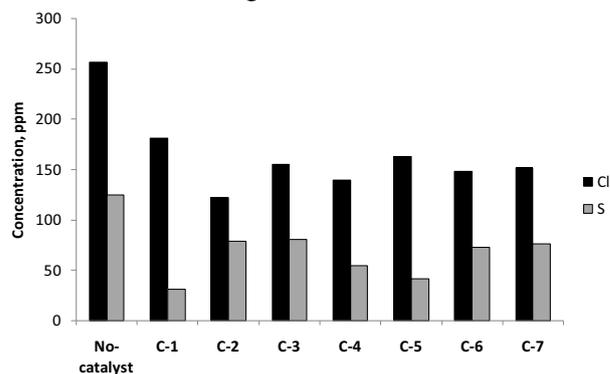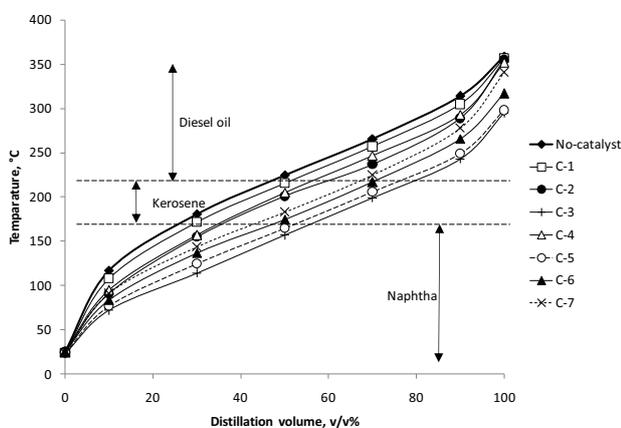

Figure 7. Chlorine and sulphur content of pyrolysis oils.

Volatile characteristic of pyrolysis oils was also followed by Engler distillation test. Figure 8 summarizes the distillation curves. The data well demonstrates, that pyrolysis oil obtained by catalyst free experiment contain nearly half of diesel oil range and 25%-25% kerosene and naphtha range hydrocarbons. In the presence of catalysts (especially HZSM-5) the portions of naphtha-like and kerosene-like hydrocarbons were higher, e.g. using HZSM-5 they were nearly 60% and 25%, respectively. It

was confirmed by earlier work, because it was demonstrated that owing to the small pore size, the HZSM-5 catalyst results especially hydrocarbons in naphtha boiling point range (Bp below 180°C) [10,11,16].

Figure 8. Engler distillation curves of pyrolysis oils.

Activated carbon had only a slight effect on the boiling point range, because the temperatures belong to specific distillation volumes, was only slightly lower than that without catalyst. MCM-41 catalyst could also slightly affect the boiling points, but its effect was most notable than in the case of activated carbon. Regarding catalyst mixtures, it was concluded, that especially the HZSM-5 containing mixtures (C-5, C-6 and C-7) could significantly increase the yield of naphtha or kerosene and decrease the yield of diesel oil.

4 Conclusion

The yields of gaseous product could be increased especially by HZSM-5 catalyst, while the yield of pyrolysis oil was increased both by HZSM-5 and MCM-41 catalyts. Activated carbon had only a slight effect on the yields and hydrocarbons in the product. Significant isomerization effect was demonstrated both in the gases and pyrolysis oils using HZSM-5 catalyst and HZSM-5 catalyst containing catalyst mixtures. MCM-41 and HZSM-5 catalyst had also an aromatization effect, and the MCM-41 catalyst with larger pore size had activity in the formation of benzene and toluene. The most benefit of activated carbon was the enormous decrease in sulphur content, while the chlorine could be decreased especially by MCM-41 catalyst, which was attributed to its large pore surface area. Volatile characteristic of pyrolysis oils

demonstrated the increase of the naphtha-like fraction content of pyrolysis oil using HZSM-5 catalyst.

References

1. H. T. Lin, M. S. Huang, J. W. Luo, L. H. Lin, C. M. Lee, and K. L. Ou, Fuel Processing Technology, **91**, 1355 (2010)
2. E. V. Antonakou, K. G. Kalogiannis, S. D. Stefanidis, S. A. Karakoulia, K. S. Triantafyllidis, A. A. Lappas, and D. S. Achilias, Polymer Degradation and Stability, **110**, 482 (2014)
3. Y. H. Lin, M. H. Yang, Journal of Molecular Catalysis A: Chemical, **231**, 113 (2005)
4. G. Elordi, M. Olazar, M. Artetxe, P. Castano, and J. Bilbao, Applied Catalysis A: General, 415-416, 89-95 (2012)
5. Y. H. Lin, H. Y. Yen, Polymer Degradation and Stability, **89**, 101 (2005)
6. W. C. Huang, M. S. Huang, C. F. Huang, C. C Chen, K. L. Ou, Fuel, **89**, 2305 (2010)
7. S. S. Kima, S. Kim, Chemical Engineering Journal, **98**, 53 (2004)
8. N. S. Akpanudoh, K. Gobin, G. Manos, Journal of Molecular Catalysis A: Chemical, **235**, 67 (2005)
9. X. Yang, L. Sun, J. Xiang, S. Hu, and S. Su, *Waste Management* 33 (2013), p. 462
10. J. F. Mastral, C. Berrueco, M. Gea, J. Ceamanos, Polymer Degradation and Stability, **91**, 3330 (2006)
11. X. Zhang, H. Lei, G. Yadavalli, L. Zhu, Y. Wei, Y. Liu, Fuel, **144**, 33 (2015)
12. J. Bozi, M. Blazsó, Journal of Analytical and Applied Pyrolysis, **97**, 189 (2012)
13. W. L. Fanchiang, Y. C. Lin, Applied Catalysis A: General, 419-420, 419 (2012)
14. R. A. García, D. P. Serrano, D. Otero, Journal of Analytical and Applied Pyrolysis, **74**, 379 (2005)
15. M. R. Jan, J. Shah, H. Gulab, Fuel, **105**, 595 (2013)
16. A. López, I. Marco, B. M. Caballero, M. F. Laresgoiti, A. Adrados, and A. Aranzabal, Applied Catalysis B: Environmental, **104**, 211 (2011)
17. K. H. Lee, Polymer Degradation and Stability, **93**, 1284 (2008)