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Environmental Saving Disposal of Contaminated Plastic Wastes by Their Pyrolysis

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The pyrolysis of different contaminated plastic wastes has been investigated in a 2.0 dm^3 autoclave at 450 and 500°C under nitrogen. Results show considerable differences in yields and quality of products applying different pre-treatings and parameters. The properties of the products were determined by standardized methods, gas chromatography and FTIR. The gaseous products of the pyrolysis were distributed in the range of C_1-C_5 and consisted of different inorganic compounds. Liquids can be characterized as hydrocarbons in the carbon atom range of 5-34, with mainly aliphatic compounds. In the liquid products were different heteroatom containing organic compounds, too. The contaminant level of products considerably can be decreased by washing of the raw materials while the parameters of pyrolysis have only negligible effect on this.

1. Introduction

Huge part of the municipal plastic wastes is from packing sector, which are basically commodity plastics. By pyrolysis they are able to convert into liquid hydrocarbons with high yields and moderate quality. The problem is that plastic wastes quite often contain solid or liquid contaminants. In case of pyrolysis contaminants also present problems because they appear in the products, too (N. Miskolczi, 2008). The degradation mechanism of plastic wastes containing heteroatoms (such as PVC, ABS, etc.) and the effect of these materials on the yields and product quality were investigated by researchers (A. López, 2010, M.N. Siddiqui, 2009). In an experimental study different catalysts were placed in a fixed bed reactor with batch operation, in which vapour phase contact was ensured between the catalysts and the products (M. Brebu, 2004). Results showed that the efficiency of the catalysts depends strongly on the composition of the raw material. In another work two steps pyrolysis of plastic wastes was carried out (T. Bhaskar, 2007). In the first step, a small amount of liquid product was accumulated with a significant contaminant level at lower temperatures. In the second step the temperature was raised at the temperature requirement of the pyrolysis. In that step high amount of quite clear liquid product was reached. Neither with catalysts nor by controlled pyrolysis was able to significantly decrease the heteroatom containing substances from the pyrolysis oil.
The goal of our work was the investigation of contaminated plastic waste pyrolysis in a batch system at 450 and 500°C. The raw materials of our work were pre-treated. The

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effect of washing of the raw materials on the yields and particularly the product qualities were investigated.

2. Material and Methods

2.1 Raw materials

To investigate the contaminants in products three contaminated plastic wastes were used: engine oil container, herbicide and detergent flasks. The first two were obtained from TERSZOL Co. and the last one from Rekultív Ltd from household collection. According to FTIR analysis the main parts of the waste polymers was HDPE (Table 1). (Acronyms: HDPE - High Density Polyethylene, LDPE – Low Density Polyethylene, PP – Polypropylene, PVC – Polyvinyl-chloride.)

Table 1: The composition of raw materials, (%)

	HDPE	LDPE	PP	PVC	Other	Water	Paper	Oil	Herbicide	Detergent
Off-grade HDPE	100.0	-	-	-	-	-	-	-	-	-
Motor oil flask	81.6	-	2.5	1.1	-	4.6	-	10.2	-	-
Herbicide flask	67.9	-	26.1	-	2.7	-	-	-	3.3	-
Detergent flask	56.6	1.0	38.2	0.9	0.6	-	0.8	-	-	1.8

To determine the effect of the contaminants in the raw materials granulated off grade HDPE from TVK Co was also pyrolyzed. In the case of herbicide and detergent flasks the washing procedure occurred by distilled water, while in the case of the motor oil flasks the solvent was light naphtha. In the first case distilled water was chosen because the herbicide and detergent contamination are polar so a polar solvent was used. In the case of motor oil flask light naphtha was chosen because a non-polar solvent was needed to remove the oil contamination.

2.2 Pyrolysis process

The process was carried out under nitrogen at two different temperatures (450°C and 500°C) in an electrically heated fixed bed reactor with 2.0 dm^3 volume (Figure 1).

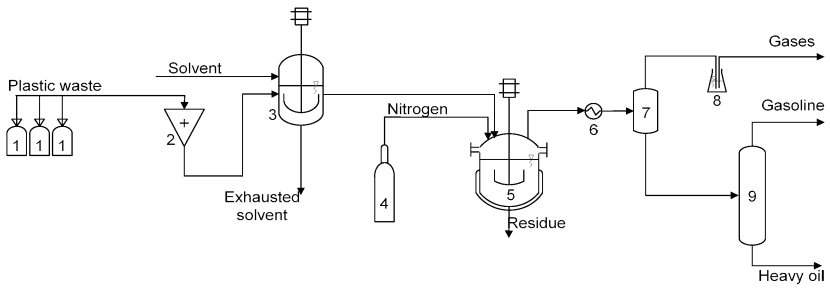

Figure 1: The layout of the process, (1, raw material; 2, shredder and grinder; 3, washer; 4, nitrogen bottle; 5, reactor; 6, condenser; 7, gas-liquid separator; 8, water trap; 9, distillation column).

The raw materials should be placed tight into the reactor to provide adequate heat transfer therefore they were shredded and milled into particles up to 3 mm in main dimension. Then one part of them was washed in a mixed vessel. 2,5 l of solvent was added to 1 kg plastic waste in a 5 l volume mixed vessel. The washing procedure took 30 minute long. The rest of raw material was not washed. After the above mentioned pre-treating, 400 g of wastes were fed into the reactor. The pre-heating of the reactor occurred by 15 °C/min. After that, the pyrolysis process was taken 2 hours long. From the reactor volatile products were driven trough a condenser and they got into a gas-liquid separator. The non-condensable gases got in a water trap where the inorganic substances were trapped. The condensable volatile products were separated in a distillation column into gasoline and heavy oil. After the pyrolysis the residue was taken off from the bottom of the reactor. Measuring of temperature occurred by thermocouple.

2.3 Analysis of pyrolysis products

DANI gas-chromatograph fitted with a 30 m x 0.32 mm Restek-Q column was used for hydrocarbon analysis of gas products. A DANI gas-chromatograph fitted with a 30 m x 0.53 mm Rtx-11column was used for hydrocarbon analysis of pyrolytic oils.

The composition of the raw material was analyzed by a TENSOR 27 type Fourier transformed infrared spectrometer in the 4000–400 cm^{-1} wave number ranges.

For chlorine determination a Mitsubishi TOX-100 type instrument was used. The temperature was 900 °C, and argon was used as inert gas.

Determination of heating value, melting point, nitrogen and sulphur content of fractions were performed by using standardized methods: MSZ EN ISO 12185:1996, MSZ 24000-5:1978, MSZ 3252:1973, ASTMD 6428 99 and ASTMD 6366 99, respectively.

3. Results and Discussion

3.1. Product yields

Yields are shown in Figures 2 and 3. Due to the lower thermal stability of the C-C bonds at higher temperature, the yields of the volatile products were significantly less in case of pyrolysis at 450°C then those of at 500°C.

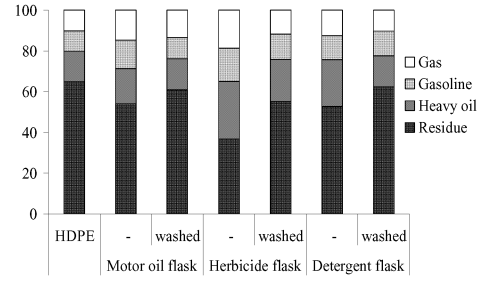

Figure 2: Product yields at 450°C

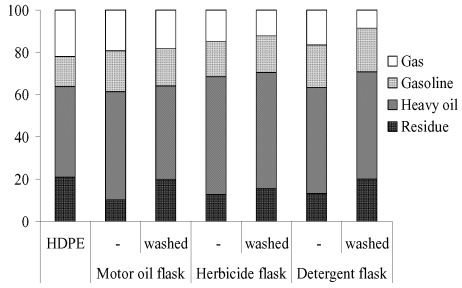

Figure 3.: Product yields at 500°C

The amounts of residues have changed between 36.8 and 64.8 wt% at 450°C, while that of between 10.2 and 21.0 wt% at 500°C. It was found that washing has also notable effect on product yields. Volatile product yields obtained from degradation of contami-

nated plastics were higher than those of from original or not washed raw material pyrolysis. The least volatile products could be reached from the pyrolysis of the original raw material. The reason for that could be explained by following: contaminants should be initiating the degradation of the polymer via free radical mechanism. The highest yields of volatile products were found from the not washed herbicide flasks pyrolysis (18.8% gas 16.3% gasoline and 28.1% heavy oil) at 500°C and not washed motor oil flasks pyrolysis (19.3% gas, 19.3% gasoline and 51.3% heavy oil) at 450°C.

3.1 Gases

Compositions of gas products from pyrolysis are shown in Tables 2 and 3. All the gaseous products were in the carbon number range of C_1-C_5. Because of the structure of HDPE, the carbon number distributions show two maximums at C_2 and C_4. Owing to the lower thermal stability of C-C bonds at higher temperature, less C_4 hydrocarbons were observed in the pyrolysis gases at 500°C. It is also clear that washing procedure could not affect the hydrocarbon composition of gaseous fractions. Whereas the originality of raw materials had affected the gas composition. Pyrolysis of detergent flasks with high PP content resulted in C_3 reach gases. Based on experimental data, the calculated heating values of the gases have changed between 46.3 MJ/kg and 46.9 MJ/kg.

Table 2: Composition of gases obtained from pyrolysis of not washed raw materials

Carbon number	Original raw material		Motor oil flasks		Herbicide flasks		Detergent flasks	
	450°C	500°C	450°C	500°C	450°C	500°C	450°C	500°C
C1	5.3	6.6	4.3	4.4	4.9	5.4	3.9	5.8
C2	29.6	29.0	30.7	28.5	27.6	29.9	23.0	24.4
C3	6.1	5.7	11.2	7.6	9.2	9.5	17.5	28.1
C4	31.3	32.8	30.0	31.8	32.3	31.5	37.2	24.5
C5	27.7	25.9	23.8	27.7	26.0	23.7	18.4	17.2

Table 3: Composition of gases obtained from pyrolysis of washed raw materials

Carbon number	Motor oil flasks		Herbicide flasks		Detergent flasks	
	450°C	500°C	450°C	500°C	450°C	500°C
C1	3.6	3.9	4.4	6.3	4.4	5.3
C2	29.4	30.3	28.0	28.8	22.3	24.3
C3	10.6	11.6	12.1	13.0	29.6	28.7
C4	29.9	27.8	31.3	29.8	23.4	21.2
C5	26.5	26.4	24.2	22.1	18.3	18.5

3.2 Liquid products

Two different liquid products were obtained in the pyrolysis process: gasoline and heavy oil. The compositions of gasoline are shown in Figures 4 and 5 and the compositions of heavy oils are in Figures 6 and 7. Gasoline contains n-paraffin, n-olefin, branched hydrocarbons and aromatic compounds in the carbon number range of 5-17. Aromatic compounds were in the form of benzene, toluene, ethyl-benzene, xylenes, styrene, cumene, n-propylbenzene and p-cymene. Heavy oil consisted of hydrocarbons from C_9 to C_{34}, but they did not contain aromatics. It was found that washing did not have effect on the composition of the liquid products, but some differences were found

among products obtained from different raw materials. The PP reach detergent flasks have given high concentrations of branched components in all cases. For what the structure of PP is blamed. As the results show temperature has also deteriorated the composition of the products. E.g. in the case of gasoline the amount of n-paraffins decreased by 17-27% if the temperature was increased from 450°C to 500°C.

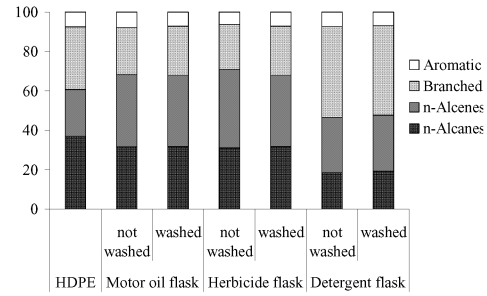

Figure 4: Gasoline at 450°C

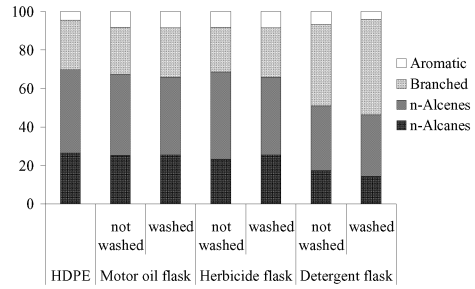

Figure 5.:Gasoline at 500°C

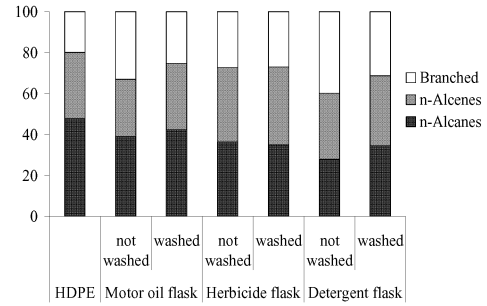

Figure 6: Heavy oil at 450°C

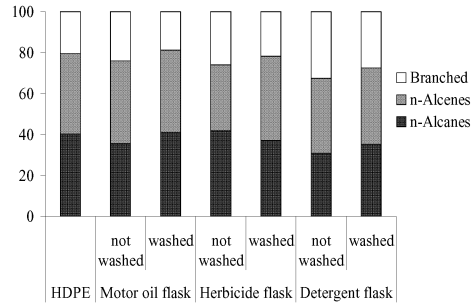

Figure 7: Heavy oil at 500°C

3.3 Residue

Different residues could be obtained at the two different temperatures: they were waxy-like at 450°C and solid carbon-like at 500°C. The residues had melting points between 83 and 88°C and heating values between 39.3 and 40.6 MJ/kg. The chlorine content of the residues had also analyzed, what was changed between 0 ppm (original HDPE) and 1300 ppm (not washed detergent flask at 450°C). The chlorine content could be decreased only by washing of the raw materials.

3.4 Contaminant level of products

Contaminant level of pyrolysis products obtained from not washed and washed raw materials are shown in Table 4. Due to the presence of herbicides, the contaminants in products obtained from non-washed herbicide flasks were the highest, especially in case of nitrogen. Generally heavy oils had the highest chlorine and sulphur content, but the highest nitrogen content was observed in the case of the gasoline. The effect of washing was very significant in case of all products: chlorine, sulphur and nitrogen content of the products could be decreased by this way. Washing decreased the chlorine content approximately by 50%, the sulphur content by 40-75% and the nitrogen content by 50-75%. Glancing the temperature effect, it needs to remark, that the level of impurities were significantly lower in case of gasoline and heavy oil at higher temperature.

Table 4: Contaminants in pyrolysis products, (ppm)

		Original		Motor oil flask				Herbicide flask				Detergent flask			
		450°C	500°C	450°C		500°C		450°C		500°C		450°C		500°C	
Washing				no	yes	no	yes	no	yes	no	yes	no	yes	no	yes
	Cl	0	0	21	10	23	12	58	37	57	39	26	18	25	14
Gas	S	1	1	9	5	3	2	20	8	18	13	2	1	3	1
	N	2	2	33	31	53	50	700	690	682	689	87	47	222	85
	Cl	0	0	22	15	18	14	127	84	108	86	46	0	43	0
Gasoline	S	3	2	321	89	181	85	108	91	104	80	57	37	59	33
	N	3	3	355	110	318	127	3491	1247	3469	1009	932	505	1148	612
	Cl	0	0	43	19	67	26	267	225	281	240	157	40	163	43
Heavy oil	S	1	2	469	157	248	148	151	134	203	105	96	46	82	58
	N	0	1	847	403	132	56	2366	1843	1176	1004	491	119	175	93

4. Conclusion

In this work the effect of the washing of different raw materials on the pyrolysis product yields, composition and contaminant level was investigated. It was found that washing decreased the volatile product yields but the amount of the heteroatom containing substances in the pyrolysis products, too. Washing has not affected the carbon number distribution of the products. The quantity of contaminants decreased significantly but they could not be fully removed this way.

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