High Energy Containing Fractions from Plastic Wastes by Their Chemical Recycling

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Summary: Different conventional fractions of oil industry were produced by the cracking of real plastic wastes under mild conditions in a horizontal tube reactor. The influence of the raw material (HDPE, PP, HDPE/PS and HDPE/PP/PS/PA/PVC) on the characteristic of the cracked products was studied. It was found that waste polymers could be converted into valuable lighter fractions (gas, naphtha, middle distillates or light oil) with yields of 30–60% depending on the applied cracking parameters. The gas and liquid products had significant content of unsaturated hydrocarbons, mainly α-olefins, but their types (vinyl or vinilydene) were considerably affected by the composition of raw materials. Lighter naphtha-like fractions had high octane numbers ($83 < \text{RON} < 94$), while high cetane numbers (>68) in case of middle distillates. Products from suitable raw materials had very low sulphur, nitrogen and hetroatom content (<10 ppm) or products are sulphur and nitrogen free. Due to the high energy content of products there is a good chance of energetic utilization, but the possibility of their application is mainly depending on the composition of feed plastics.

Keywords: cracking; energy containing fractions; waste plastics

Introduction

The suitable treatment of plastic wastes is one of the key questions of the waste management. The problem of waste materials is important from energetic, environmental, humanbiologic and political aspects. Modern societies and the increase rate of their GDPs are unimaginable without plastics. In 2005 the plastic consumption was about 250 Mt worldwide, and it is growing by 4–8% annually.[1–4] The main motive power of researches is the increasing energy demand. As it well known the global reserves of fossil fuels are limited but plastic wastes have high so called hidden energy content, therefore there are efforts to convert wastes into valuable feed stocks. On the other hand some legal measures stimulate the higher rate of recycling (e.g. in the member countries of the EU recycle of 30% of plastic wastes is aimed at in 2010). Recently the amount of recycled waste plastics is less than 5–10%. According to forecasts the problem of plastics and other household and industrial wastes are cannot be solved by the other commonly used routes of utilizations (such as landfilling and incineration).[2,4,5–8]

One prospective way of the solutions of problems is the chemical recycling of waste plastics, which is virtually a thermal or thermo-catalytic initiated degradation. In cracking reactions C–C bonds of polymers are cracked resulting in lighter but considerably more valuable fractions of hydrocarbons. According to publications several researchers investigate the route of different degradation of plastic wastes to valuable products furthermore several methods have been suggested for solving of this problem.[5,6,8,9,12–17] Usually batch experiments were carried out in a small, laboratory sizes using one or two types of polymers, which were clean and not waste polymers. However batch system has numerous disadvantages and problems when researchers ought to

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make its size increasing therefore in this case the continuous system is favoured. Both yields and chemical properties of products can be modified with catalysts. In batch reactions catalysts can be added easily, but in a continuous system it might be problematical, because e.g. the maintenance of fluid beds depends on the changing properties of wastes. A further problem is the handling of the deactivated catalysts, what have to be separated from the residue and reactivated. To eliminate these problems rather fluidized reactors are used, but they operating costs is high. Therefore more researchers investigate the application of tubular reactors with or without catalysts.[11,14–20] Further utilization possibilities of products obtained by cracking reactions are a key point of the technology. One possibility of their utilization is the energetic (e.g. feed stock-like) application or mixing in fuels as blending component. From these possibilities mainly the fuel-like application was investigated. End fractions of cracking have high olefin content therefore they are to be saturated with hydrogen, or hydroisomerized before their application. These steps result in a high quality synthetic diesel fuel, with high cetane number, which are theoretically free from sulphur, nitrogen and metals.[11,15,17,21] According to preliminary calculations the cost of refineries could be considerably decreased with recycled wastes. Big oil companies (e.g. TEXACO, BP, Shell) developed plastic waste recycling processes, and numerous other laboratories also worked on solving the problem.[10,11,14,18,19]

The goal of our experimental work was the investigation of the cracking behaviour of a different plastic wastes (HDPE, PP, HDPE/PS and HDPE/PP/PS/PA/PVC) in a horizontal tube reactor. The effects of cracking parameters (especially the composition of feed polymer) on the product properties were investigated.

Experimental

Raw Materials

Commercial waste plastics (HDPE, LDPE, PP, PS, PA and PVC) were used as raw materials from different area of human life (from packaging industry to agriculture). Each polymer contained sulphur and nitrogen from additives (e.g. sulphur containing anti-flame or antioxidant additives, etc). The main properties of raw materials are shown in Table 1.

In the selection of waste polymer the main consideration was the possibility of collection and the purity of products. Therefore fundamentally polyolefins and polystyrene was chosen, seeing that these plastics represent the ruling part (80–85%) of polymer wastes. The difference in proportion of polyolefins and polystyrene inside the used and waste plastics is a consequence of the costumer and user customs. Sample 1 (S-1) and 2 (S-2) contained only HDPE and PP, while Sample 3 (S-3) was the mixture of 90% HDPE and 10% PS. The Sample 4 (S-4) contained 44% HDPE, 44% PP, 10% PS and 1-1% polyamide and poly-vinyl-chloride too, because with this last composition we ought to model the decomposition of municipal plastic waste (MPW).

Table 1.
The main properties of cracked waste polymers.

Properties	HDPE	PP	PS	PA 6.6	PVC
Origin	Agricultural	Service industry	Packaging industry	Autoelectronic industry	Electronic industry
MFI, g/10 min.	0.538	0.367	1.040	1.129	0.374
Density, g/cm^3	0.962	0.909	1.045	1.129	1.076
Ash content, %	0.89	0.71	0.08	1.32	0.57
Cl, %	n.d.	n.d.	n.d.	n.d.	55.8
S, ppm	12.6	14.8	16.2	n.d.	17.1
N, ppm (%)	6.1	8.5	7.3	12.6(1)	n.d.

(1) in %.

Cracking Apparatus

The cracking equipment consisted of three main parts: an extruder, a tube reactor and a separation section, which is schematically shown in Figure 1. The waste polymers with suitable grain size were fed by an extruder (where the polymer was preheated up to 250–280 °C) then the preheated polymer was driven from the extruder into the reactor. Inside the reactor the polymers were melted and their carbon chain cracked into low molecular fragments. The reactor wall temperature was 500 °C and residence time of 23 min was used. In preliminary separator the formed hydrocarbons were separated into volatile products and heavy oil. The volatile fraction was cooled with water and the non condensed hydrocarbons were separated by atmospheric and vacuum distillations. Three other products were formed by distillations: naphtha, middle distillates and light oil. These products were further analysed. Non-condensable gases were passed through a flow meter and then flared.

Analysis of Products

Each fraction was analyzed using the following standardized test methods: liquid density measurement (MSZ EN ISO 12185), determination of distillation curve (ASTM-D 1078), of sulphur and nitrogen content of naphtha and middle distillate fractions (ASTMD 6428 99 and ASTMD 6366 99), of flash point (ISO 2719:2002 and MSZ 15967:1979), of CFPP (MSZ EN 116:1999), of kinematic viscosity (MSZ ISO 3105:1998), corrosion test (MSZ EN ISO2160:2000). Gases were analyzed using a Carlo-Erba Vega Series GC 6000 gas chromatograph provided with a 50 m × 0.32 mm fused silica column with Al_2O_3/KCl coating, at 40 °C. Liquid products were analyzed by gas chromatographs using a TRACE GC gas chromatograph with a flame ionization detector. It was provided with a 30 m × 0.32 mm Rtx®-1 (Crossbond® 100% Dimethylpolysiloxane) column. The olefin content of liquids was determined with infrared technique by a TENSOR 27 type Fourier transformed infrared spectrometer (resolution: 2 cm^{-1}, illumination: SiC Globar light, monocromator: Littrow prism, detector: RT-DLaTGS (Deutero L-α-Alanine Triglycin-Sulphate) type detector with KBr window) in the 400-4000 cm^{-1} wave number range. The concentration of sulphur and chlorine in light and heavy oils were followed with energy dispersive X-ray fluorescent technique by a PHILLIPS PW 4025/02 instrument, while Research and Motor Octane Numbers and Cetane Number were determined from their infrared spectra with a ZX-101c type instrument.

Results and discussion

Yields

In our experimental work the cracking behaviour of real plastic wastes was investi-

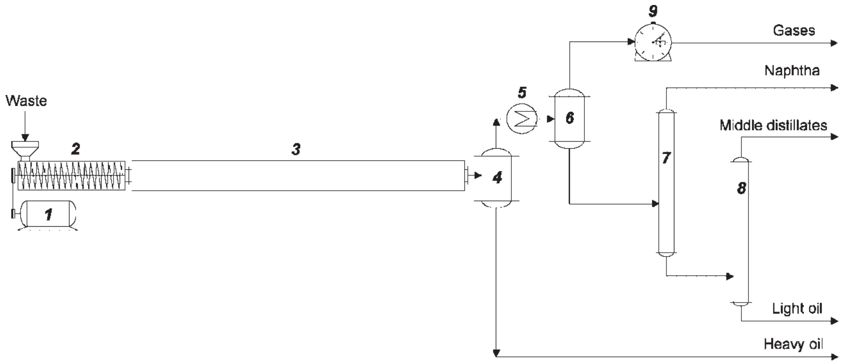

Figure 1.

Cracking apparatus: 1. Motor, 2. Extruder, 3. Reactor, 4. Preliminary separator, 5. Condenser, 6. Separator, 7. Atmospheric distillation, 8. Vacuum distillation, 9. Gas-flow meter.

gated. The yield of products is a very important view of the technology because of its capable for life. The highest yield of valuable volatile product is better prospect to the economical working. It is known that the yield of valuable products is increasable with temperature and residence time but the higher the temperature and longer the residence time, the greater the possibility of cracking and other unfavourable reactions.[17,21] Therefore moderate, mild condition (500 °C) was chosen. It was found that the composition of feed polymers had a significant effect on the yields of lighter fraction obtained in the cracking process, which could be caused by the differences in the thermal stability of polymer chains. The highest conversion was observed in the cracking of S-4 sample, which contained HDPE, PP, PS, PA and PVC. Fig. 2 shows the yields of products formed in cracking reactions. The considerably differences in the product yields was the consequence of the variance in the activation energy of polymer cracking. As it well known the activation energy of destruction is considerably lower in case of PP and PS than that of HDPE or PA. Furthermore the PVC cracked in more steps and the first step has very low activation energy. According to Fig. 2 HDPE was convertible into valuable volatile products with the lowest yield. It is very interesting phenomena that there is much difference in conversion of cracking between S-2 or S-3 and S-4 samples. S-2 sample was only PP, while S-4 the mixture of HDPE, LDPE, PP, PS, PA and PVC.

As data show there was not notable difference observed in the respect of conversion of S-2 and S-3 but the overyield in case of S-4 sample was more than it was expected from its composition. This phenomena is shows a possible interaction between preliminary products of cracking of different plastics. Inside the used plastics the lowest activation energy of cracking was the first step of PVC destruction. According to results presumably these radical fragments from preliminary degradation could be reacted with other still not degraded molecules and initiated their cracking. Similar phenomenon was observed by R. Miranda et al. who investigated interactions among the cracking products of plastic wastes during thermal destruction.[22]

Products

The degraded hydrocarbons formed in the cracking reactions were separated with vacuum distillation following atmospheric distillation into different products: gases (G), naphtha (N), middle distillates (MD), light (LO) and heavy oils (HO). These fractions were analyzed by gas chromatograph and qualify as conventional products of refinery by standardized methods.

The composition of gases in case of HDPE degradation contained mostly C_2, and C_4 hydrocarbons, while that of C_3 in case of PP cracking, which was the consequence of structure of polyethylenes and polypropylene because the thermal degradation of polymers results mainly in monomers and oligomers. S-3 and S-4 had

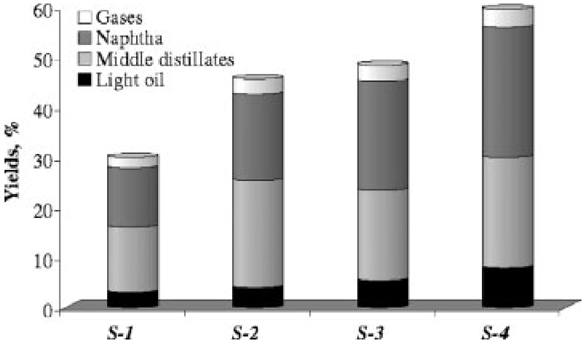

Figure 2.
The yields of volatile products.

approximately same content of aliphatic olefins and paraffins from methane to butane. Calculated heating value of gases were 46-47 MJ/kg, which were quite high to use of gases in energy generation (e.g. to provide the heat requirement of cracking with gas products of degradation).

The carbon number distribution of naphtha and middle distillates are shown in Figures 3 and 4. These columns show considerably differences among different fractions of cracking.

According to the results of gas-chromatography analysis the naphtha contained C_5–C_{17} hydrocarbons. The carbon chain distribution of products obtained by HDPE cracking resulted Gauss-like distribution while in case of PP the triple sequence could be observed in case of aliphatic compounds (C_6, C_9, C_{12} hydrocarbons have been present in the highest concentration) due to the chemical structure of polymer chains. Polypropylene had tertiary carbon atoms in every second member of main chain. Due to the lower thermal stability of tertiary carbon atoms the carbon chain was cracked in these points, resulted that triple sequence. The carbon atom distribution of lighter products in case of S-3 and S-4 shows a large peak at carbon number of 8, which was the appearance of styrene and ethyl-benzene from polystyrene. The hydrocarbon distribution of each fraction is shown in Table 2. As data in table shows the hydrocarbon composition did not changed significantly with the composition of raw materials. The naphtha like fractions had C_5–C_{17} hydrocarbons. Each fraction had approximately half of olefin content, mainly α-olefins (vinyl and vinylidene).

In the composition of naphtha obtained by the cracking of PS containing plastic wastes (S-3 and S-4) 35–40% aromatic content was observed due to cracking of polystyrene, because under mild conditions the formations of aromatics is negligible from polyolefines. The middle distillates had considerably lower concentration of aromatics than it was observed in case of lighter fractions. Furthermore the fraction of middle distillates had almost only aliphatic compounds which might be characterized with carbon number of 12–27, but hydrocarbons with the highest concentration posses with carbon number of 15–18. In case of each middle distillate fractions its concentration was not more than 1%, because aromatics with lower boiling point stayed in the naphtha. Similarly as it was above mentioned also middle distillates had favourable properties for further fuel-like application. The olefin content was a bit smaller, than in case of naphtha-like fractions. The heavy residue of cracking (bp.> 410 °C) mainly had paraffins, olefins and aromatics. The aromatics were mainly the oligomers of styrene with higher carbon

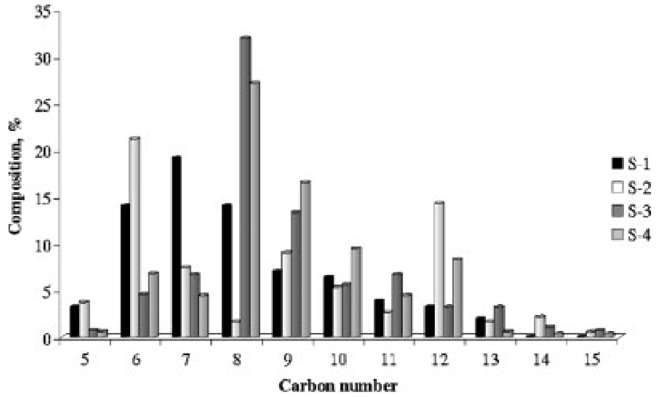

Figure 3.
The composition of naphtha-like fractions.

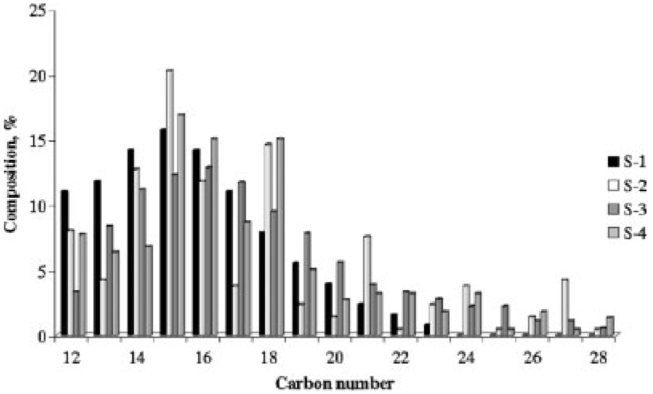

Figure 4.
The composition of middle distillates.

number, which could not be distilled from melted polymers. Figs. 5 and 6 give more information about the aromatics in naphtha-like fractions.

In the respect to aromatics the dominant concentration of ethyl-benzene and styrene - the building elements of polystyrene - was found. This result was the consequence of the characteristic of polystyrene because its cracking results high yield of aromatics. It means that the monomer and ethyl-benzene formed in the highest probability, beside formation of benzene, toluene, xylenes and other aromatics could be observed at a smaller extent. The other important properties of separated fractions are appeared in Table 3.

The data in table show that fractions had favourable properties for further fuel-like utilization of products in case of suitable composition of raw materials. In naphtha-like (N) fraction their octane numbers were high due to the aromatic content, but their sensibilities were high too. Both cetane numbers and diesel indexes of products were high enough, while the CFPP was rather low in case of middle distillates (MD). The light oil fractions (LO) had olefin and paraffin content without aromatics and naphthenes. These fractions are appeared rather in solid phase at room temperature because the hydrocarbons had boiling point of 240–410 °C of these fractions. The heaviest fraction was the heavy oil (HO). Their melting points of were about 110 °C and they have molecular weight of 1200–1500g/mol. It is well observable that the average molecular weight was the lowest in case of residue of the mixture of HDPE, LDPE, PP, PS, PA and PVC cracking. This phenomenon could be attributed to the greater degree of degradation of this mixture, in consequence of initiating effect of preliminary radicals from e.g. PVC on C–C bond cracking. Their caloric values were about 41.0 MJ/kg, which is quite high to

Table 2.
The hydrocarbon composition products.

	S-1				S-2				S-3				S-4			
	N	MD	LO	HO	N	MD	LO	HO	N	MD	LO	HO	N	MD	LO	HO
Aliphatic parafins	52.8	53.2	56.5	61.1	51.1	56.0	57.8	62.8	24.0	58.5	59.1	64.1	26.8	58.3	58.2	63.9
Aliphatic olefins	47.3	46.8	43.5	38.9	48.9	44.0	42.2	37.2	40.5	41.3	40.9	23.4	35.7	41.6	41.8	22.2
Vinyl*	95	94	96	94	7	6	8	8	97	96	96	94	34	32	35	33
Vinylidene*	2	3	3	4	90	91	88	89	1	3	2	2	62	63	60	64
Vinylene*	3	3	1	2	3	3	4	3	2	1	2	4	4	5	5	3
Aromatics	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	35.5	0.2	n.d.	12.5	37.5	0.1	n.d.	13.9

n.d.-not detectable.
* -in the percentage of aliphatic content of fractions.

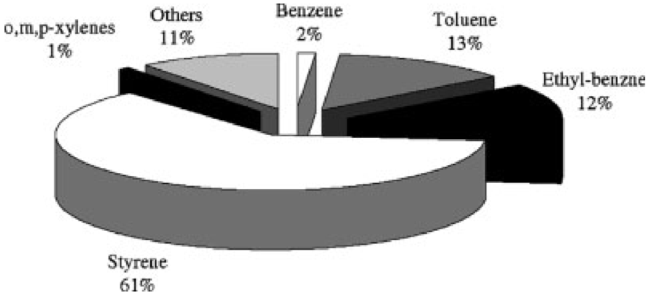

Figure 5.
The aromatic composition of naptha obtained by cracking of S-3.

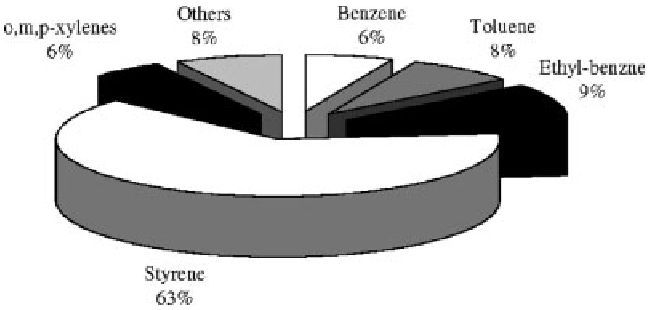

Figure 6.
The aromatic composition of naptha obtained by cracking of S-4.

Table 3.
The main properties of products.

Samples	S-1				S-2				S-3				S-4			
Fractions	N	MD	LO	HO	N	MD	LO	HO	N	MD	LO	HO	N	MD	LO	HO
ROM	74	–	–	–	76	–	–	–	85	–	–	–	86	–	–	–
MON	70	–	–	–	72	–	–	–	75	–	–	–	74	–	–	–
Cetane number	–	62	–	–	–	61	–	–	–	62	–	–	–	62	–	–
Viscosity, mm^2/s	–	2,26	4,42	–	–	2,18	4,37			2,24	4,40			2,19	4,32	
Flash point, °C	–	89	169	231	–	83	165	225	–	86	170	234	–	85	172	220
Melting point, °C	–	–	–	109	–	–	–	102	–	–	–	108	–	–	–	103
CFPP, °C	–	4	–	–	–	0	–	–	–	1	–	–	–	2	–	–
S content, ppm	3	9	8	n.d.	5	3	4	n.d.	5	2	3	2	9	3	5	8
N content, ppm	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1570	1957	1872	n.m.
Cl content, ppm	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2384	3211	4281	9500
Ash content, %	–	–	–	0,36	–	–	–	0,34	–	–	–	0,34	–	–	–	0,33
Caloric value MJ/kg	–	–	–	41,6	–	–	–	41,5	–	–	–	41,5	–	–	–	41
M, g/mol	119	242	301	1510	110	240	299	1340	115	241	294	1350	113	239	299	1220
Distillation data, °C																
IBP	36	86	241	–	36	89	242	–	38	86	234	–	39	93	242	–
20	75	166	306	–	73	163	314	–	78	165	315	–	71	171	316	–
50	110	195	348	–	115	190	350	–	108	196	345	–	108	183	351	–
70	148	218	370	–	143	224	376	–	148	225	378	–	145	220	381	–
FBP	207	250	403	–	205	251	401	–	210	252	404	–	212	253	406	–

n.d. -not detectable.
n.m.-not measured.

application of these fractions for energy producing. Fuel-like fractions obtained by thermal recycling of waste polymers consisted of sulphur max. 10ppm and they were nitrogen free apart products from S-4 sample. Unfortunately the favourable properties were depreciated in the presence of PA 6.6 and PVC, because both the nitrogen and chlorine content of products was high in this case. Apart from the heteroatom content the favourable properties of fractions are not changed notable with the composition of raw materials.

Conclusions

In our experimental work the thermal cracking of waste polymers (LDPE, HDPE, PP and PS) and the utilization possibilities of products were investigated. It was found that the mixtures of waste polymers were converted into valuable lighter hydrocarbons with yields of 30–60%. The volatile liquids had high octane number and diesel index in case of naphtha and middle distillates furthermore each fraction contained low amounts of heteroatoms (S and N). Lighter fractions (gases, naphtha and middle distillates) might be used for energy generation or as fuel-like feed stocks. The yields of each lighter fraction obtained in the cracking process (gases, naphtha and middle distillates) considerably increased both with residence time and temperature, whereas yields also were the dependence of feed polymers. Unfortunately the favourable properties were depreciated in the presence of PA 6.6 and PVC, because both the nitrogen and chlorine content of products was high in this case, however the other favourable properties not changed with compositions of the raw materials.

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