THERMAL CRACKING OF THE MODEL SEVEN COMPONENTS MIXED PLASTICS INTO OILS/WAXES

Martin Bajus, Elena Hájeková

Slovak University of Technology, Faculty of Chemical and Food Technology, Institute of Organic Chemistry, Catalysis and Petrochemistry, Radlinského 9, SK-812 37 Bratislava, Slovakia, e-mail : martin.bajus@ stuba.sk

Abstract

In a previous paper we have reported thermal cracking of individual and mixed plastics into oil/waxes. Now we are getting insight into thermal cracking of model seven components mixed plastics. Thermal cracking of mixture composed of high-density polyethylene (HDPE) /low-density polyethylene (LDPE) /linear-low-density polyethylene (LLDPE) /polypropylene (PP)/polyvinyl chloride (PVC)/ polyethyleneterephthalate (PET) /polystyrene PS/ (HDPE/LDPE/LLPE/PP/PS/PET/ PVC = 34.6/17.3/17.3/9.6/.9.6./10.6/1.1 %wt.) was carried out in the batch reactor at temperatures from 350 to 500°C in atmospheric pressure. The main objective of this study was converting the seven components mixed plastics into oil/wax product for use as hydrocarbon fuel oil or chemical feedstock. The effect of temeperature and reaction time have been studied to ascertain the optimum conditions necessary for the production as well as to investigate the effects of these parameters on the composition of pyrolysis products, with special emphasis on the oil/waxes.

Keywords: Thermal cracking; pyrolysis; mixed plastics; oil/waxes; characterization.

1. Introduction

Pyrolysis is one of the best methods for preserving valuable petroleum resources in addition to protecting the environment by decreasing the volume of non-degradable waste. Pyrolysis of waste plastics is favored because of the high rates of conversion into oil, which can be used as fuel or feedstock in refinery. The gaseous products coming from the pyrolysis process with high caloric value may also be used as fuel. Recycling by pyrolysis has high potential for heterogeneous waste plastic materials, as the separation is not economical. There has been a plethora of research work on the pyrolysis of individual and mixed plastics.

Plastic polymers make up a high proportion of waste and this is expected to continue in the future with the dramatic increase in the volume and range of plastic products in use. The two main types of plastic are: thermoplastics which soften when heated and harden again when cooled and thermosets which harden by curing and cannot be re-moulded. Thermoplastics are by far the most common types of plastics comprising almost 80% of the plastics used in Western Europe. There are six main component plastics in European municipal solid waste which are high-density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC) and polyethyleneterephthalate (PET). However, the polyethylene plastics, LDPE and HDPE make up over 40% of the total plastic content of municipal solid waste. The consumption of plastics in Western Europe is of the order of 38 million tones per year [1] and it is estimated that only 50% of the plastics produced are available for collection and recycling.

The low grade uses for mixed plastic recycled materials has led to research into alternative processing methods to produce higher value products. One example is via chemical recycling where the plastic waste materials are processed back to produce basic petrochemicals, that can be used as feedstock to make virgin plastic [2, 3]. Feedstock recycling can be via hydrogenation at high temperature and pressure to thermally degrade the plastics. Pyrolysis of waste plastics is a recycling option that shows great potential and has been investigated by a number of researchers [4-9]. Pyrolysis is the thermal degradation of the plastics in an inert

atmosphere and produces gas, oil and solid char products. The yield and composition of the products is influenced by a range process parameters, including the type of waste plastic and reactor system, but also other factors, such as the gas residence time, temperature and pressure ranges, presence of catalyst, and presence of hydrogen gas or hydrogen donor compounds [10-14].

In our previous reports, we have also reported on the copyrolysis of individual low-density polyethylene and polypropylene with naphtha [8], copyrolysis of two component mixture (LDPE/PP) [9, 15] and three component mixture (LDPE/HDPE/PP) [9, 15] with naphtha. The composition of gaseous and liquid products during copyrolysis was studied at 780°C and 820°C. The utilization of oils/waxes obtained from thermal cracking of individual LDPE, HDPE, LLDPE, PP or cracking mixed polymers PP/LDPE, HDPE/LDPE/PP and HDPE/LDPE/LLDPE/PP for the production of automotive gasolines and diesel fuels was overviewed [11].

Polystyrene degraded at around 350°C, mainly into viscous dark-colored oil. The formation of char was dramatically enhanced at 450 and 500°C, reaching up to 30% wt.. The oil product from PS even at 350°C consisted almost entirely of aromatic compounds especially toluene, ethylbenzene and styrene [12, 14]. In the work Almazán – Almazan et al. [6] carbonization time and carbonization temperature were a major factors in the composition of products during PET pyrolysis. Pyrolysis of mixed plastics containing PVC produces inorganic and organic chlorine compounds during the initial stages of pyrolysis process [5, 19]. The presence of PET in municipal waste plastic (MWP) produced the additional chlorinated hydrocarbons.

In the present investigation, we report the thermal degradation of the model seven components mixed waste plastics carried out in the batch reactor at 450°C in atmospheric pressure. The effect of PS, PET and PVC in model mixed plastics on the quality of liquid products was presented. The detailed investigation on the distribution PS, PET and PVC in various degradation products is discussed. GC was used for the analysis of liquid products obtained from PE/PP/PS/PVC/PS/PET thermal degradation.

In this study, HDPE/LDPE/LLDPE/PP/PS/PVC/PET represents common plastics usually present in high proportion in the plastic waste stream of municipal solid waste. The main objective of this study was to convert the waste plastics into oil/wax product for use as a hydrocarbon fuel oil or raw chemical feedstock. The effects of temperature and reaction time have been studied to ascertain the optimum conditions necessary for the production of oil/wax as well as to investigate the effects of these parameters on the compositions of reaction products, with a special emphasis on the oil/waxes. Reaction (residence) time here refers to the length of time (run in minutes) for which an experiment was held at a particular (constant) temperature. The choice of this term is intended to avoid the confusion of using the term, reaction time, residence time and run time which would inadvertently include both the reactor heat-up time and actual reaction time or residence time.

2. Experimental

2.1. Materials

The feedstocks used in our presented work were obtained from the Slovak Republic. The characteristic for all feedstocks have been evaluated for the temperature 25°C.

2.1.1. Polymers

Main characteristic of used polymers is in table 1. Polymers were virgin plastics in the form of pellets, except of PET (bottle) and PVC (powder).

Table 1 Characteristic of used polymers

Polymer	$\bar{M}_w$	$\bar{M}_n$	ρ, kg.m^{-3}	producer
HDPE	33 800	6 950	950	Slovnaft, a.s.
LDPE	292 000	22 000	919	Slovnaft, a.s.
LLDPE	112 110	30 300	919	Slovnaft, a.s.
PP	200 000	65 000	903	Slovnaft, a.s.
PS	-	135 135	1 050	Plastika, a.s.
PVC	173 000	86 500	1 380	Plastika, a.s.
PET	62 500	25 000	920	waste

2.2. Thermal cracking of polymer blend

We used a similar apparatus as in our previous works [8, 11], with cooler traps operating at 70°C. 10 %wt. solution of sodium hydroxide was used for gas produced from seven-component mixture for catching of chlorine, which is present in the PVC. The presence of halogen compounds in the oils/waxes prevents the oils/waxes to be used as fuel or refinery feedstock. The presence of chlorine in the oil/wax cannot exceed 10 ppm [5, 19]. The batch reactor was fed with 17 g of feedstock and closed. Nitrogen as inert gas (50 ml.min^{-1}) was fed into the apparatus to prevent the presence of oxygen in the reactor. Thermal cracking took 92 min. at 450°C and 116 min at 500°C. The following program for thermal cracking of polymer blend was used: heating rate of 16.5°C.min^{-1} to 350°C, 8 min temperature stabilization, heating rate of 9 °C.min^{-1} up to 440°C, heating rate of 7.5 °C.min^{-1} up to 480°C. However, final real temperature in the reactor was 450°C. The temperature was controlled by thermocouples. The convenient rate heating and duration of polymers cracking for the production of high yields of oil/waxes was determined to be 92 min. and 116 min. as result of the optimization procedure. Detailed description of thermal cracking is given in literature [8, 11]. Obtained products were: yellow oils/waxes collected in the separator, gas collected in the gas sample, brown residue in the reactor.

The composition of seven-components polymer blend used as feedstock is shown in Table 2. In many countries, plastic is collected from commercial and industrial sources as separate plastic fractions, much of which is recycled directly back into the plastic product manufacturing process. Although plastic make up between 5 and 15 mass % of municipal solid waste it comprises 20 – 30% of the volume [1]. There are five main plastics which arise in Slovakia municipal solid waste. PE (65 mass %), PP (9%), PS (9%), PET (10%), PVC (1%), rest (PA, ABS, PMMA, and others) (6%) [16].

Table 2 The composition of polymer blend

Plastic sample	weight [g]	mass %	Plastic sample	weight [g]	mass %
HDPE	5.87	34.57	PS	1.63	9.57
LDPE	2.94	17.29	PET	1.81	10.64
LLDPE	2.94	17.29	PVC	0.18	1.07
PP	1.63	9.57	Total	17.00	100.00

2.3. Analysis of gaseous and liquid products from thermal cracking

Analysis of the gases obtained from thermal cracking of polymer blend was performed with the gas chromatograph Hewlet Packard HP 6890+. The three-PLOT chromatographic column system consists of two parallelly installed detectors FID and TCD and of three switching valves. Helium was used as a carrier gas. The temperature in the injection chamber was 150°C. The time of analysis was about 40 min.

The liquids obtained from thermal cracking were analyzed with the gas chromatograph CHROM 5. The gas chromatograph system consists of the DB-PETRO column and the FID detector. Helium was used as a carrier gas. The temperature in the injection chamber was 240°C. The time of analysis was about 80 min. The analytical procedure was described in detail in [8, 9].

2.4. Results and discussion

The thermal cracking of HDPE/LDPE/LLDPE/PP/PS/PVC/PET blend was performed under atmospheric pressure at 450°C and 500°C. The products of plastic cracking were classified into three groups: gas, liquid (oil/wax) and solid residue. Table 2 shows the yields of thermal cracking products. Thermal cracking of HDPE/LDPE/LLDPE/PP/PS/PVC/PET blend resulted in 30.5 – 35.5 % wt. of gas, 62.3- 65.9 % wt. of oil/waxes and 2.1-3.6 % wt. of brown solid residues. The oil/waxes (62.3- 65.9 % wt.) produced with the seven components polymer blend were lower than yield of oil/wax for individual polyethylenes (~ 79 – 80 % wt.), PP (85 % wt.) and mixed polymers 79 – 82 mass %) [10, 11]. It is clear from the Table 3 and Table 4 that the presence of PS, PVC and PET has predominant effect on the formation and yields of gases and oil/waxes in the comparison with the thermal cracking of individual and mixed polymers (Table 4).

Table 3 Products yield of thermal cracking at 450°C and 500°C

Temperature, °C	450			500		
	Yield			Yield		
	Oil/w	Gas	Solid residue	Oil/wax	Gas	Solid residue
g	11.20	5.18	0.61	10.60	6.04	0.36
%wt.	65.94	30.47	3.59	62.35	35.53	2.12

Table 4 Product composition obtained during thermal cracking of polymers at 450°C [10,11]

Feedstock	Yield, Y/ %wt.		
	Oil/wax	Gas	Residue
LDPE	79.8	15.1	5.1
HDPE	79.8	17.0	3.2
LLDPE	79.1	12.6	8.3
PP	85.0	14.2	0.9
LDPE/PP	79.4	17.2	3.4
LDPE/HDPE/PP	82.4	13.8	3.8
LDPE/HDPE/LLDPE/PP	79.7	14.4	5.9
LDPE/HDPE/LLDPE/PP/PVC/PS/PET [a]	75.4	21.9	2.7

a)   LDPE/HDPE/LLDPE/PP/PVC/PS/PET in % wt. 16.0/32.0/16.0/32.0/0.8/2.5/0.8/

This results has not been found only in the actual monitored representation of PS (9.6 % wt.), PVC (1.1 %wt.) and PET (1.6 %wt.), but it has been found also in a considerably lesser representation of PS (2.5 %wt.), PVC (2.7 %wt.) and PET (0.8 %wt.) in a previously pyrolysed mixture with published results [10]. The most difficult problems arose during pyrolysis of the actual PET. While on pyrolysis of pure PS at 450°C a dark-yellow even brown liquid occurs in amount of approximately 90 %, the decomposition to gaseous products runs only within 10 %. The dominant component in the pyroliquid is styrene. At 470°C styrene occurs as 86 % wt. of the yield [17]. The thermal cracking of pure PET starts already at 390°C and it is accompanied by a considerable production of coke. As a follow up of intensive coking, the reactor gets plugged (especially the cooling system) by passing-over pyrolysis products, even in the case of various forms (shapes) of the used PET in the batch reactor. The material balance of the products was poor, only at 70 %wt., out of which gases represented 20 %wt., residue materials were at 28.7 %wt. and coke was at 20 %wt. [17]. When PET is pyrolysed, usually a large amount of residue is formed, even at 700°C (30 %wt.) [22].

Changes in composition of gaseous pyrolysis products were observed during heating HDPE/LDPE/LLDPE/PP/PS/PVC/PET/mixture to final temperatures. After the pyrolysis processes were finalised, the representative composition of liquid products was found out gas-chromatographically. The overall material balances of the pyrolysis processes at end temperatures 450°C and 500°C (Tab. 3) were calculated as subtraction of the mass of solid residue and of the mass of liquid product from the mass of the raw material, by which procedure the theoretical mass of yielded gases was found out. In the case of the end-temperature 450°C, the samples of the yielded gases were taken at temperatures 350°C, 400°C, 450°C and one hour isothermically after reaching the temperature 450°C. In the case of the end-temperature 500°C, the samples were taken at 400°C, 450°C, 500°C and one hour isothermically after reaching the temperature 500°C.

The chromatographic analysis of gases has shown that gaseous pyrolysis products from a seven-component mixture of plastic materials consist most of all from oxides of carbon (Tab. 5 and Tab. 6.) Production of carbon dioxide sharply plunged with temperature rising to 450°C: from 6.4 % wt. to 0.1 % wt. At 500°C the trend was from 4.2 mass% to 0.1 % wt. However, in a similar but reverse dependence, production of carbon monoxide gets quickly prevalent. The averaged measured data have shown that pyrolysis of a seven-component mixture of plastics produces about ten-times more carbon monoxide compared to carbon dioxide. Carbon oxides (CO and CO_2) are yielded in such a large amount owing to thermal decarboxylation of PET. Gases and volatile solid products appear in similar amounts. On the contrary, liquid products are barely observed during thermal cracking of pure PET at 700°C [22]. The gas consists mainly of carbon

oxides (32 %wt.), while the solid products show a broad spectrum of different components with poor economic value. Especially organic acids, as benzoic acid (4.2 % wt.), terephthalic acid was not quantified, can cause corrosion and blocking problems in recycling facilities [22].

Table 4 Product distribution (%wt.) of components in gases obtained by thermal cracking of polymer blend at 450°C

Temperature, °C	350	400	450	450	Average composition of gas
Time of experiment, min.	17	24	32	92	
Components, %wt.		Composition, %wt.			%wt.
Carbon dioxide	6.4	1.0	0.8	0.1	2.1
Carbon monoxide	-	-	59.0	31.2	22.6
Methane	1.6	1.8	3.1	6.7	3.3
Ethane	9.2	9.3	4.3	12.8	8.9
Ethylene	11.8	13.1	12.1	14.0	12.7
Propane	11.4	11.4	2.4	8.9	8.5
Propene	29.9	31.1	6.7	16.1	21.0
Methylpropane	traces	traces	traces	0.1	traces
Butane	4.8	5.1	0.7	2.1	3.2
trans-2-Butene	1.6	1.7	0.2	0.3	0.9
1-Butene	10.1	10.8	1.8	2.8	6.4
Methylpropene	3.6	3.7	0.7	1.2	2.3
1,3- Butadiene	2.2	2.4	0.3	0.4	1.3
1,3-Pentadiene	0.3	0.3	traces	traces	0.1
cis-2-Butene	1.2	1.2	0.1	0.2	0.7
C_4-hydrocarbons	0.8	1.1	6.1	1.6	2.4
Pentane	3.1	3.7	1.6	1.2	2.4
2 -Methyl-2-butene	1.0	1.1	0.1	traces	0.6
1- Pentene	traces	traces	traces	0.2	0.1
C_5 - hydrocarbons	0.4	0.5	traces	0.1	0.2
Benzene	0.7	0.7	0.1	traces	0.4

Table 5 Product distribution (%wt.) of components in gases obtained by thermal cracking of polymer blend at 500°C

Temperature, °C	400	450	500	500	Average composition of gas
Time of experiment, min.	26	36	46	116	
Components, % wt.					
Carbon dioxide	2.3	4.2	0.4	0.1	1.8
Carbon monoxide	traces	32.0	55.9	12.0	25.0
Methane	3.1	3.4	4.3	7.8	4.6
Ethane	8.8	5.4	5.9	16.9	9.2
Ethylene	10.5	12.5	14.9	14.2	13.0
Propane	8.8	4.1	2.5	13.0	7.1
Propene	25.3	13.9	7.2	21.9	17.1
Methylpropene	traces	traces	0.1	0.2	0.1
Butane	5.1	2.2	0.6	3.3	2.8
trans-2- Butene	2.9	1.4	0.1	0.5	1.2
1- Butene	11.4	5.5	1.5	4.0	5.6
Methylpropene	4.5	3.0	0.7	2.0	2.5
cis - 2 - Butene	2.2	1.1	0.1	0.4	0.9
C_4 - hydrocarbons	0.4	0.4	0.4	0.8	0.5
1,3 - Butadiene	1.9	1.0	0.1	0.6	0.9
1,3- Pentadiene	0.8	0.4	traces	traces	0.3
Pentane	5.0	4.5	1.3	1.8	3.1
2-Methyl-2-butene	2.4	1.3	0.1	traces	0.9
1 - Pentene	traces	traces	traces	0.3	0.1
C_5- hydrocarbons	1.8	1.7	4.0	0.2	1.9
Benzene	3.0	2.0	0.1	traces	1.7

As to forming hydrocarbon gases that are produced during heating to 450°C and 500°C, it can be stated that with increasing temperature production of methane is favoured at both temperatures. Rising temperature has a positive effect also on production of ethane (from 9.2 %wt. to 12.8 %wt.) and ethylene (from 11.8 %wt. to 14 %wt.). Nevertheless, the production of higher carbohydrates C_3^+ gets lower, at 450°C: propane from 11.4 %wt. to 8.9 %wt.; propene from 29.9 %wt. to 16.1 %wt.; butane from 4.8 %wt. to 2.1 %wt.; trans-2-butene from 1.6 %wt. to 0.3 %wt.; 1-butene from 10.1 %wt. to 2.8 %wt.; methylpropene from 2.2 %wt. to 0.4 %wt.; pentane from 3.1 %wt. to 1.1 %wt. and benzene from 0.7 %wt. to trace amounts (Tab. 5). Even at higher temperature, within the temperature interval from 400°C to 500°C, the amount of methane in the reaction products increases, from 3.1 %wt. to 7.8 %wt.. The amount of ethylene grows as well, from 10.5 %wt. to 14.1 %wt.. In a similar but reverse dependence, the production of ethane falls from 8.8 %wt. to 5.9 %wt.; propane from 8.8 %wt. to 2.5 %wt.; propene from 25.3 %wt. to 7.2 %wt.; butane from 5.1 %wt. to 0.6 %wt.; trans-2-butene from 1.9 mass% to 0.1 mass%; pentane from 5.0 mass% to 1.3 mass% and benzene from 3.0 %wt. to 0.1 %wt.. At isothermal conditions, at 500 °C and reaction period 116 min, the production of higher gaseous hydrocarbons from C_3^+ is on increase (Tab. 6).

On thermal cracking of mixed plastics at 450 °C and 500°C, no production of hydrogen occurred. It is no surprise, because in comparable reaction conditions hydrogen was not yielded in thermal cracking of individual (LDPE; LLDPE; PP) or mixed plastics (LDPE/PP; HDPE/LDPE; HDPE/LDPE/LLDPE/PP; LLDPE/LDPE/PP/HDPE/PVC/PET/PS) [10, 15]. A pleasant surprise is a prevailing representation of propene alongside ethylene. Formation of propene and ethylene is welcome. These gaseous monomers belong to basic petrochemicals, even in pyrolysis of hydrocarbons coming from crude oil fractions (naphtha) and from natural gas (ethane, propane). Gaseous product obtained from pyrolysis runs at these different temperatures mostly comprised $C_1 - C_4$ hydrocarbon compounds that have high caloric value. Consequently, the gaseous products could be utilized to supply the energy involved in the pyrolysis process. The calculated caloric value valid for gaseous products formed at these different temperatures was between 50.8 and 52.7 MJ/kg, which is comparable to that pure methane gas with caloric value of 55.7 MJ/kg [18].

After each of the experiments had been finished, the pyroliquid of dark-green colour and smell after pyrolytic gasoline was taken away from the drip. At 450°C oil-waxes were obtained in 65.9 % yield and at 500°C in 62.4 % yield, compared to the feedstock (Tab. 3). The oil-waxes represent a mixture of valuable hydrocarbons that can be utilised to synthesize secondary chemicals in petrochemistry. The oil-waxes are of alkenic-aromatic character. At first place they are 1-alkenes (α- olefins) that are formed by thermal decomposition of polyethylene and polypropylene, in agreement with the radical mechanism. The aromates $C_6 - C_8$ are mostly represented by styrene, as a result of thermal decomposition of polystyrene, PET and PVC (Tab. 7).

Because PVC is present in the feedstock, gaseous and liquid chlorinated compounds, of both organic and inorganic character, evolve during thermal cracking. To eliminate them, washing by solution of sodium hydroxide was applied into the procedure. A caustic soda wash traps mostly gaseous HCl that evolves by dehydrochlorination. In this work chlorinated products from the reactions were not studied in detail as PVC in the feedstock was present in quite a small amount (approximately 1 % mass). Meszaros [20] reported that the pyrolysis of MWP in an Auger kiln reactor contained 3% mass of PVC (Conrad Recycling Process). Lime was used in order to trap the HCl evolved, which resulted in liquid products with 25 ppm of chlorine. The chlorinated hydrocarbons found in PE/PP/PS/PVC degraded liquid products were also observed in PE/PP/PS/PVC/PET and MWP degraded liquid products. The presence of PET in MWP produced the additional chlorinated hydrocarbons that are similar to chlorinated hydrocarbons observed during the PE/PP/PS/PVC/PET degradation liquid products. In addition, the presence of PET facilitated the formation of higher organic chlorine content in liquid products and drastic decrease in the formation of inorganic chlorine content [5, 19, 21].

Formation of aromatic hydrocarbons is characteristic for pyrolysis of mixed plastics comprising PS, PET and PVC (Tab. 7). At 450°C the aromates $C_6 - C_8$ are represented by 17.4 %wt. and at 500°C they are represented by 16.7 %wt.. Benzene, toluene, xylene, ethylbenzene and styrene are represented in the yield by about 17 %wt., owing to the thermal decomposition of polystyrene, polyethylene terephthalate and polyvinylchloride.

Table 7 The yields of gaseous and liquids components from thermal cracking of polymer blend at 450°C and 500°C

Temperature, °C	450	500
Time of experiment, min.	92	116
Conversion to gases and liquids, %	0.964	0.979
Component	Yields, % wt.	
Carbon dioxide	0.6	0.6
Carbon monoxide	6.8	7.1
Methane	1.0	1.6
Ethane	2.7	3.3
Ethylene	3.9	4.6
Propane	2.6	2.5
Propene	6.4	6.1
Methylpropane	traces	traces
Butane	1.0	1.0
trans-2- Butene	0.3	0.4
1-Butene	1.9	2.0
Methylpropene	0.7	0.9
1,3-Butadiene	0.4	0.3
1,3-Pentadiene	0,1	0,1
cis-2-Butene	0.2	0.3
C_4-hydrocarbons (unknown)	0.7	1.7
Pentane	3.2	2.0
1-Pentene	1.0	0.8
C_5-hydrocarbons (unknown)	0.1	0.7
2-Methyl-2-butene	0.2	0.3
Benzene	2.6	4.0
1-Hexene	2.7	3.1
1-Heptene	1.8	1.9
Heptane	1.9	1.2
Toluene	2.8	2.0
1-Octene	1.4	1.6
1-Octane	1.6	1.1
Ethylbenzene	1.8	2.0
p- + m-Xylene	1.0	0.9
Styrene	7.5	6.1
o-Xylene	1.7	1.6
Nonane	1.4	0.9
1-Decene	1.6	1.9
Decane	1.0	0.9
1-Undecene	1.6	1.7
Undecane	1.4	0.9
1-Dodecene	1.3	1.3
Dodecane	1.1	1.1
1-Tridecene	1.2	1.2
Tridecane	1.1	1.0
1-Tetradecene	1.2	1.1
Tetradecane	0.8	0.8
1-Pentadecene	0.8	0.8
Pentadecane	0.8	0.7
1-Hexadecene	0.5	0.6
Hexadecane	0.6	0.5
1-Heptadecene	0.5	0.5
Heptadecane	0.5	0.4
Unknown	18.6	19.5

The pure PS starts degrading around 300-400°C giving mainly styrene monomer, benzene, toluene, some dimers and trimers as volatile products [23-27] and a cross-linked

residue above 400°C. It has been reported [23-28] that small amounts of C_1-C_4 hydrocarbons are also produced during the pyrolysis of PS. The yields of the main degradation products from pure PS increases with temperature except that of styrene-trimer. There is a considerable decrease in the yields of all the degradation products with the 2,5 %wt. loading of PVC in the PS matrix [23]. The stabilization effect has been explained on the basis of mechanism involving interaction between the degrading products from the polymer components, thus leading to a stable polymer network. The extend of interaction and hence the stabilization.

The thermal cracking of the PET with following the decarboxylation and the reduction of oxygen-containing compounds led to an increasing yield of aromatic hydrocarbons. Especially benzene, toluene, styrene, naphthalene and biphenyls were obtained in high yields from pure PET during thermal cracking at 700°C [22]. $Ca(OH)_2$ can be used for the decarboxylation of polyester as PET under pyrolysis conditions.

Thermal decomposition of a polymerous material (such as PE, PP), according to our process, does not occur in the presence of polystyrene (PS), polyvinyl chloride (PVC), or polyethylene terephthalate (PET). The point is that PS, PVC and PET decrease fuel production and deteriorate the quality thereof. In the presence of PS, the production of aromatic compounds that are not environmentally acceptable is increased. PVC and PET are also among restrictive raw materials because in their presence an increased formation of coke occurs on account of liquid products. The same results have recently been obtained by other authors. PS degraded at around 350°C, mainly into viscous dark-coloured oil. The formation of char only increased marginally up to 425°C, but dramatically increased at 450°C and 500°C, reaching up to 30 wt %. The oil products from PS even at 350°C, consisted almost entirely of aromatic compounds, especially toluene, ethyl benzene and styrene. Under increasing temperatures and residence times, the oil product from PS was preferentially converted into char [14].

The mass rate of PE and PP volatilization was decreased in the presence of PVC, especially at lower degradation temperatures (360°C to 450°C) and with increasing amounts of PVC. This could be explained by the involvement of PE degradation fragments in reactions of polyene structures resulting from DHC of PVC thus increasing the amount of high molecular weight compounds that could not leave the reactor and thus remained in the reactor content. Indeed, a considerable amount of reactor content corresponding to 10 wt % of the input needed to be withdrawn every 30 minutes in order to avoid excessive accumulation of material inside the reactor. In contrast, negligible accumulation was observed during continuous flow degradation of PE and PP in the absence of PVC [29]].

Our process uses only one batch reactor system. References to the advantageous use of the batch reactor as compared to the continuous flow reactor are also made by other authors [13]. The key difference is that the batch reaction system showed a relatively high fraction of gasoline and a low fraction of heavy oil, whereas conversely the continuous reaction system had a low fraction of gasoline and high fraction of heavy oil. The batch reaction showed slightly faster production in the cumulative yield distribution of the liquid product under the same degradation temperature programming in relation to that of the continuous reaction system.

However, the maximum production rate of liquid products was obtained at a similar elapsed time point, i.e. about 80 minutes: this was more strongly influenced by the degradation temperature programming than by the reaction system itself. At the high degradation temperature of 450°C, the heavy hydrocarbons were cracked into light hydrocarbons, that is to say, gasoline-range products, and they were significantly more cracked due to the longer elapsed time of the reactants in the reactor.

The batch reaction system showed a relatively high fraction of liquid components with a low carbon number in the gasoline range, and a low fraction of heavy oil in relation to the yields of the continuous reaction system.

3. Conclusion

This study presents results from investigation of the possibility for thermal cracking of the model seven components mixed plastics into oils/waxes. The products of plastic cracking were classified into three groups: gas, liquid (oil/wax) and solid residue. The presence of PS, PVC and PET in the feedstock has predominant effect on the formation and yields of gases and oil/waxes in the comparison with the thermal cracking of individual and mixed polymers. It is found that the presence of PS, PVC and PET in model mixed plastics increased

the formulation of carbon monoxide and carbon dioxide in the gas and benzene, toluene, xylenes, styrene in the liquid (oil/waxes) products.

Acknowledgement

References

[1]   Wiliams, P.T.: Waste Treatment and Disposal, John Wiley and Sons, Chichester, UK, 2005, pp. 380.
[2]   Scheirs, J., Kaminsky,W. (Eds.) : Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels, John Wiley and Sons, Chichester, 2006, pp 785.
[3]   Aguado, J., Serrano, D. : Feedstock Recycling of Plastic Wastes, The Royal Society of Chemistry, Cambridge, 1999, p. 192.
[4]   H. Jung, S.H., Cho, M.H., Kang, B.S., Kim, J.S. : Fuel Processing Technology 91 (2010) 277-284.
[5]   Bhaskar, T., et al.: J. Anal. Appl. Pyrolysis 70 (2003) 579-589.
[6]   Almazán-Almazán,M.C. et al.: Fuel Processing Technology 91 ((2010) 236-242.
[7]   Lee, K.H., Nam, K.Y.: Fuel Processing, Technology 91 (2010) 514-519.
[8]   Hájeková,E., Bajus, M.: J. Anal. Appl. Pyrolysis 74 (2005) 270-281.
[9]   Hájeková, E., Mlynková, B, Bajus, M., Špodová, L.: J. Anal. Appl. Pyrolysis 79 (2007) 196-204.
[10]   Mlynková, B., Hájeková, E., Bajus, M.: Fuel Processing Technology 89 (2008) 1047-1055.
[11]   Mlynková, B., Bajus, M., Hájeková, E., Kostrab, G. Mravec, D.: Chemical Papers 64 (1) (2010) 15-24.
[12]   Miskolczi, N., Bartha, L., Deák, Gy.: Polymer Degradation and Stability 91 (2006) 517-526.
[13]   Lee, K.-H.: J. Anal. Appl. Pyrolysis 86 (2009) 348-353.
[14]   Onwudili, J. A., Insura, N., Williams, P.T.: J. Anal Appl. Pyrolysis 86 (2009) 293-303.
[15]   Hájeková, E., Špodová,L., Bajus,M., Mlynková,B.: Chem. Pap. 61 (4) (2007) 262-270.
[16]   http :// www.recfond.sk pdf/VUSPL.pdf.
[17]   Bajus, M., Hájeková, E., Špodová, L.: APROCHEM 2005. Proceedings from 14th International Conference, 24.-26.2005, Milovy, Czech. Republic.
[18]   Perry, R. H., Green, D. W. (Eds.): Perry˙s Chemical Engineers˙ Handbook, 7[th]edition Mc Graw-Hill, New York, 1997.
[19]   T. Bhaskar, M. Tanabe, A. Muto, Y. Sakata, Ch.-F. Liu, M.-D. ChenChih C. Chao, Polym. Degrad. Stab. 89 (2005) 38-42.
[20]   Meszaros, M. W., in Andrews, G. D, Subramanian P.M., (Eds.): ACS Symposium Series 609, American Chemical Society, Washington, DC 1996, 170 (Chapter 15).
[21]   Bhaskar,T., Kanekoo,J., Muto, A., Sakata, Y., Jakab, E., Matsui, T., Uddin,Md A.: Anal. Appl. Pyrolysis 72 (2004) 27-33.
[22]   Grause, G., Yoshioka, T., Handa.T., Otani,S., Inomata, H., Mizoguchi,T., Okuwaki,A.: Feedstock Recycling of Plastics, M. Müller-Hagedorn, H.Bockhorn (Edts), Selected Papers Presented at the Third International Symposium on Feedstock Recycling of Plastics Techniques, Karlsruhe, Germany, September 25-29, 2005.
[23]   Ahmad,Z., Al-Sagheer, F., Al-Awadi, N.A.: J. Anal. Appl. Pyrolysis 87 (2010) 99-107.
[24]   Kaminska,A., Sanyal,S., Kaczmarek, H.: J. Therm.. Anal. 35 2135-2141.
[25]   Qiang,Y., Charles,W.A.: J Polym. Mater. Sci. Eng., 83 (2000) 98.
[26]   Qiang,Y., Charles,W.A.: J. Vinyl Addit. Technol. 7 (1) (2001) 26.
[27]   Haba,Y., M. Narkis,M.: Polym. Eng. Sci 44 (8) (2004) 1473-1483.
[28]   Karaduman, A., Simsek, E.H., Cicek, B., Bilgesu, A.Y.:J. Anal. Appl. Pyrol. 60 (2001) 19-186.
[29]   Murata,K., Brebu,M., Sakata,Y.: J. Anal. Appl. Pyrolysis 86 (2009) 33-38.