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Recycling of mixed plastics by pyrolysis in a fluidised bed

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SUMMARY: Mixtures of plastics and a plastic light fraction from DSD, Germany, were used as feedstocks. The fluidised bed was heated indirectly and fluidised by pyrolysis gas, nitrogen or preheated steam. By a pyrolysis temperature of 510°C up to 90 wt % of the feedstock was obtained as oil or waxy products. The content of aromatics is low and lies between 0.1 and 0.3 wt %. The liquid product can be used as feedstock for a steam cracker and as a substitute for naphtha. By a higher pyrolysis temperature of 690 to 735°C and pyrolysis gas as fluidising gas the experiment yielded about 40 wt % of an oil which consists mainly of benzene, toluene and xylene (BTX-aromatics). The organic chlorine content in the low boiling oil is less than 10 ppm and therefore useful in the petrochemistry.

The present report describes the pyrolysis of a light fraction (LF) of mixed plastic waste (MPW) in a fluidised bed lab scale reactor. The main components of the waste were polyethylene (PE) and polypropylene (PP) with a small amount of polystyrene (PS) (<4 %). The aim of the investigation was to yield the monomers ethene and propene. Therefore steam was used to fluidise the bed. Nine test runs were made with reactor temperatures between 545 and 750°C and residence times from 2.3 to 3.6 s.To compare experiments which are different in both parameters temperature and residence time, the crack severity was calculated for each experiment. The crack severity shows the same influence on the product distribution as it does on naphtha in technical steam crackers.

At temperatures between 700 and 750°C high amounts of olefins were obtained. There are 21-29 wt % ethene, 16-21 wt % propene and 5.6-6.6 wt % butadiene. These results are similar to the products of naphtha cracked in steam crackers.

Introduction

The pyrolysis of mixed plastics is currently receiving renewed interest as a route for disposal of the large quantities of plastic wastes collected by different collecting systems. The pyrolytic route is favoured because of the high rates of conversion into valuable oil and gas which can be obtained. Additionally the main part of all fillers, impurities and heavy metals are fixed in the residue.

Since the early nineties recycling became an important subject in German public because of

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the packaging decree of the German government. In Germany a system was established to collect packaging waste from households for recycling. Some waste materials like glass or paper have already been recycled for years. However, recycling of old plastics was not done because the procedure of washing and separating the different types of plastic was seen as a expenditure. Caused by the new decree the plastics industry is now forced to develop possibilities for recycling post-consumer plastic waste. During the last few years many companies and scientific institutes investigated different methods of plastics recycling1).

There is a market for recycled pure plastics, especially for polyethylene and the residues from the plastics manufacturing industry. But many materials such as composites, heavily filled plastics, elastomers and duroplasts are inherently not suitable for regranulation and recycling.

Other than combustion under utilization of the energy content of the wastes, high molecular weight substances cannot be purified by physical processes like distillation, extraction or crystallisation. They can only be recycled via cleavage (pyrolysis) of the macromolecules into smaller fragments. The pyrolysate may then be suitable for the common petrochemical separation processes.

The thermal cracking of hydrocarbons is a well known process because of its importance in petrochemistry, e.g. visbreaking, cat-cracking, gasification etc. Pyrolysis of plastics is the thermal degradation of macromolecules in the absence of air. Pyrolysis simultaneously generates oils and gases, which are suited for chemical utilisation or generation of energy. The advantage of pyrolysis over combustion is a reduction in the volume of product gases by a factor of 5 to 20 which leads to considerable savings in the gas conditioning equipment. Furthermore, the pollutants are concentrated in a coke-like residue matrix. It is possible to obtain hydrocarbon compounds as a gas or oil.

The pyrolysis is complicated by the fact that plastics show poor thermal conductivity while the degradation of macromolecules requires considerable amounts of energy.

The pyrolysis of plastic wastes and used tires has been studied in melting vessels, blast furnaces, autoclaves, tube reactors, rotary kilns, cooking chambers and fluidised bed reactors2-5).

Rotary kiln processes are particularly numerous. They are marked by relatively long residence times of the solid wastes in the reactor of 20 minutes and more whereas dwell times in fluidised bed reactors hardly a few seconds to a 1.5 minute maximum. Due to the large temperature gradient inside the rotary kiln the product spectrum is very diverse. For this reason the gases and oils generated in the process are normally used for the direct generation of energy (heat).

In this article the thermal cracking of mixed plastic waste MPW in a fluidised bed reactor is described. This type of reactor has advantages which are specified by Kunii and Levenspiel6).

In cooperation with different companies and the Ministry of Education and Research (BMBF), pyrolysis of mixed plastics has been carried out at the University of Hamburg in a laboratory (1-3 kg/h) and technical (20-50 kg/h) scale.

The Hamburg pyrolysis process was developed to produce a petrochemical oil consisting mainly of benzene, toluene and xylene (BTX-aromatics) from plastic waste7,8). Since a few years other variants have been investigated :

- at lower temperatures waxes and aliphatic oils are formed which can be used as feed for petrochemical plants as steam cracker or fluid cat cracker9,10),
- poly(methyl methacrylate)11) and polystyrene12) depolymerise selectively to their monomers at temperatures between 450 and 550°C,
- with steam as fluidising agent polyolefins build high amounts of the monomers: ethene, propene and butene13).

Since the implementation of the “Duales System Deutschland GmbH“ (DSD) in Germany, the development of separation and preparation of MPW has made a big progress. Therefore it is possible to receive the polyolefins almost pure without PVC and with only small amounts of PS (<5 %). The input material of our investigation, which came from the waste combustion plant MVA Stapelfeld had such a composition. Furthermore the polyolefins dominate the production and waste of plastics (1997 production in Germany: polyethylene 1,9 mill.t, 16 % of all plastics, polypropylene 1,1 mill.t, 9 % 14)) so we concentrated our work on optimising the yield of ethene and propene out of mixed polyolefins.

Experimental part

Fluidised bed reactor

A lab scale pyrolysis reactor with a throughput of 1 - 2 kg/h of the University of Hamburg was used for the experiments (Fig. 1). The 154 mm wide tube of temperature-resistant stainless steel with a height of 670 mm was filled with 9 kg sand with a granulation of 0.3-0.5 mm. The gas distributor at the bottom consisted of a steel plate with 108 tubes which were formed in hooks so that no sand could fall through the gas distributor. The reactor was heated with a filament heating with 5 kW. Steam was generated in two consecutive electrically heated vessels and preheated up to 600-800°C. With a system of two screw conveyors the input material was fed into the reactor. In the reactor the material was rapidly heated and converted into volatiles. The products were caught in a separation unit which consisted of a cyclone, several coolers and an electrostatic precipitator. The pressure was controlled manually and excess gas was sucked off by a compressor and burned in a flare after some samples were taken.

Input material

Two input materials were used. Both were light fractions of mixed plastic waste collected from German households by the Duales System Deutschland GmbH (DSD). The first material (LF1) consisted of several plastic package materials, the second (LF2) only of plastic bottles and boxes. Both were washed and cut up. Then a light fraction of PE, PP and PS was segregated by density separation with water and agglomerated in an extruder to pellets of 5 mm in diameter.

The light fractions were analysed by elementary analysis and ashing at 815°C. The proportion of PS was quantified by solving in toluene. The results are documented in table 1. The C/H-ratio indicates that the material was nearly of pure polyolefin. LF1 had a bit higher C/H-ratio than LF2 because of its higher amount of PS. The ash in the MPW came from the inorganic filling materials that are used for compounding plastic materials. Chlorine could not be verified in the material thus there was no PVC in the feed material.

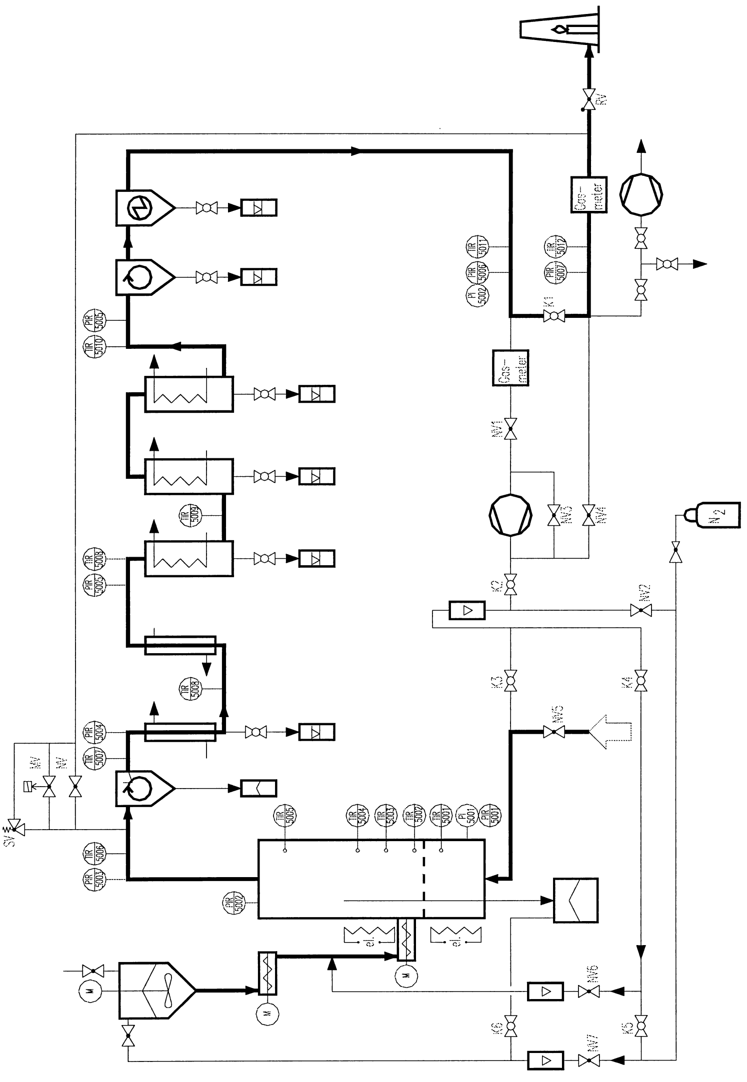

Fig. 1. Flow scheme of the lab scale fluidised bed reactor

Tab. 1. Composition of the input material

	C, wt %	H, wt %	C/H- ratio	ash, wt %	PS, wt %
LF1	85.1	13.7	0.52	1.3	3.6
LF2	84.7	14.2	0.50	1.1	<1

Experimental runs

In Table 2 the parameters of the experiments are shown.

The residence time of the product gases in the reactor was between 2.3 and 3.6 s. This time does not include the time needed for heating, melting and cracking so that the total time of the pyrolysis was longer. The fluidised bed temperature varied between 545 and 750°C.

The kinetic crack severity function KSF was calculated by the using fluidised bed temperature, the freeboard temperature and the residence time.

Work off and analytical methods

The experiments yielded gas, solid residues and an emulsion of oil and water. A representative sample of the liquids was destillated up to 210°C at 133 mbar to receive the oil fraction, water and a destillation residue. The pyrolysis gas and the oil fraction were analysed by gas chromatography. The oil fraction and the destillation residue were analysed by elementary analysis and the solid and destillation residue by ashing.

Results and discussion

Table 3 shows the mass balance and the distribution of organic products. The main interests lies in the product gas fraction, which contains the monomers ethene, propene and butadiene, and oil with the aromatics benzene, toluene, xylene and styrene.

The total yield of gas increases up to a crack severity of 2.5 and than stays at about 73 wt %. First the oil yield falls to a severity of 2.5 and then stays at the amount of about 20 wt %. To interprete this result it is necessary to look at the composition of the fractions.

The gas fraction

Ethene and propene are the two main components of the gas. In each run they represent about 60 wt % of the total gas yield. The third component is methane with 8 to 14 wt % of gas and then comes 1,3-butadiene with about 7 to 9 wt % of gas. Butane and ethane are other basic components. The amount of ethene and methane rises with the severity while

Tab. 2. Parameters of the pyrolysis experiments

Experiment	V1	V2	V3	V4	V5	V6	V7	V8	V9
Temperarutre fluidized bed, °C	545	660	665	695	710	715	722	750	750
Residence time reactor, s	2.5	2.3	2.3	3.6	2,7	2.6	2.7	2.9	3.0
Crack severity	0.4	0.9	1.0	1.8	2.0	2.3	2.9	5.4	6.4
Input material	LF1	LF1	LF1	LF2	LF2	LF2	LF2	LF2	LF2
Input, kg	6.7	4.4	6.0	2.7	4.1	2.9	4.3	4.4	2.9
Experiment time, h	3.1	4.3	6.5	4.0	1.7	2.4	4.7	2.6	3.0
Feed rate, kg/h	2.2	1.0	0.9	0.7	2.4	1.2	0.9	1.7	1.0
water throughput, kg/h	3.5	2.7	2.7	2.1	2.1	2.8	2.7	2.1	2.2

Tab. 3. Product distribution (refering to total input)

Experiment	V1	V2	V3	V4	V5	V6	V7	V8	V9
Crack severity	0.2	0.5	0.5	0.9	1.0	1.2	1.5	2.7	3.2
Gases, wt %	27	45	49	63	68	72	72	73	73
Hydrogen, wt %	0.12	0.24	0.29	0.30	0.45	0.41	0.45	0.39	0.72
Methane, wt %	2.1	4.6	4.9	5.9	7.0	7.5	8.3	8.4	10
Ethene, wt %	7.7	13	15	21	23	24	24	25	29
Propene, wt %	8.2	13	14	18	19	19	20	20	16
Butadiene, wt %	1.9	3.8	3.9	5.7	5.8	5.8	6.4	6.2	5.8
Oil, wt %	44	41	35	30	20	24	23	22	19
Aliphatics, wt %	34	24	22	15	13	10	10	11	7.4
Aromatics, wt %	5.9	5.9	5.7	7.0	5.6	8.0	11	9.8	11
Benzene	0.55	1.6	1.8	2.9	2.9	4.2	4.2	5.6	6.6
Toluene	0.82	1.9	2.0	2.0	1.6	2.8	2.5	2.5	2.4
Xylene	0.76	1.1	0.94	0.81	0.33	0.43	0.37	0.29	0.23
Styrene	3.5	3.4	3.7	0.82	0.51	1.2	3.9	0.99	1.0
C/H ratio	0.61	0.65	0.65	0.71	0.73	0.82	0.86	0.88	0.90
Destillation residue, wt %	29	14	15	3.6	8.3	0.9	3.0	3.4	6.1

that of propene and butadiene reach a maximum at about 2. Ethene and methane need a high activation energy to be built by pyrolysis. Therefore the yield rises with severity. It can be assumed that there is a maximum at a definite severity out of the test scale after which also the amounts of ethene and methane are falling. They are like all other gas molecules except hydrogen thermodynamically instable at the test conditions and therefore intermediate products at pyrolysis. For this reason it can be supposed that the total amount of the gas fraction will fall at higher severity. The same behaviour of crack reactions is described for naphtha in steam crackers in literature[15,16)].

The oil fraction

The oil consists of 2 main fractions. The aliphatics contain mainly α-alkene and some alkane and α,ω-alkadiene. At low severity they take one third of the total organic and decrease to 14 wt %. The most part of the aromatics are benzene, toluene, xylene and styrene. They start with 6 wt % at the lowest severity and increase up to 11 wt %. At first the influence of the aliphathics is much bigger than of the aromatics so that the total oil yield decrease. Then the amounts of aromatics increase and overrides the falling tendency of the aliphatics. The C/H ratio of the oil supports this theory. With the severity the C/H ratio grows and indicates the higher aromatic character. At severities higher than the test scale the oil yield will theoretically grow because more aromatics will be built. The contrary behaviour of the two main fractions aliphatics and aromatics will lead to a minimum like in a steam cracker [15,16)]. Attention should be paid to styrene. It is meanly built by polystyrene PS which has a bigger part (4 wt %) in V1, V2, V3 and V7. If the yield of styrene would be fitted in this runs the trend of the aromatics would be more definite.

Conclusions

The presented results show that the pyrolysis of used polyolefins in a fluidised bed reactor with steam can yield amounts of the monomers ethene and propene like a commercial steam cracker. The feed material is available in large quantities by the German recycling system. Therefore it might be possible that technical plants would run profitable.

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