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Recycling of polymers by pyrolysis

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ABSTRACT

The pyrolysis of plastic waste, scrap tires and other polymeric materials in a fluidized bed has been carried out based on a scale up program (laboratory plants 70 g/h, 500 g/h, 3000 g/h, and pilot plant 20-50 kg/h). The fluidized bed shows short residence times and high heat and mass transfers, and is heated indirectly up to 600 - 800 °C. In the case of poly(methylmethacrylate) (PMMA) or polystyrene as feedstock up to 97 wt.% of the monomer can be recovered. Other polymers give a more unspecific product spectrum. Depending on the process parameters between 30 and 60 % of the polymeric material could be recovered as oil which is comparable to that of a mixture of light benzene and bituminous coal tar if the pyrolysis gas is used as fluidizing gas. The other fractions are gas and a residue containing fillers and impurities (heavy metals). The gas fraction contains mainly methane, ethane, ethene, and propene, the oil fraction benzene, toluene, xylene, and naphthalene.

INTRODUCTION

The recycling of plastics and rubber is of increasing importance as landfilling and incineration becomes more expensive and the acceptance of these methods is decreasing. Most polymers are produced from oil and can be pyrolyzed into petrochemicals.

There is a market for the recycling of pure plastics, especially of polyethylene but also residues from the plastic manufacturing industry. The collection of plastics, the mechanical sorting of wastes and the utilization of used cars, however, give plastic wastes that are mixed or contaminated and are expensive to separate and recycle.

Many composites like filled plastics, elastomers, and duroplasts are not suited for regranulation and recycling on principle.

Other than combustion under utilization of the energy content of the wastes, high molecular weight substances, that cannot be purified by physical processes like distillation, extraction, or crystallization, can only be recycled via thermal degradation (pyrolysis) of the macromolecules into smaller fragments. The pyrolyzate is then suited for the common petrochemical separation processes. Pyrolysis is the

thermal cleavage in the absence or at least a lack of air with simultaneous generation of pyrolysis oils and gases, suited for chemical utilization 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. Furthermore, the pollutants are concentrated in a coke-like residue surrounding them as a matrix. On top of this it is possible to obtain hydrocarbon compounds and some processes even recover valuable crude chemicals.

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

PROCESSES

The pyrolysis of plastic wastes, used tires, and biopolymers has been studied in melting vessels, blast furnaces, autoclaves, tube reactors, rotary kilns, coking chambers and fluidized bed reactors [1-9].

In the course of the development rotary kilns and fluidized beds have turned out to be the most suitable pyrolysis aggregates.

Meltable plastic wastes can also be decomposed in agitator vessels. The vessels can be heated externally or by means of internal piping.

Other processes are operating in autoclaves for the hydrogenation of plastics at 300 °C and 200 - 400 bar hydrogen pressure. Rotary kiln processes are particularly numerous. They are marked by relatively long residence times of the waste in the reactor of 20 Minutes and more, whereas dwell times in fluidized bed reactors hardly exceed a few seconds with a 1,5 minute maximum.

One of the first processes was the Kobe Steel process [10] using a rotary kiln for the pyrolysis of scrap tires. The process ran over a long period and was combined with a cement factory. The pyrolysis products were used instead of heating oil.

The core of the Salzgitter pyrolysis is an externally heated rotary kiln. This 26 m long reactor with a diameter of 2,8 m is subdivided into six segments in the reactor at temperatures of 400 - 700 °C and yields pyrolysis gas and oil as well as solid residues. The purified pyrolysis gas is used as a fuel for operating the plant and excess gas is converted to electricity in a linked power plant.

The fluidized bed has a number of special advantages for the pyrolysis, because it is characterized by an excellent heat and mass transfer as well as constant temperature throughout the reactor which results in

- largely uniform product spectra
- absence of moving parts in the hot zone of the reactor
- completely closed system, i.e. the reactor can easily be sealed.

The fluidized bed is generated by a flow of air or an inert gas that is directed from below through a layer of fine grained material, e.g. sand or carbon black, at a flow rate that is sufficient to create a

swirl in the bed. At this stage the fluidized bed behaves like a liquid.

In Japan fluidized bed pyrolysis plants are operated with air or oxygen feed [10]. The partial oxidation generates a part of the necessary fission energy while on the other hand a part of the products is burnt. The product oils are partly oxidized and their energy content is some 10 % below that of pure hydrocarbons.

FLUIDIZED BED

A number of projects that have been conducted at the University of Hamburg in recent years were aimed at determining the suitability of plastic wastes, used tires, and waste oil residues as a source of raw materials after pyrolysis in an indirect heated fluidized bed reactor. Laboratory plants with capacities for 60 - 3000 g/h and two pilot plants for 10 - 40 kg/h of plastic and 120 kg/h of used tires were installed and run at the Institute of Technical and Macromolecular Chemistry with financial support from BMFT, Verband Kunststoffherzeugende Industrie (VKE), C.R. Eckelmann company (CRE), and Asea Brown Boveri (ABB) [11-15].

Figure 1 shows the scheme of the pilot plant for the pyrolysis of plastics. The core of the plant is a fluidized bed reactor with inner diameter of 450 mm. An auxiliary fluidized bed of quartz sand with a temperature of 600 to 900 °C is used for the pyrolysis of plastics that are fed into the reactor through a double flap gate or a screw. Pyrolysis gas preheated to 400 °C is used to create the swirl in the fluidized bed. The heat input takes place indirectly through heat radiation fire pipes which are heated by pyrolysis gas.

The exhaust gases are then directed through a heat exchanger. The product gases emerging from the fluidized bed are separated from residual carbon and fine dust in a cyclone and then cooled to room temperature by product oil in a condenser. The gas flow is then directed through two packed condensation columns.

The condensed oil fractions are distilled in two distillation columns using the fraction boiling from 135-145 °C (mostly xylenes) as a quenching medium. Also produced are tar with a high boiling range as well as two fractions, one rich in toluene and the other in benzene.

The gas, largely stripped of liquid products, passes to an electrostatic precipitator where it is freed from small droplets. Subsequently, it is compressed in five membrane compressors, connected in parallel, and stored in three gas tanks, each 0,5 m³ in volume. Part of the gas serves as fuel for the radiation heating tubes, while the remainder, preheated by hot fuel gases in the heat exchanger, is used for fluidizing the sand bed. The excess gas is burnt in a torch.

Up to 50 % of the input material may be retrieved in liquid form, which corresponds to a mixture of light benzene and bituminous coal tar with about 95 % aromatics. The oil may be processed into chemical products according to the usual petrochemical methods. Optimal reaction management aims at high yields of aromatics. Comparable raw material value analysis showed that the chemical processing of this type of high aromatic oil is better converted to valuable raw materials than used for heating or propulsion purposes.

The product gases are a highly energetic fuel gas with a calorific value of about 50 MJ/ m³. Only about 40 % of them are needed as fuel for the radiation fire tubes, the rest is available as excess gas.

Any kind of plastic waste can be pyrolyzed even when it is soiled.

In Table 1 the input plastics and rubber which have been investigated, are summarized.

TABLE 1 Pyrolysis of Plastic Waste in a Fluidized Bed. Different Feeds and their Products

Feed	Pyrolysis (Temp. °C)	Gas (wt.%)	Oil (wt.%)	Residue (wt.%)	Others (wt.%)
Polyethylene PE	760	55,8	42,4	1,8 C	64,9 Styrene
Polypropylene PP	740	49,6	48,8	1,6 C	
Polystyrene PS	580	9,9	24,6	0,6	64,9 Styrene
Mixture PE/PP/PS	750	52,0	46,6	1,4	
Polyester	768	50,8	40,0	7,1	2,1 H ₂ O
Polyurethane	760	37,9	56,3	0,5	5,0 H ₂ O; 0,3 HCN
Polyamid PA-G	760	39,2	56,8	0,6	3,4 HCN
Polycarbonate	710	26,5	46,4	24,6	2,5 H ₂ O
Poly(methyl meth- acrylate)	450	1,25	1,4	0,15 C	97,2 MMA
Poly(vinyl chloride)	740	6,8	28,1	8,8	56,3 HCl
Poly(tetrafluoro- ethylene)	760	89,3	10,4	0,3	
Medical syringes	720	56,3	36,4	5,8	1,5 steel
Plastic from house- hold separation	787	43,6	26,4	25,4	4,6 H ₂ O
Plastic from car- shreddering	733	29,9	26,7	27,6	14,0 metals; 1,8 H ₂ O
EPDM-Rubber*	700	32,3	19,2	47,5	1,0 H ₂ O
SB-Rubber**	740	25,1	31,9	42,8	0,2 H ₂ S
Scrap tires	700	22,4	27,1	39,0	11,5 steel
Lignin	500	3,4	29,9	49,3	17,4 H ₂ O
Cellulose (Wood)	700	47,1	23,0	18,6 C	11,3 H ₂ O
Sewage Sludge	600	34,3	27,7	33,2	4,8 H ₂ O

* EPDM: Ethene-Propene-Diene-Monomers

** SB: Styrene-Butadiene

Normally it is difficult to win back the monomers by pyrolysis. So the yields of ethene and propene produced from polyolefins, does not exceed a maximum of 60 %. The situation is different when poly(methylmethacrylate) (PMMA) or polystyrene is used; about 64 % of the monomeric styrene could be recovered by pyrolysis. The liquid has to be purified in an expensive process to give polymerization-grade monomer. In contrast to this the fluidized bed pyrolysis of PMMA gave very large amounts (97 %) of monomeric methyl methacrylate [16].

In the case of PVC the product consists mainly of hydrogen chloride (56 %) and carbon black, while the composition of the component is similar to that of polyethylene. Carbon dioxide and carbon monoxide

are formed from polyester, polyurethanes, polyamides and cellulose-containing materials. The collected plastic fraction from household separation contains 57 % polyolefins, 14 % poly(vinylchloride) (PVC), 19 % polystyrene, 5 % other plastics or paper, and 5 % inorganic materials (sand, salts).

Table 2 shows the pyrolysis conditions for three runs in the technical plant. The composition of the products of mixed plastics and some other plastics (polyethylene, polyester, polyurethanes) are summarized in Table 3. The main compounds in the gas are methane, ethane, ethene, propene, and in the oil benzene, toluene, and naphthalene. The yield of oily products can be raised at the expense of lower gas yields when aromatics are alkylated by olefinic gases (ethene, propene) in the presence of zeolithes. This increases the weight fraction of liquid products up to 70 %. Plastic wastes obtained from separate collection contain about 15 % PVC.

TABLE 2 Pyrolysis Conditions of Three Runs at Different Temperatures of Mixed Plastics (Temperature 790 °C)

Throughput of plastics	(kg)	130
Throughput of dolomite	(kg)	4,5 (lime)
Pyrolysis time	(h)	6,8
Flow rate of fluidizing gas	(kg/h)	19
Pressure before fluidized bed	(mbar)	136
Pressure after cyclone	(mbar)	36
Temperature in the quench coolers	(°C)	3
Stock of xylene in the coolers	(kg)	155
Stock of sand in the fluidized bed	(kg)	171

By addition of lime to the fluidized bed, the hydrogen chloride from the decomposition of PVC can be bound chemically. The calcium chloride that is formed in the process, however, has a tendency to clog the fluidized bed at higher concentrations. Therefore it is attempted to eliminate HCl gas in a preliminary step at 300-400 °C before more extensive cracking reactions take place. The dry HCl gas would then be available for further use.

The residual content of organic chlorine is of great importance for the value of the pyrolysis oils. For processing in existing petrochemical plants the chlorine content should not exceed 10 ppm. Oils that are obtained from the pyrolysis of plastic mixtures contain between 50 and 200 ppm of organically bound chlorine. Fortunately, no chlorinated dibenzodioxines were found among these chloroorganic compounds. This was confirmed by numerous analyses in other institutes in connection with a BMFT project.

When the dioxines in question are present in the material to be pyrolyzed, e.g. sewage sludge, their concentration is reduced to 75 % by a single pyrolysis cycle in the fluidized bed.

A further dehalogenation of the pyrolysis oil was achieved by dosing sodium vapour into the flow of pyrolysis gas by analogy with the Degussa process in which chlorine containing oils are dehalogenated within a few minutes in the liquid phase using sodium. In the gas phase at 500 °C the same process takes only seconds. Another possi-

TABLE 3 Components (wt.%) by the Pyrolysis of Different Plastic Wastes in a Fluidized Bed Process

Feed	Poly-ethylene	Plastics from household separation	Poly-ester	Poly-urethanes
Temperature (°C)	740	790	768	760
Hydrogen	0,75	0,70	0,30	0,23
Methane	23,6	17,5	3,8	3,5
Ethane	6,7	2,9	0,24	0,76
Ethene	19,8	9,8	1,5	5,4
Propane	0,08	0,08	0,01	0,01
Propene	5,5	1,3	0,08	1,7
Butenes	0,54	0,13	0,01	-
Butadiene	1,6	0,44	0,04	1,2
CO ₂	-	2,3	17,2	14,4
CO	-	1,2	27,4	8,7
HCN	-	-	-	0,31
HCl (CaCl ₂)	-	7,2	-	-
Hexenes	0,02	0,002	0,02	0,2
Benzene	19,1	13,8	18,3	5,0
Toluene	3,9	5,6	2,5	1,8
Styrene	0,5	3,1	2,1	0,01
Indene	0,25	1,0	0,41	1,1
Naphthalene	2,8	3,8	1,4	1,5
Methylnaphthalenes	0,63	0,84	0,25	0,69
Biphenyl	0,30	0,41	1,47	0,15
Fluorene	0,20	0,22	0,18	0,27
Phenanthrene/ Anthracene	0,52	0,66	0,08	0,62
Phenylnaphthalenes	0,08	0,36	0,21	0,01
Fluoranthene	0,08	0,26	0,02	0,01
Acetonitrile	-	-	-	0,58
Acrylnitrile	-	-	-	0,95
Benzonitrile	-	-	-	1,8
Ketones, Acetales	-	-	0,15	9,2
Acetophenone	-	-	1,4	0,3
Other compounds	11,3	9,0	11,7	34,1
Carbon black	1,75	6,4	7,1	0,5
Water	-	2,6	2,1	5,0
Inorganic compounds	-	5,3	-	-

bility is to carry the hydrogen chloride out of the reactor with ammonia. The ammonium chloride can be washed out easily [17].

Through a combination of waste oil dehalogenation with sodium, distillation of the oil, and pyrolysis of the distillation residue it is possible to regenerate more than 90% of pure hydrocarbons from waste oil. The common purification processes using sulfuric acid produce about 25 % of acid resins that are difficult to dispose of.

A semi-industrial plant that is working according to the Hamburg process of fluidized bed pyrolysis was built in Ebenhausen near

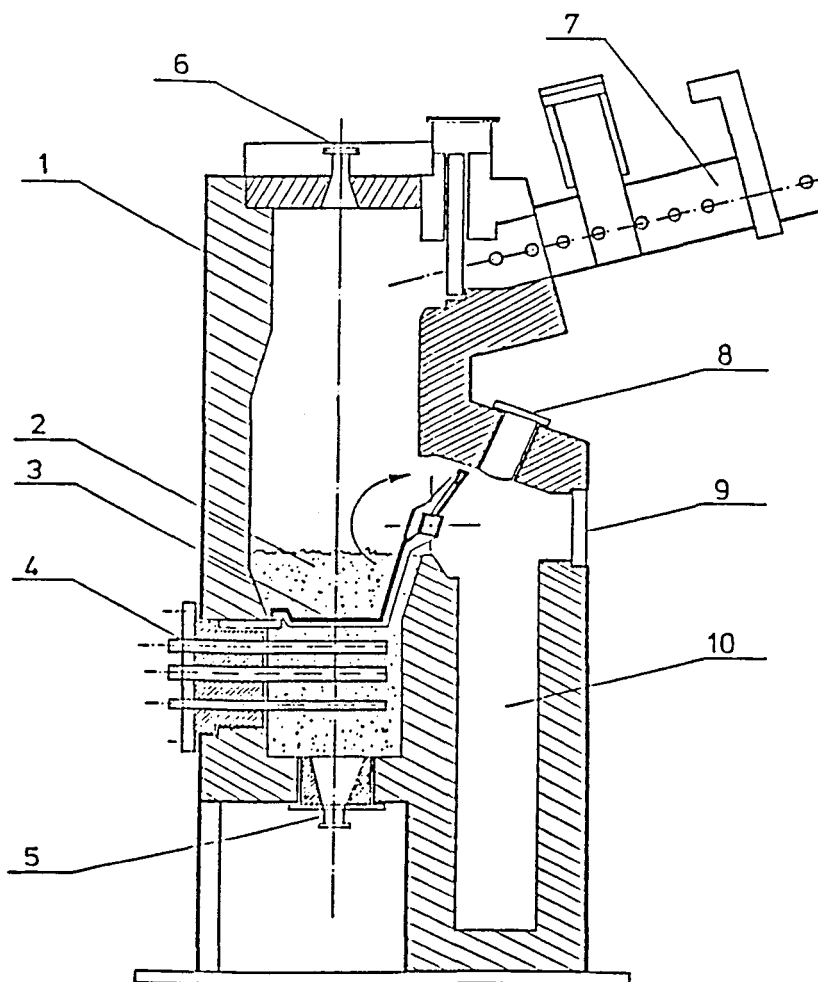


Figure 2 Flow Diagram of the Prototype Reactor for Whole-Tire Pyrolysis. (1) steel wall with fireproof bricking; (2) fluidized bed; (3) tiltable grate; (4) radiation fire tubes; (5) nozzles to remove sand and metal; (6, 8, 9) flange for observation and repairs; (7) gas tight lock; (10) shaft for steel cord

Ingolstadt and operated by the Asea Brown Boveri company (ABB) with a throughput of 5000 t/a.

The process has been shown to be successful for the pyrolysis of polyolefins. To process plastics with high PVC content it is necessary to scale down by one step (250 kg/h) and test the plant in continuous operation.

PYROLYSIS OF RUBBER

After experiments on the pyrolysis of plastic wastes had shown how individual pieces that were only slightly smaller than the reactor's inner diameter could be pyrolyzed in the fluidized bed a larger pilot plant with a 90 cm square fluid bed was used to decompose whole used tires (Fig. 2).

The tires were introduced to the reactor through a lock with pneumatic gates. The steel parts remaining in the reactor, after the pyrolysis was complete, were forked out of the fluidized bed by means of a grate at programmable intervals and deposited in a silo. The solid powdery products were carried out of the reactor by the gas stream and separated in a cyclone.

By pyrolysis of more than 4500 kg of whole used tires in several series of experiments it could be shown that whole tires with a maximum weight of 20 kg were completely pyrolyzed within 1,5 to 4 minutes at temperatures above 650 °C. The amount of pyrolysis gas produced in the process was sufficient to heat the reactor without additional supply of energy.

The products of the pyrolysis were obtained in the following five fractions (weight %):

Gas	15-20
Oil	20-30
Water	5-10
Carbon black and filling materials	30-40
Steel cord	5-20

Main components next to the solids carbon black and steel cord are methane, ethylene, ethane, benzene, and toluene.

It is also remarkable about the product spectrum that the hydrogen sulfide content was found to be below 0,3 wt-% in all experiments although some 2,0 % of sulfur are incorporated in the rubber. After the pyrolysis the main portion of sulfur is found in the carbon black fraction in the form of zinc or calcium sulfide. During the pyrolysis a reaction of sulfur containing fission products with alkaline filling materials takes place. The carbon black that is obtained is suitable for recycling as filling materials.

OUTLOOK

The necessity of economizing on the amount of raw materials taken from natural deposits to preserve sufficient amounts of resources for future generations and the need to minimize the production of wastes calls for an extensive recycling of raw materials.

Through pyrolysis of plastic wastes, used tires, waste oil residues

and other organic waste materials it is possible to obtain hydrocarbons and to generate petrochemicals and reusable carbon black from rubber products. Separate collection and sorting of wastes, as they are carried out in many industrialized nations at the moment, produce increasing amounts of materials that are suitable for recycling through pyrolysis. The new recycling processes also help to relieve the waste disposal problem and cut down the emission of pollutants. Several pyrolysis plants have been tested for years. Since oil and gas are generated as valuable substances, the profitability of the process depends largely on the price of mineral oil. It is to be expected that some of the processes can be established in the market under more favourable conditions as they are given by new waste collection laws.

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