Plastic recycling chemically using fluidized bed pyrolysis

Biplab Mohapatra
College of Engineering Bhubaneswar, Biju Patnaik University of Technology, Odhisa

ABSTRACT

Fluidized beds are used in the chemical recycling of many types of mixed, filthy, or filled plastic trash. Utilizing a fluidized bed reactor has several benefits, one of which is its high heat transmission. There are fewer adverse responses and a quick cracking process. Polyolefin is pyrolyzed to create olefins and oil. Aromatics are created if the pyrolysis gas is cycled while the fluidizing gas is present. By pyrolyzing poly(methylmethacrylate), one can extract up to 98% of methylmethacrylate and 77% of styrene from polystyrene. Terephthalic acid and very little soot were produced during the hydrolysis and pyrolysis of polyester. Large volumes of plastic trash may be recycled on an expensive scale through the pyrolysis of plastics in a fluidized bed.

Keywords: Chemical recycling Pyrolysis, Fluidized bed Polyolefin Plastics Monomer Recovery

1. Introduction

As a means of conserving resources and the environment, collecting and recycling plastic garbage has gained a lot of attention in recent years [1, 2]. Over the course of the last 30 years, plastics consumption has grown significantly more globally than that of other materials, rising from 100 million tons in 1989 to 369 million tons in 2019 [3]. Almost half of the plastics produced are wasted after being used for packaging or short-lived item and ends as waste. Cleaning and sorting the waste into various pure plastic types and then reusing these as raw materials to make new plastic items would be the most environmentally friendly approach. The entire amount of plastics collected cannot be recycled mechanically since many of the pieces of plastic are contaminated with metals, paper, other polymers, and/or fillers. Currently, in EU countries, about 30% of plastic trash is recycled and 70% is burned or dumped in landfills [3]. Since nearly all plastics are produced from crude oil and natural gas products, landfilling and incineration with a low energy recovery is not a long turn option. The chemical recycling can be a good alternative for miXed and contaminated plastics, to produce the valuable products [4]. Even articles obtained from mechanical recycled plastics will become a waste again. The number of recycle processes is limited, because extrusion process, depending on the polyolefin type, leads to chain scission with and without cross-linking, which reduces the mechanical properties of the final product [5].After the high increase of the crude oil prise in 1975, there was first interest in feedstock recycling of polymers to obtain back oil and gas from this hydrocarbon source. Another goal was to prevent the nature from landfilling of plastic materials decompose very slowly [6]. Today there are more different processes described for thermal cracking of polymer [7–10].

The low heat transfer coefficient, high energy required and the different impurities such as inorganic fillers, food residues, and paper, are the main problems of the plastics pyrolysis industry [11, 12]. An indirect heated fluidized bed pyrolysis process was used for the first time at the University of Hamburg which was able to recycle filled and contaminated plastics with the advantage of an excellent heat transfer [13]. The indirect heating prevents a miXture of incineration exhaust gases with the pyrolysis product gases. Up to this time, there were described only few fluidized bed processes for plastics cracking in Japan using air as fluidizing gas and the partially incineration by oXygen to cover the cracking heat. Polystyrene bottles were pyrolyzed by the Japan Fluid Cracking process (JFC) in a fluid sand bed reactor of 500 mm diameter and with a capacity of 1 t/day [14]. The oily products were contaminated by oXidized compounds. Later also polyolefin was pyrolyzed in a fluidized bed reactor [15].Catalytic cracking of plastics is a suitable way to change the product composition and reduce the required energy [16–19]. Catalysts lower the needed pyrolysis temperature, increase the reaction rate and the formation of isoalkanes and aromatics which are desirable for diesel fuel. The use of molecular sieves and amorphous silica-alumina catalysts for cracking of polyolefins into hydrocarbons has been widely studied [20, 21]. Fluid catalytic cracking is a possibility to increase the depolymerisation rate. The coke formation, fast catalyst deactivation, and often high catalyst/plastic ratio (5-10%) are the major problems in the catalytic pyrolysis of miXed plastics [22, 23]. Other pyrolysis processes for plastics use indirect or direct heated melting vessels, shaft reactors, rotary kilns all with a 5-10 times lower heat transfer [24, 25]. Gasification by partial incineration is another way for chemical recycling of plastics which results in the small number of formed compounds and easy separation. Another way to obtain higher product quality is the stepwise pyrolysis of plastic waste [26].In the Hamburg Institute, fluidized bed reactors were build up indifferent size which continuously work with plastics throughput of 30 g/ h up to 50 kg/h [14, 27].

The small laboratory reactors heated up electrically from outside, and the pilot plants by heating tubes with the incineration of gas (for starting propane, later in a run by pyrolysis gas). The advantage of the pyrolysis in a fluidized bed reactor is the excellent heat and mass transfer and process in the continuous mode. In the optimum fluidized bed reactors, the heat transfer is about 10 times better than in a melting vessel or tube reactor [28]. By decreasing residence time, the polymer is degraded under fast pyrolysis and resulted in less secondary reactions and side products [29]. By the pyrolysis of plastics in a fluidized bed reactor it is possible to receive mainly waxy products, oil, gas, or monomers in dependence of the used polymers and process parameters [30, 31]. The Hamburg process can be varied by two main process parameters such as pyrolysis temperature and kind of fluidizing gas (nitrogen, steam, cycled pyrolysis gas) to produce different products from plastic waste. Some plastics such as polystyrene (PS), poly (methyl methacrylate) (PMMA), or polytetrafluoroethylene (PTFE), can be pyrolyzed back into monomers [26]. Another possibility in the Hamburg process, is the pyrolysis of tires for recovery of oil and carbon black [28, 32].The experiments in the University of Hamburg were the start-ups for the building of three pilot plants by companies. The first pilot was built up in 1982 in Ebenhausen/Bavaria by DRP/ABB using a fluidized bed reactor with a diameter of 1800 mm and a capacity of 800 kg/h of miXed plastics and whole tires [33].

The second plant was built up in Grim- ma/GDR in 1984 for whole tires with a capacity of 5000 t/year. Also BP Chemicals has carried out first experiments in 1992 at the University of Hamburg and built then a pilot plant in Grangemouth/Scotland with a capacity of about 5000 t/year to obtain waxy products from miXed plastics, mainly polyolefin. These waxy products should be used as feedstock for naphtha-crackers. One benefit is that the waxy compounds can be tested for toxins prior to being added to crackers together with naphtha. The pilot plants only operate for a few years, mostly because it was not feasible to run them profitably at a time when the price of crude oil was falling.

Additionally, biomass such as wood (flash pyrolysis), lignin, bark, oil seed, and fat can be recovered along with oil, gas, and carbon black from oil sand and oil shale using the Hamburg process [34, 35].

2. Fluidized bed process

The fluidized bed pyrolysis process due to the short residence time, proper design, high contact surface, suitable heat and mass transfer, can create the good platform for the industrialization of the plastic pyrolysis process [18,36,37]. Accordingly, over the past few decades, the University of Hamburg has conducted extensive studies on gas phase pyrolysis and build up several plants. The arrangements of the different fluidized bed plants build up in the Hamburg institute are similar. The size and the heating are different. Small plants are heated from outside, the technical plant by fire tubes. Fig. 1 shows the scheme of a technical plant with a throughput of 10–30 kg/h [14]. Heart of the plant is a fluidized bed reactor with an inside diameter of

450 mm and a height of 900 mm.This sand bed is followed by a 1075 mm long free board zone in which no sand is fluidizing. The fluidized sand bed has a height of 650 mm and the sand a size of 0.3–0.7 mm.

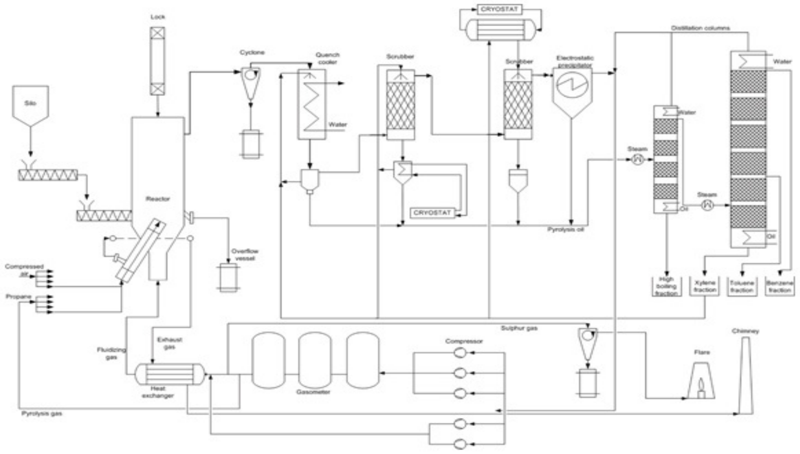

Fig. 1. Scheme of the pilot plant of the Hamburg process for pyrolysis of 30 kg plastics/hour in a fluidized bed reactor.

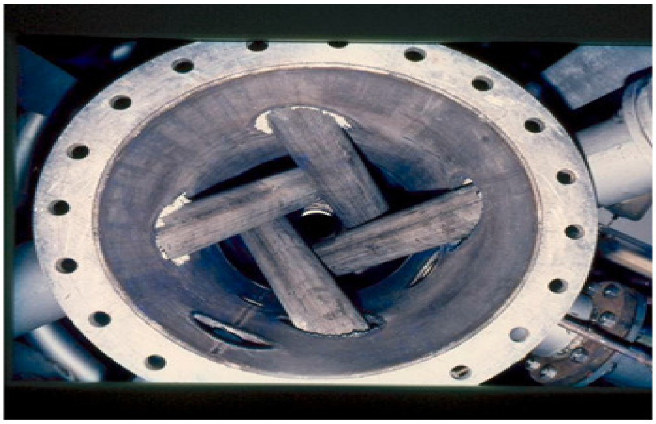

Fig. 2. View inside the fluidized bed reactor from the bottom with four heating tubes and the holes for feeding and empty residues.

The fluidized bed reactor isheated by four steel heating tubes which are using propane or the excess gas of the pyrolysis products. Fig. 2 shows a view inside the reactor. The four heating tubes can be seen as well as the side holes for the input of the plastics and one for the removal of impurities in the waste. For feeding, there are three possibilities of a screw conveyor, a tube for liquid feed from the side, and a look with two flap valves for material from the top of the reactor. The feeding system consist of a screw conveyor nearer which controls the amount of the feed and a fast moving screw conveyor directly at the reactor which brings the feed into the fluidized bed very fast to avoid the formation of glue and constipation. The screw conveyor is cooled by a water double jacket. The lock with the two flap valves is used for big parts of plastics or for material with a high viscosity. The capacity of plastics pyrolyzed the pilot plant is about 10–30 kg plastics/hour [14]. The bottom of the fluidized bed has an incline of about 15 ◦ and carries the bent gas-inlet tubes. These tubes are movable vertically so that their distance from the bottom of the fluidized bed can be varied. With this arrangement, there is a variable settling zone for small metal pieces and stones which cause in as impurities of the plastic waste [14]. Behind the fluidized bed reactor follows a cyclone for separation of solids. Then the product gases pass a washing cooler; in this cooler, Xylene is cycled and used as cooling medium and solvent. It washes the cooler free from waxes and other high boiling products. The heat transfer happens by a tube heat exchanger. After this, the cooled product gases pass two packed columns in which also Xylene is used as a quenching medium. This solvent is cooled down to –5 ◦C by a cryostat running with ethanol. Before the gas is compressed, it is cleaned up from fog by an electrostatic precipitator (electro-filter). The compression happens by 5 membrane compressors. Two of them transport the gas directly into the fluidized bed. The other three presses the gas into three steel gasometer.

From this a part of the gas is used for fluidizing the bed; it can be controlled and is miXed with the other gases. The right flow gas rate is the sum of both gases. If a high amount of flow gas rate is necessary, also three membrane compressors can directly pump the gas into the fluidized bed. The capacity of a compressor is higher if the pressure is less. The excess gas of the pyrolysis can be burned in the fire tubes or in a flare on top of the building [14].In a separate room (sure of explosion) the distillation and quenching columns are installed. In the two distillation columns, four distillation boiling cuts can be obtained from the pyrolysis oil. In the first column with a diameter of 150 mm and a length of 10.5 m, the fraction with a boiling point of more than 180 ◦C is separated from the distillation residue. In the second column with a diameter of 80 mm and a height of 8 m are obtained cuts of 80 ◦C, 110 ◦C, and 140 ◦C (Xylene). The xylene is used as quenching oil also in the coolers [14].

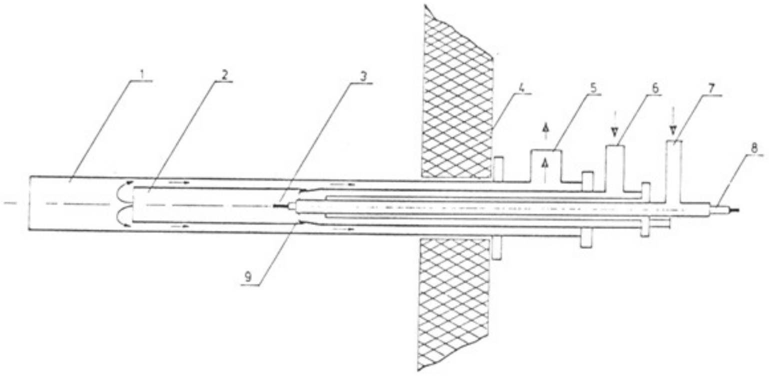

Fig. 3. Tube for heating of the fluidized bed . 1: Closed outer tube, 2: open inner tube, 3: burner head, 4: reactorwall, 5: outlet for exhaust gas, 6: inlet for air, 7: inlet for propane or pyrolysis gas, 8: spark plug, 9: burner head.

The plant is controlled by a process computer and equipped with numerous data-collecting instruments. Surveillance is carried out by continuous analysis of the room air as well as by explosion-limit controls. The pyrolysis gas is analyzed automatically by a gas chromatograph. All data obtained are registered to enable calculation of energy- and mass-balances. Some basic components are continuously monitored by infrared spectroscopy, i.e. ethylene in the pyrolysis gas, sulphur dioXide and oXygen in the exhaust gas [14].The heating of the fluidized bed by fire tubes was the demand to up- scale the plant. The heating value of the pyrolysis gas used for the tubes reaches 13.5 kWh/m3. The other larger demonstration plants build up in Ebenhausen and Grimma used the heating tubes, too. A scheme of the heating tube is shown in Fig. 3 [14].

The heating tube consists of two tubes. The outer tube is closed in front, while the inner tube is open. The flame is started at the burner lead and the exhaust gases passes between inner and outer tube. They are collected outside the reactor and go through a heat exchanger in which the incoming gas for fluidizing is heated up. There is no miXing of exhaust and product gas.The whole reactor is shown in Fig. 4. The steel reactor is isolated by rock wool and has a size of 220 cm. In one run, 200 to 500 kg of plastic materials can be pyrolyzed and between 50 and 150 litre of oil and 20 to 290 kg gas are obtained. The products are analyzed by GC and GC-MS [14] Fig. 5.

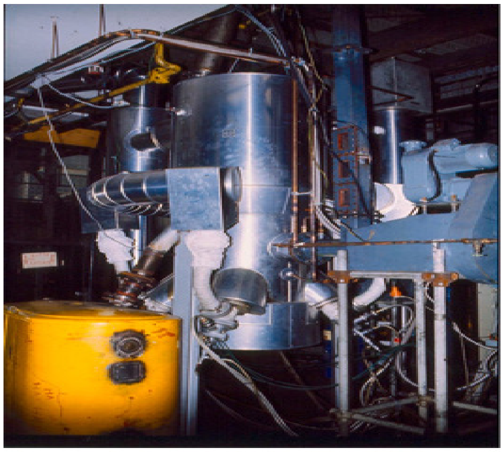

Fig. 4. Isolated fluidized bed reactor with the outside fire tubes (middle), the screw conveyor for feeding (right) and the drump for inorganic fillers from the overflow (left).

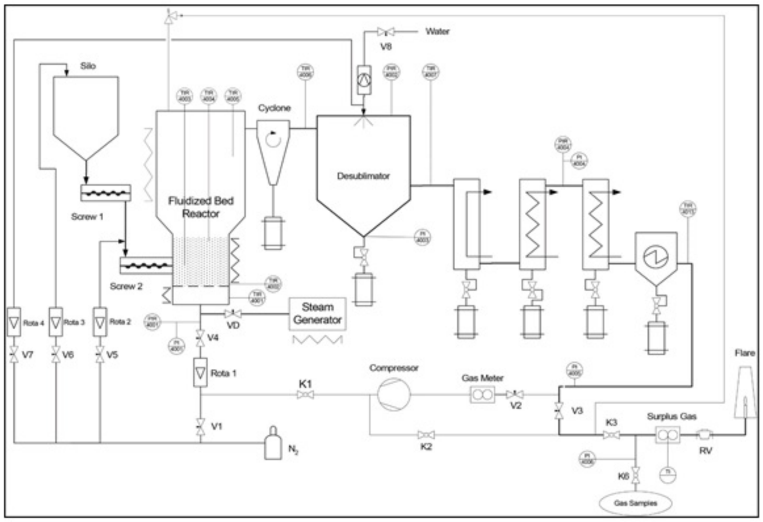

Fig. 5. Scheme of a 2-5 kg/h laboratory scale plant for the pyrolysis and hydrolysis of PET. From the right: feeding system, fluidized bed reactor, cyclone, steam generator, desublimator for terephthalic acid, cooling system and electro filter.

3. Pyrolysis of polyolefin

Nearly 50% of plastic waste consists of polyolefin in Europe [38]. This fraction can be separated and enriched by the density. A real plastic waste (B) collected by the German Dual System (DSD) from municipal packaging show a composition of 65% polyolefin, 25% polystyrene (PS), 1.2% polyvinylchloride (PVC), 1.5% polyester (PET) and paper, 1.3% other plastics, 4.1% water, and 1.9% fillers and metals. Table 1 show some detailed product composition of polyethylene, polypropylene, used syringes, and a miXed plastic fraction (B) from DSD pyrolyzed in a fluidized bed process [39,40] . The syringes were collected in a hospital. The gas and oil fractions were analyzed by GC, GC/MS and elementary analysis.

It can be seen that high amounts of methane, olefins and aromatics are formed at a pyrolysis temperature of 700–750 ◦C. The methane content varied between 8 and 20 wt %. It is the lowest at a pyrolysis temperature of 700 ◦C and using steam as fluidizing gas and increased by a higher temperature. The yield of ethylene is 10–30 wt%, of propene 7–15 wt%, of butenes 1–5 wt%, and of butadiene 1–6 wt%. The sum of olefins reaches more than 59 wt%. The other components produced are benzene with 7–18 wt%, toluene with 2–7 wt%. The product composi- tion of the pyrolysis of PE with pyrolysis gas is very similar to that ob- tained by a naphtha cracker. In general, depending on the type and design of the reactor, residence time, type of feed, reactor temperature and carrier gas, the products produced can change clearly [18,41,42].

To receive a maximum on olefins and butadiene from recycling polyolefin, it is necessary to have a short residence time of the product gases in the fluidized bed zone to have no secondary reactions. Long residence times can intensify the secondary reactions and produce more aromatics and coke [41,43,44]. The pyrolysis gas should not be circu- lated and used as fluidizing gas. For some experiment, steam was used as fluidizing gas [45,46]. An easy separation of the hydrocarbon products is possible by condensation the steam to water in a cooler. The results are shown in the last line of Table 1. Steam reduces the formation of soot in according to literature [47]. 30 wt% of ethylene and 15 wt% of propene are obtained using steam as fluidizing gas. These are amounts similar to those obtained by a naphtha cracker [47]. The pyrolysis of polypropylene gives similar results as the pyrolysis of polyethylene. The amount of methane and benzene is slightly higher the amount of ethylene and propene is lower. Similar results can be obtained if nitro- gen is used instead of steam as the fluidizing gas.Up to 50 wt% can be obtained as aromatics if the pyrolysis gas is cycled and used as fluidizing gas. The other 50 % are gas components. The benzene content reaches 18 wt% at a pyrolysis temperature of 740 ◦using PP as feed. If nitrogen or steam is used as fluidizing gas the con- centration of olefins in the fluidized bed reaction zone is less than the half compared to a run were the fluidizing gas which contains olefins is recycled. The aromatics are formed mainly by condensation reactions of olefins. Other main components of the polyolefin pyrolysis are ethylene and butene as gas, and toluene, naphthalene as aromatics. The amount of carbon soot is low. The light olefins in the pyrolysis gas can take part in the bimolecular reactions and increase the aromatics clearly [41,44]. Plastic fractions from household waste separation used syringes gives similar high amounts of olefins and aromatics. The styrene content is higher because of PS in the waste.

Table 1
Pyrolysis of polyethylene (PE), polypropylene (PP), used syringes (A), and mixed plastics (B) using pyrolysis gas (Pgas) or steam as fluidizing gas. Products in wt %, +: traces.

Feed Material	PE	PP	A	B	PE/ PP
Fluidizing Gas Pgas Pgas Pgas Pgas steam					
Temperature°C	740	740	720	740	700
Hydrogen	0.5	0.6	0.5	0.7	0.6
Methane	16.1	20.6	19.1	20.5	8.8
Ethane	5.3	4.4	6.6	2.2	2.8
Ethylene	25.4	13.3	15.4	10.3	30.0
Propane	+	0.2	0.1	0.1	0.1
Propene	9.0	7.1	9.9	8.0	15.0
Butene	0.5	2.4	3.0	1.1	3.8
Butadiene	2.8	2.0	1.4	1.0	6.4
Isoprene	+	0.1	0.3	0.1	0.1
Cyclopentadiene	1.0	0.5	2.1	0.3	0.2
Other aliphatic compounds	13.3	0.7	3.1	6.4	5.2
Benzene	12.2	18.1	13.6	17.4	7.4
Toluene	3.6	6.7	4.2	3.9	2.4
Styrene	1.1	0.1	0.5	8.7	1.4
Indane, Indene	0.3	0.8	0.5	2.5	0.6
Naphthalene	0.7	3.7	2.5	7.2	0.8
Methylnaphthalene	0.2	1.0	0.9	0.1	+
Diphenyl	+	0.4	0.3	0.1	+
Fluorene	+	0.3	0.2	0.2	+
Phenanthrene	+	0.6	0.5	0.6	0.1
Other aromatic compounds	5.1	5.4	8.2	6.6	4.6
Carbon monoXide	-	-	-	1.3	1.4
Carbon dioXide	-	-	-	0.6	1.3
Fillers	0.9	1.6	5.8	5.5	0.9

The hydrogen chloride (HCl) coming out from PVC in the miXed plastic waste is quantitatively absorbed by calcium oXide which was added in 5 % weight to the feed. The formed CaCl2 is separated in the cyclone after the fluidized bed reactor. There was found no chlorine in the gas fraction. The oil (feed material B) contains 15 ppm chloro- organic compounds, mainly chlorobenzene, the soot separated by the cyclone contains 18.4 wt%

$CaCl_2$. In the oil were no chlorinated dibenzodioXines (TCDD) or furane (TCDF) found (detection limit 0.01 ng/g). The results shows that there are no problems to recycle a real plastic waste in a fluidized bed process as long as the PVC content is less than 3 wt%.As shown, it is possible by a chemical recycling of polyolefin waste in a fluidized bed process at pyrolysis temperatures of 700-750◦C, to receive high amounts of olefins similar to that of a naphtha cracker and high amounts of aromatics.

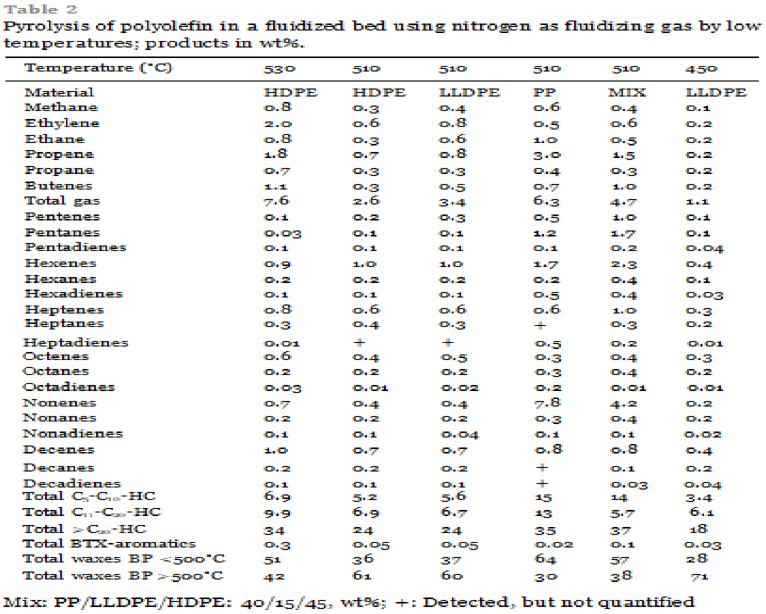

Table 2

Pyrolysis of polyolefin in a fluidized bed using nitrogen as fluidizing gas by low temperatures; products in wt%.

Temperature (°C)	530	510	510	510	510	450
Material	HDPE	HDPE	LLDPE	PP	MIX	LLDPE
Methane	0.8	0.3	0.4	0.6	0.4	0.1
Ethylene	2.0	0.6	0.8	0.5	0.6	0.2
Ethane	0.8	0.3	0.6	1.0	0.5	0.2
Propene	1.8	0.7	0.8	3.0	1.5	0.2
Propane	0.7	0.3	0.3	0.4	0.3	0.2
Butenes	1.1	0.3	0.5	0.7	1.0	0.2
Total gas	7.6	2.6	3.4	6.3	4.7	1.1
Pentenes	0.1	0.2	0.3	0.5	1.0	0.1
Pentanes	0.03	0.1	0.1	1.2	1.7	0.1
Pentadienes	0.1	0.1	0.1	0.1	0.2	0.04
Hexenes	0.9	1.0	1.0	1.7	2.3	0.4
Hexanes	0.2	0.2	0.2	0.2	0.4	0.1
Hexadienes	0.1	0.1	0.1	0.5	0.4	0.03
Heptenes	0.8	0.6	0.6	0.6	1.0	0.3
Heptanes	0.3	0.4	0.3	+	0.3	0.2
Heptadienes	0.01	+	+	0.5	0.2	0.01
Octenes	0.6	0.4	0.5	0.3	0.4	0.3
Octanes	0.2	0.2	0.2	0.3	0.4	0.2
Octadienes	0.03	0.01	0.02	0.2	0.01	0.01
Nonenes	0.7	0.4	0.4	7.8	4.2	0.2
Nonanes	0.2	0.2	0.2	0.3	0.4	0.2
Nonadienes	0.1	0.1	0.04	0.1	0.1	0.02
Decenes	1.0	0.7	0.7	0.8	0.8	0.4
Decanes	0.2	0.2	0.2	+	0.1	0.2
Decadienes	0.1	0.1	0.1	+	0.03	0.04
Total C_5-C_{10}-HC	6.9	5.2	5.6	15	14	3.4
Total C_{11}-C_{20}-HC	9.9	6.9	6.7	13	5.7	6.1
Total $>C_{20}$-HC	34	24	24	35	37	18
Total BTX-aromatics	0.3	0.05	0.05	0.02	0.1	0.03
Total waxes BP <500°C	51	36	37	64	57	28
Total waxes BP >500°C	42	61	60	30	38	71

Mix: PP/LLDPE/HDPE: 40/15/45, wt%; +: Detected, but not quantified

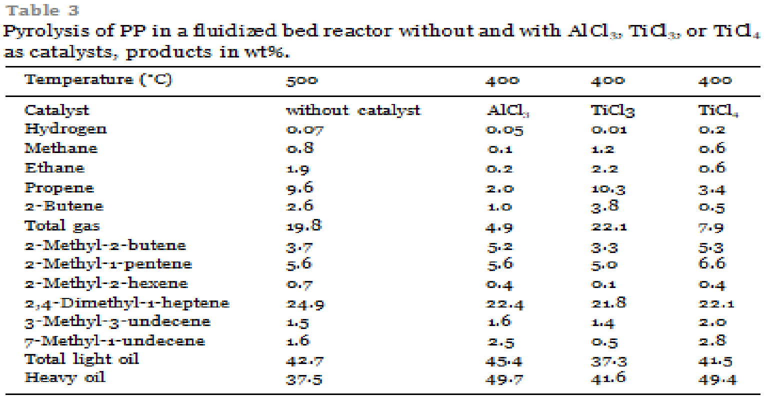

Table 3

Pyrolysis of PP in a fluidized bed reactor without and with $AlCl_3$, $TiCl_3$, or $TiCl_4$ as catalysts, products in wt%.

Temperature (°C)	500	400	400	400
Catalyst	without catalyst	$AlCl_3$	TiCl3	$TiCl_4$
Hydrogen	0.07	0.05	0.01	0.2
Methane	0.8	0.1	1.2	0.6
Ethane	1.9	0.2	2.2	0.6
Propene	9.6	2.0	10.3	3.4
2-Butene	2.6	1.0	3.8	0.5
Total gas	19.8	4.9	22.1	7.9
2-Methyl-2-butene	3.7	5.2	3.3	5.3
2-Methyl-1-pentene	5.6	5.6	5.0	6.6
2-Methyl-2-hexene	0.7	0.4	0.1	0.4
2,4-Dimethyl-1-heptene	24.9	22.4	21.8	22.1
3-Methyl-3-undecene	1.5	1.6	1.4	2.0
7-Methyl-1-undecene	1.6	2.5	0.5	2.8
Total light oil	42.7	45.4	37.3	41.5
Heavy oil	37.5	49.7	41.6	49.4

High boiling aliphatic oil or waxy products with only small amounts of gas and aromatics can be obtained by pyrolysis temperatures of 430–550 ◦C [48]. By increasing the pyrolysis temperature, the molecular weight of the final product is reduced and at higher temperatures (> 800 ◦C), and results in the light olefins [49]. Table 2 shows the product results using different kinds of pure polyolefin, high density poly- ethylene (HDPE), linear low density polyethylene (LLDPE), PP, and a miXture of 15% LLDPE, 45% HDPE, 40% PP (material MiX). Only 1 to 8 wt% of gas is produced depending on the temperature. At a pyrolysis temperature of 450 ◦C and LLDPE as feed only 1.1% gas is formed. Propene is the main gas component from PP. With a heat of combustion of some 47 MJ/kg, it can be used for the indirect heating of the fluidized bed. The waxes form a homologous series when pure polyethylene is used as feedstock. The alkenes, alkanes, and alkadienes of each group are main components [50]. The total amount of waxes reaches 93 to 99 wt%, while the total amount of aromatics is less than 0.5 wt%. The waxy products formed from real plastic waste can analysed on poisons and if free used as fuel or as feedstock for naphtha crackers [51]. This is a concept of British Petroleum (BP) who builds up a pilot plant with a capacity of 400t/year at BPs Grangemouth site in the UK. The polymers are introduced into a bubbling fluidized bed at a temperature of 500 ◦C. A Venturi loop system condenses the gas to give a waxy hydrocarbon product. The waxy product is filtered to remove fine solid particles and miXed with naphtha at a level of about 20%. This miXture can be used without danger in a steam cracker to give classic petrochemical products. Saturated olefins can be obtained by a combination of thermal cracking of polyolefin and hydro reforming using catalysts and hydrogen [52]. For heating the fluidized bed reactor by heating tubes up to a temperature of 550–700 ◦C and to compensate the cracking energy about 15% of the produced pyrolysis gas are used. Catalysts can reduce the pyrolysis temperature by about 100◦C offering a similar product composition and save cracking energy [53, 54]. Lewis- acids such as AlCl3 were investigated because these are in the gas phase under pyrolysis condition and by this very effective [55, 56]. Only 0.1% of catalyst has to be added to the polyolefin instead of 5 % using zeolithes as catalyst. It is possible to pyrolysis polypropylene at 400 ◦C adding AlCl3, TiCl3 or TiCl4 as catalysts. Without a catalyst the pyrolysis of PP is not possible at 400◦C in a continuously running fluidized bed process because the sand bed is blocked by not pyrolyzed PP. Table 3 shows the obtained pyrolysis products compared to an experiment without catalyst at 500 ◦C otherwise similar conditions. The catalyst is added together with the polypropylene.The product composition is similar of the pyrolysis at 500 ◦C without catalyst and at 400 ◦C with TiCl3 as catalyst. It shows that the use of only0.1 wt% of catalyst reduces the necessary pyrolysis temperature by 100 ◦C and save heating energy. Main single component at 400 ◦C is 2,4- dimethyl-1-heptene with about 22 wt%, a trimeric propene. The reason for this high amount of trimeric propene may be the homogeneous temperature in the fluidized bed. Other single components are propene, 2-butene, 2-methyl-2-butene, and 2-methyl-1-pentene. AlCl3 and TiCl4 produce less propene and other gas components than TiCl3. The sum of light oil and heavy oil is about 80 wt%. These fractions are useful as feedstock (syncrude oil) for a naphtha cracker. When higher amounts of catalysts were added secondary reactions were caused and the selectivity of the catalysts decreased. Running the reaction at temperatures over 500 ◦C with these catalysts, the decomposition of the catalysts was caused. There were found no chlorinated hydrocarbons in the products. The amount of 0.1 wt% of catalyst is too low. Also no aromatics could be analysed. Using zeolites as catalysts aromatics could be obtained in high quantities [55, 56].

3. Monomer recovery from PMMA

The pyrolysis of PMMA waste is one of the few technical processes for chemical recycling of plastics which works economically [57]. The reason for this is the relatively high price of PMMA compared to stan- dard plastics and the possibility to recover up to 95 % of methyl- methacrylate (MMA) as monomer [58–60]. If PMMA is heated to a temperature of more than 400◦C, it will decompose almost completelyinto the monomer [60].For the depolymerisation of PMMA, molten metal bath, dry distil- lation, extruder processes and fluidized bed processes are used [61,62]. The depolymerisation reactor of a molten metal bath consists essentially of a gas or oil heated metal bath. The metals used are those which have a low melting point such as tin and lead. The PMMA regrind is fed from the storage silos onto the stirred metal bath. Bath temperature and a residence time of some minutes are important for a good yield and quality of the MMA [57,63,64].

In contrast to this, the residence time of the products in a fluidized bed lies between 1 and 5 s [65]. Other advantages in using a fluidized bed reactor for the depolymerization are the low contamination of organometallic compounds in the products and the possibility to use filled PMMA [66]. The filler will contaminate the molten metal bath while in a fluidized bed the often expensive fillers can be recovered. Today, PMMA is mainly filled by silica, quartz, aluminium hydroXide and other inorganic fillers. For special uses, the polymer is crosslinked. These facts give a lot of problems for a material but not for a chemical recycling [66].

Temperatures of 450–550 ◦C were used for pyrolysis of PMMA in a fluidized bed process. Table 4 shows the results of three runs with pure pellets and one with tinted waste from collected automobile rear lights (Waste). Main product is the monomer MMA with a maximum con- centration of 97% [66].The influence of temperature on the monomer concentration is small in the range of 450 to 490 ◦C but is drastically in the temperature range from 490 to 590 ◦C. The MMA concentration decreases to 51% at a pyrolysis temperature of 590 ◦C. Even from waste material 91% of MMA can be recovered. The other liquid components (1,2 wt%) are mainly small amounts of methyl isobutyrate and methyl acrylate (MA). The amount of gas increases with raising the temperature from 2 wt% at 450 ◦C to 42 wt% at 590 ◦C. The gas consists mainly of methane, ethylene, propene, carbon monoXide, and carbon dioXide. The amount of carbon black (soot) is small [66].Mechanistically, the pyrolytic conversion of PMMA to its monomer is a radical process [57].The purity of the recovered MMA is high enough to be polymerized again to PMMA without any further purification [66].

Table 4

Products of PMMA pyrolysis at different temperatures (components in wt%).

Temperature	Pure pellets 450 °C	Waste 490 °C	590 °C	490 °C
Carbon monoXide	0.1	0.4	13.6	1.1
Carbon dioXide	1.1	1.5	8.7	4.1
Methane	0.2	0.3	3.9	0.8
Ethylene	0.1	0.1	2.5	0.3
Ethane	0.3	0.6	0.9	0.2
Propene	0.1	0.2	7.0	0.5
Butene	0.1	0.2	1.2	0.6
Pentene	0.1	0.2	0.6	0.2
Other gases	0.1	0.2	3.8	0.3
Methyl isobutyrate	0.1	0.1	0.3	0.1
Methyl acrylate	0.3	0.3	1.4	0.2
Methyl methacrylate	97.2	95.5	54.9	91.0
Other esters	0.1	0.2	0.9	0.1
Carbon black	0.1	0.2	0.3	0.5

Table 5

Pyrolysis of PS in a fluidized bed reactor, products in wt%, +: traces.

Temperature (°C)	515	540	540	515
Residence time (s)	3.2	3.2	1.5	1.5
Methane	0.2	0.5	0.2	0.1
Ethylene	0.3	0.6	0.4	0.1
Ethane	0.1	0.2	0.1	0.0
Propene	0.2	0.3	0.2	0.1
Total gas	0.8	2.0	0.9	0.3
Benzene	0.3	0.1	0.1	0.1
Toluene	2.2	2.9	2.3	2.0
Ethylbenzene	0.7	0.9	0.3	0.4
Styrene	71.9	68.7	73.4	74.9
Methylstyrene	2.3	3.2	2.2	2.3
Indene	0.4	0.6	0.5	0.3
Diphenylethane	1.3	2.2	1.7	0.9
Diphenylpropane	2.0	3.1	2.5	1.4
Styrene dimer	6.6	4.3	6.1	4.9
Phenylnaphthaline	1.1	0.7	0.2	0.2
Higher styrene oligomers	4.8	9.1	7.3	9.3
Other components	4.8	1.4	2.2	3.0
Total oil	98.9	97.8	99.0	99.7
Soot	0.2	0.4	0.1	0.2

5. Pyrolysis of polystyrene (PS)

Polystyrene is another polymer which can be pyrolyzed mainly into the monomer [67–69]. The needed pyrolysis temperature is higher than in the case of PMMA as feedstock. The pyrolysis temperature can be reduced using catalysts such as iron oXides [70].EXperiments in the fluidized bed reactor were carried out between 515 and 540 ◦C and with residence times of the gas in the fluidized bed reactor of 3.2 and 1.5 seconds. A higher gas flow rate of the fluidizing gas gives a shorter residence time of all gases in the fluidized bed. The molecular weight of the used unfilled PS was 225000. The whole product composition is shown in Table 5. Main product in all runs is the liquid. Up to 99.7 % can be obtained. The produced gas fraction is with 0.3–2 wt% very low and contains mainly of methane, ethylene, ethane, and propene. The gas content increases with the pyrolysis temperature. The oil content is decreasing with increasing pyrolysis temperature and decreasing residence time representing less secondary reactions. The styrene content is decreasing with increasing temperature and reaches 74.9 wt% by 519 ◦C and the shorter residence time of 1.5 s. Other main liquid components are dimeric and other oligomeric styrene components. The content reaches 14 wt% of these oligomers. Other components formed by the pyrolysis of polystyrene are toluene, methylstyrene, diphenylethane/propane, and other aromatics. The styrene oligomers show secondary isomerization reactions. These make it difficult to pyrolyze them in a following step into higher amounts of styrene. Other aromatics but not styrene are obtained by the degradation of the styrene oligomers. This means that the optimum recovery of styrene from PS is about 75 wt% and cannot be increased to higher values. For a polymerization into new PS the liquid must be cleaned up by distillation.

6. Hydrolysis of polyester (PET)

Polyester like poly (ethylene terephthalate) (PET) is a polymer with a fast growing market not only for the production of bottles but also for films, fibers, and tapes. Material recycling is the most used methods for the recycling of PET. This technic is not possible for a miXed and contaminated or with solid material filled polyester. For these wastes the feedstock recycling by pyrolysis or by hydrolysis is a possibility to receive petrochemicals [71–73]. The hydrolysis of PET plastic waste is increased in alkaline medium [74]. The pyrolysis of PET in a fluidized bed leads to CO, CH4, other gases and mainly aromatic compounds and using catalysts such as Ca(OH)2 to a high yield of benzene [75–77]. Terephthalic acid can be obtained in the fluidized bed process if steam is used as fluidizing gas. The ester is hydrolysed into terephthalic acid and glycol which decomposes at the pyrolysis temperature to gas compounds.To include the hydrolysis step into the process the pyrolysis plant has to be added by a desublimator for the terephthalic acid. Fig. 3 shows the laboratory scheme for the hydrothermal pyrolysis of 1–3 kg/h PET.

The electrically heated fluidized bed reactor of stainless steel has a diameter of 130 mm. Quartz sand (9 kg) with diameters between 0.3 and 0.5 mm led to a high of 480 mm of the fluidized bed. The steam is produced by a steam generator and heated up to 400 –500 ◦C in the fluidized bed. The PET pellets enter the reactor by a screw conveyor system. The gaseous products leave the reactor into a separation and cooling part. In a cyclone sand and fillers are removed and enter at 160–180◦C cooled down desublimator in which the terephthalic acid is condensed. After that the remaining gas is cooled to 10◦C in additional coolers to remove water and other products. Aerosols are removed in an electrostatic precipitator. The cleaned gaseous products are measured by a gas meter and analysed by GC-FID and HPLC-MS. Table 6 shows the result of the hydrothermic pyrolysis of PET by different temperatures [76,77]. For three of the experiment pure PET pellets were used, for the run by 485 ◦C pellets from PET waste. In all experiments terephthalic acid is the main product. The best yield is given by a temperature of 450 ◦C. Other main products are the oligomers, monoterephthalate glycol ester (TG) and diterephthalate glycol ester (TGT). While the concentration of terephtalic acid is nearly constant, the amount of TG decreased with an increasing pyrolysis temperature from 15 wt% by 401 ◦C to 5.3 wt% at 505 ◦C. The content of TGT increases with the temperature. Differences in the residence time of the gas (mainly steam) in the fluidized bed show nearly no effect. Real PET waste gives very similar results as the use of pure PET pellets. Compared to the content of terephthalic acid in the PET by the hydrothermic pyrolysis in a fluidized bed about 95 wt% can be recov- ered as acid, TG, and GTG. The main part of the glycol is destroyed into gaseous products [76,77].

7. Pyrolysis of other polymers

Beside the described polymers also polyamide (PA), polyurethane (PUR), and polytetrafluoroethylene (PTFE), were used as feedstock for pyrolysis [78–80]. The fluidized bed process is very flexible for different feeds and process parameters. The pyrolysis of pure polyvinylchloride (PVC) waste is difficult because the main product formed is HCl next to coke. Up to 3 wt% of PVC in the plastic waste can be handled by adding calcium oXide into the fluidized bed to absorb the HCl. The formation of chlorinated dioXins like PCDF is under the detection limit [81].Table 7 shows the pyrolysis products of PA and PUR using the laboratory plant at different temperatures. PA66 (Nylon) is formed by polycondensation of hexamethylenediamine and adipiic acid. Two different polyurethanes are the polyaddition product of methylene-4-4’- diphenyl-diisocyanate (MDI) and propyleneoXide-polyethylene glycol (PUR I) and toluylene-diisocyanate (TDI) and polypropyleneoXide glycol (PUR II) [82]. For the pyrolysis of PA and PUR II pyrolysis gas was used for fluidizing and for PUR I steam. The pyrolysis of PA66 produces at a temperature of 510 ◦C only few gas components (4.2 wt%) and high amounts of a high boiling oil fraction (50.8 wt%).Much more gas (30.3 wt%) is formed at a pyrolysis temperature of 630 ◦C and less high boiling oil (24.7 wt%). The main components in the gas fraction are carbon oXides, methane, ethene and propene. Some nitriles up to 3 wt% were analyzed. Hydrogen cyanide is formed only in traces. The amount of aromatics is low at a pyrolysis temperature of 510◦C. and reaches 15.8 wt% at a temperature of 630

◦C. The total oil content is 90 wt% and contains a lot of oXygen and nitrogen containing compounds [82]. The composition of products is different if polyurethanes are pyrolyzed at a temperature of 750 ◦C (Table 7, PUR I and PUR II). High amounts of gases are formed (65 wt%). Main components are carbon monoXide, methane and ethylene. In contrast to the pyrolysis of poly- amide hydrogen cyanide (HCN) is formed. The amount HCN can be reduced to a tenth using partially steam as fluidising gas (PUR I). The other differences in the product composition are small between PUR I and PUR II. The sum of nitriles is comparable for the pyrolysis of polyamides and polyurethanes with values of about 3 wt%. The amount of high boiling oil is much lower. The obtained oil from polyamides and polyurethanes have a high caloric value of 50 MJ/kg [82].

In miXed plastic fractions from house hold waste separation are normally less than 2 % of polyamides and polyurethanes. If this part is based on the calculated composition of a wet pyrolysis gas, the toXic hydrogen cyanide is less than 5 ppm and the amount of nitriles in the oil is less than 50 ppm. With these concentrations the oil can be used as feedstock for naphtha crackers or other parts [82].Fluoropolymers are technical polymers with very special properties and applications. Their properties are derived mainly from the strong carbon-fluorine bond energy of 507 kJ mol—1, compared with typical energies of 415 kJ mol—1 for C-H or 348 kJ mol—1 for C-C bonds [83, 84]. The most important fluoropolymer is polytetrafluoroethylene (PTFE). In order to improve the properties of PTFE it is often com- pounded with glass fibers, carbon fibers, coal/soot, bronze, steel, molybdenum sulphide or polymers like polyimides or poly(phenylene sulphide) [83,85].

Slow decomposition of PTFE occurs above the application temperature of 260 ◦C. However, for a noticeable decomposition to occur, temperatures above 400 ◦C are needed. The primary decomposition products are tetrafluoroethylene (TFE) and difluorocarbondiradicals (CF2). Further products are formed by secondary reactions depending on temperature, reaction pressure and reaction atmosphere. The typical main products are TFE, hexafluoropropene (HFP), cycloperfluorobutane (c-C4F8) and other fluorocarbons. Most of these substances are non-toXic but highly toXic substances like perfluoroisobutene or fluorophosgene are also formed under some reaction conditions. Early results were reported on the pyrolysis of PTFE at a temperature of 600 ◦C and under vacuum (7 × 102 Pa) receiving 97 % of TFE as product [86, 87]. Under an atmospheric pressure of 1.103 × 105 Pa this yield dropped down to only 16 %, whereas the yields of HFP and c-C4F8 increased. In a fluidized bed the pyrolysis can be carried out under normal pressure using nitrogen as fluidizing gas (Table 8) [83].

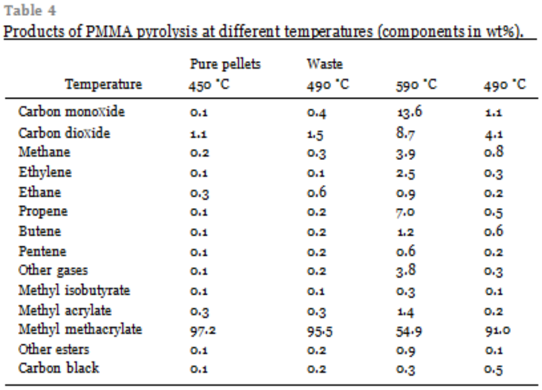

Table 4

Products of PMMA pyrolysis at different temperatures (components in wt%).

Temperature	Pure pellets 450 ˚C	Waste 490 ˚C	590 ˚C	490 ˚C
Carbon monoXide	0.1	0.4	13.6	1.1
Carbon dioXide	1.1	1.5	8.7	4.1
Methane	0.2	0.3	3.9	0.8
Ethylene	0.1	0.1	2.5	0.3
Ethane	0.3	0.6	0.9	0.2
Propene	0.1	0.2	7.0	0.5
Butene	0.1	0.2	1.2	0.6
Pentene	0.1	0.2	0.6	0.2
Other gases	0.1	0.2	3.8	0.3
Methyl isobutyrate	0.1	0.1	0.3	0.1
Methyl acrylate	0.3	0.3	1.4	0.2
Methyl methacrylate	97.2	95.5	54.9	91.0
Other esters	0.1	0.2	0.9	0.1
Carbon black	0.1	0.2	0.3	0.5

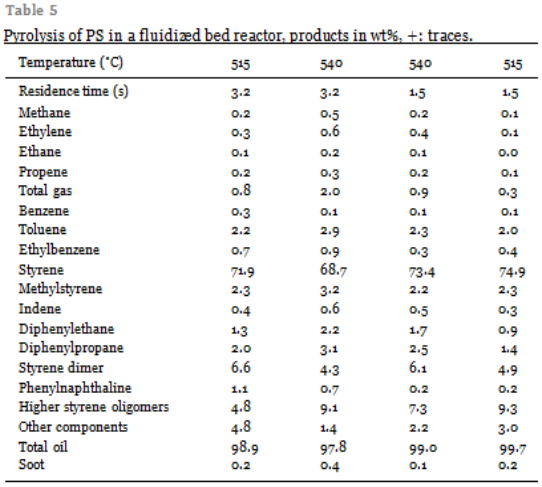

Table 5

Pyrolysis of PS in a fluidizæd bed reactor, products in wt%, +: traces.

Temperature (˚C)	515	540	540	515
Residence time (s)	3.2	3.2	1.5	1.5
Methane	0.2	0.5	0.2	0.1
Ethylene	0.3	0.6	0.4	0.1
Ethane	0.1	0.2	0.1	0.0
Propene	0.2	0.3	0.2	0.1
Total gas	0.8	2.0	0.9	0.3
Benzene	0.3	0.1	0.1	0.1
Toluene	2.2	2.9	2.3	2.0
Ethylbenzene	0.7	0.9	0.3	0.4
Styrene	71.9	68.7	73.4	74.9
Methylstyrene	2.3	3.2	2.2	2.3
Indene	0.4	0.6	0.5	0.3
Diphenylethane	1.3	2.2	1.7	0.9
Diphenylpropane	2.0	3.1	2.5	1.4
Styrene dimer	6.6	4.3	6.1	4.9
Phenylnaphthaline	1.1	0.7	0.2	0.2
Higher styrene oligomers	4.8	9.1	7.3	9.3
Other components	4.8	1.4	2.2	3.0
Total oil	98.9	97.8	99.0	99.7
Soot	0.2	0.4	0.1	0.2

Main pyrolysis products are TFE, c-C4F8, and HFP. 78.5 wt% of TFE can be obtained at a pyrolysis temperature of 605 ◦C. The amount of c- C4F8 increases from 4.6 wt % at 605 ◦C to 5.9 wt % at 650 ◦C and 16.1 wt% at 700 ◦C. Other fluorocarbons and carbon oXides were found only in traces. SiF4 and soot are formed by reactions of fluorocarbons with sand used as fluidizing medium.The amou nt of SiF4 increased with increasing temperature. It is possible to use also filled PTFE material for the pyrolysis. For a bronze filled PTFE the yield of TFE is significantly reduced to 60 wt% at a temperature of 600 ◦C by a catalytic effect. Other fillers show no effect [86,87].

8.Conclusions

The pyrolysis of mixed, contaminated, or packed plastics is an alternate technique for recycling plastics, recovering petrochemicals, and protecting the environment because the entire waste of plastics cannot be mechanically recycled. It might be demonstrated that pyrolysis of several plastic types in a fluidized bed reactor is feasible and produces a variety of monomers, hydrocarbon gas, and oil. The procedure is highly adaptable and operates continually. Less side reactions occur because of the fluidized bed's quick reaction time, which is facilitated by the good heat transfer. Polyolefin can yield high concentrations of ethylene and propene. About 15% of the product gas or oil must be utilized for heating the plant; the remaining 85% must be used for other purposes. The potential for pyrolysis of plastics based on the fluidized bed process parameters is compiled in Table 9. around 400–550 °C, polyethylene (PE) and polypropylene (PP) mostly produce waxy compounds; around 700 °C, they produce gas and oil. Furnaces are created by fluidizing pyrolysis gas. In order to reproduce ethylene and propylene for the synthesis of fresh polyolefin, naphtha crackers can be fed with the waxy product and heavy oil. Pyrolysis in a fluidized bed technique can recover large quantities of monomers from specific polymers. PMMA wastes can yield up to 98 weight percent of MMA when they are pure, filled, or colored. PMMA wastes that are pure, filled, or colored can provide up to 98 weight percent of MMA. The percentage of recoverable styrene in polystyrene is only approximately 77 weight percent; oligomers make up the remaining portion. Steam is used as a fluidizing gas in a fluidized bed process to hydrolyze polyester (PET). At low temperatures, aromatics and gas are produced by polyamides. Soot formation is minimal. It is possible to pyrolyze PTFE to produce large quantities of monomers like TFE and HEP. One possibility for an industrial use is the pyrolysis of plastics in a fluidized bed reactor.

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