Recent Advances in the Chemical Recycling of Polymers (PP, PS, LDPE, HDPE, PVC, PC, Nylon, PMMA)

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1. Introduction

During last decades, the great population increase worldwide together with the need of people to adopt improved conditions of living led to a dramatical increase of the consumption of polymers (mainly plastics). The world's annual consumption of plastic materials has increased from around 5 million tones in the 1950s to nearly 100 million tones today. Since the duration of life of plastic wastes is very small (roughly 40% have duration of life smaller than one month), there is a vast waste stream that reaches each year to the final recipients creating a serious environmental problem. The presently most common practice of handling such waste streams is to incinerate them with energy recovery or to use them for land-filling. Disposing of the waste to landfill is becoming undesirable due to legislation pressures (waste to landfill must be reduced by 35% over the period from 1995 to 2020), rising costs and the poor biodegradability of commonly used polymers (Achilias et al., 2009). Therefore, recycling seems to be the best solution.

The recycling of waste polymers can be carried out in many ways. Four main approaches have been proposed presented in Scheme 1 (Karayannidis and Achilias, 2007; Scheirs, 1998):

1. *Primary recycling* refers to the 'in-plant' recycling of the scrap material of controlled history. This process remains the most popular as it ensures simplicity and low cost, dealing however only with the recycling of clean uncontaminated single-type waste.
2. *Mechanical recycling (or secondary recycling)*. In this approach, the polymer is separated from its associated contaminants and it can be readily reprocessed into granules by conventional melt extrusion. Mechanical recycling includes the sorting and separation of the wastes, size reduction and melt filtration. The basic polymer is not altered during the process. The main disadvantage of this type of recycling is the deterioration of product properties in every cycle. This occurs because the molecular weight of the

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recycled resin is reduced due to chain scission reactions caused by the presence of water and trace acidic impurities. Strategies for maintaining the polymer average molecular weight during reprocessing include intensive drying, reprocessing with degassing vacuum, the use of chain extender compounds, etc.

3. *Chemical or Feedstock recycling (tertiary recycling)* has been defined as the process leading in total depolymerization of PET to the monomers, or partial depolymerization to oligomers and other chemical substances. The monomers could subsequently re-polymerized to regenerate the original polymer.

4. *Energy recovery (Quaternary recycling)* refers to the recovery of plastic's energy content. Incineration aiming at the recovery of energy is currently the most effective way to reduce the volume of organic materials. Although polymers are actually high-yielding energy sources, this method has been widely accused as ecologically unacceptable owing to the health risk from air born toxic substances e.g. dioxins (in the case of chlorine containing polymers).

Apart from the aforementioned methods, direct reuse of a plastic material (i.e. PET) could be considered as a "zero order" recycling technique (Nikles and Farahat, 2005). In a lot of countries it is a common practice PET-bottles to refilled and reused. However, this should be done with a great care since plastic bottles are more likely than glass to absorb contaminants that could be released back into food when the bottle is refilled. Moreover, refill of a PET-bottle with a high-alcoholic-degree drink may lead to degradation of the macromolecular chains with unexpected results.
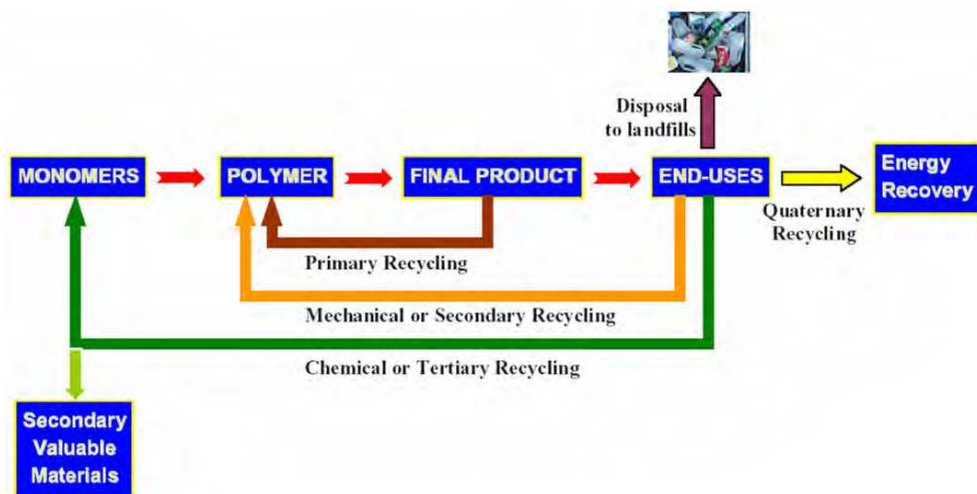
Scheme 1. Polymer Recycling Techniques.

The objective of a plastic management policy, in accordance with the principles of sustainable development (development that meets the needs of present generation without compromising the ability of future generations to meet their needs), should be not only the reuse of polymeric materials but also the production of raw materials (monomers), from which they could be reproduced, or other secondary valuable products,

which could be useful as feedstock for a variety of downstream industrial processes or as transportation fuel. In this sense, among the techniques proposed for recycling of waste polymers the most challenging method is chemical or feedstock recycling and various technologies have been successfully demonstrated and continue to be developed (Achilias and Karayannidis, 2004).

The aim of this chapter is to provide a critical review of the methods proposed and/or applied during mainly **the last decade**, on the chemical recycling of polymers. In this way, the state-of-the-art of the chemical recycling methods of several polymers will be presented. Polymers that will be studied include the widely used plastics, based on poly(ethylene terephthalate) (PET), polypropylene (PP), polystyrene (PS), low density polyethylene (LDPE), high density polyethylene (HDPE), poly(vinyl chloride) (PVC), polycarbonate (PC), poly(methyl methacrylate) (PMMA) and nylon.

2. Chemical recycling of poly(ethylene terephthalate) PET

PET is a polyester with functional ester groups that can be cleaved by some reagents, such as water (hydrolysis), alcohols (alcoholysis), acids (acidolysis), glycols (glycolysis), and amines (aminolysis). Thus, chemical recycling processes for PET are divided as follows: (i) Hydrolysis, (ii) Glycolysis, (iii) Methanolysis and (iv) other processes (Scheme 2). According to the reagent used different products are obtained (Karayannidis and Achilias, 2007; Karayannidis et al. 2006; Karayannidis et al., 2005; Karayannidis et al. 2002; Kosmidis et al., 2001). The different process options for chemical recycling of PET waste may be categorized as follows: (i) regeneration of base monomers (methanolysis for dimethyl terephthalate (DMT) and hydrolysis for producing pure Terephthalic acid (TPA) and ethylene glycol (EG)); (ii) conversion into oligomers (glycolysis or solvolysis); (iii) use of glycolyzed waste for value-added products; (iv) conversion into speciality chemicals by aminolysis or ammonolysis; (v) conversion into speciality intermediates for use in plastics and coatings.
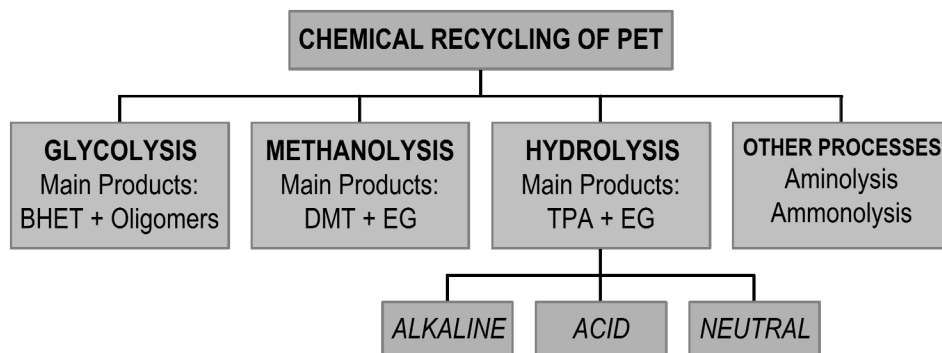
Scheme 2. Chemical recycling techniques of PET.

Recently, recycling of PET using hydrolysis, glycolysis and aminolysis under microwave irradiation has been proposed (Achilias et al., 2010; Achilias et al., 2011; Siddiqui et al., 2010). PET recycling in a microwave reactor has been proved a very beneficial method resulting not only in material recovery but also in substantial energy saving.

This section will not be presented in detail here because it is the subject of another chapter of this book. Interested reader can find extensive details on the techniques used for the chemical recycling of PET in several recent review papers appeared in literature (Scheirs, 1998; Karayannidis and Achilias, 2007).

3. Chemical recycling of polypropylene

3.1 Introduction

Condensation polymers like PET or Nylon, can undergo chemolysis with different reagents to produce mainly the monomers from which they have been produced or other oligomers. In contrast, vinyl polymers, such as polyolefins (PP and PE) cannot be degraded with simple chemicals to their monomers due to the random schission of the C-C bonds. Two main chemical recycling routes are the thermal and catalytic degradation of these polymers. In thermal degradation, the process produces a broad product range and requires high operating temperatures, typically more than 500◦C and even up to 900 ◦C. Thermal cracking of polyethylene and polypropylene is usually carried out either in high temperatures (>700 ◦C), to produce an olefin mixture (C1–C4) and aromatic compounds (mainly benzene, toluene and xylene) or in low temperature (400–500 ◦C) (thermolysis) where three fractions are received: a high-calorific value gas, condensable hydrocarbon oil and waxes. In the first case, the objective is to maximize the gas fraction and to receive the olefins, which could be used after separation as monomers for the reproduction of the corresponding polyolefins. Cracking in lower temperatures leaves a waxy product in the reactor that mainly consists of paraffins together with a carbonized char. The gaseous fraction can be used for the supply of the energy required for the pyrolysis after burning. The liquid fraction mainly consists of linear olefins and paraffins with C11–C14 carbon atoms with only traces of aromatic compounds (Aguado and Serrano, 1999). Thermal cracking of polyolefins proceeds through a random scission mechanism in four steps: initiation, depropagation, inter- or intra-molecular hydrogen transfer followed by β-scission and termination. In general, thermal cracking is more difficult in HDPE followed by LDPE and finally by PP.

Due to the low thermal conductivity of polymers together with the endotherm of cracking, thermal pyrolysis consumes large amounts of energy. Thus, catalytic technologies have been proposed to promote cracking at lower temperatures, resulting in reduced energy consumption and higher conversion rates. Furthermore, use of specific catalysts allows the process to be directed towards the formation of a narrower distribution of hydrocarbon products with a higher market value. Heterogeneous catalysis has been investigated extensively using solids with acid properties. Zeolites of the kind employed in the catalytic cracking of hydrocarbon feedstocks (Y, ZSM-5, Beta) as

well as other well-known acid solids like silica–alumina, alumina and clays are being the most studied. Mixtures of these catalysts like SAHA/ZSM-5, MCM-41/ZSM-5 have been also used. Cracking with acid catalysts takes place through the formation of carbocations, which requires the presence of strong acidic regions. Acid strength and textural properties are the main parameters dictating the performance of acid solids in the catalytic conversion of polymers. Porosity, surface area characteristics and particle size determine to a large extent the accessibility of bulky polymeric molecules to the internal catalytic acid sites of the solids. Thus, while catalyst HZSM-5 presents bigger reactivity from HMCM-41 in the cracking of HDPE and LDPE, at the decomposition of the large molecules of PP the transformation is almost the same with that of thermal cracking, because cross-section of polymer is very big in order to enter in catalysts' micropores (Achilias et al., 2007).

These facts strongly limit their applicability and especially increase the higher cost of feedstock recycling for waste plastic treatment. Therefore, catalytic degradation provides a means to address these problems. The addition of catalyst is expected to reduce decomposition temperature, to promote decomposition speed, and to modify the products. The catalytic degradation of polymeric materials has been reported for a range of model catalysts centred on the active components in a range of different model catalysts, including amorphous silica–aluminas, zeolites Y, mordinite and ZSM-5 and the family of mesoporous MCM-41 materials. However, these catalysts have been used that even if performing well, they can be unfeasible from the point of view of practical use due to the cost of manufacturing and the high sensitivity of the process to the cost of the catalyst. Another option for the chemical recycling of polymer wastes by using fluidized catalytic cracking (FCC) catalysts is attractive. Therefore, an alternative improvement of processing the recycling via catalytic cracking would operate in mixing the polymer waste with fluid catalytic cracking (FCC) commercial catalysts.

Recently, much attention has been paid to the recycling of waste polymers by thermal or catalytic pyrolysis as a method to recover value added products or energy via the production of high-value petrochemical feedstock or synthetic fuel fractions. The following review is rather selective and not extensive. Detailed reviews on the thermal and catalytic pyrolysis of PP based plastics can be found in an excellent recently published book by Scheirs and Kaminsky, 2006 and in Achilias et al., 2006.

3.2 Pyrolysis

Achilias et al., 2007, studied the technique of pyrolysis of polypropylene in a laboratory fixed bed reactor using as raw materials either model PP or waste products based on these polymer. The conclusions are very interesting. The oil and gaseous fractions recovered presented a mainly aliphatic composition consisting of a series of alkanes and alkenes of different carbon number with a great potential to be recycled back into the petrochemical industry as a feedstock for the production of new plastics or refined fuels. Details are presented in section 5.

Hayashi et al., 1998 studied pyrolysis of polypropylene in the presence of oxygen. The polypropylene was coated on porous α-alumina particles and then pyrolyzed in a flow of helium or a mixture of helium–oxygen at atmospheric pressure. The mass release from PP

was dramatically enhanced in the presence of oxygen at temperatures in the range of 200–300°C. The net mass release rate in the presence of oxygen followed first-order kinetics with respect to the oxygen partial pressure and was controlled by the formation of peroxide on tertiary carbon of PP. The activation energy was 60–70 kJ/mol. The oxidative pyrolysis at 250°C converted 90% of PP into volatiles which mainly consisted of CS -soluble oils having a number-average chain length of 10.

Dawood et al. 2001 studied the influence of γ-irradiation on the thermal degradation of polypropylene by performing thermogravimetric analysis at three constant heating rates and at a constant temperature. At all the heating rates it can be indicated that the TG curves of the irradiated samples shifted to lower temperatures in comparison with the unirradiated one. The shift clearly increased with increasing irradiation dose, which means that the pyrolysis was enhanced by the irradiation. Since the difference in TG curves between the unirradiated sample and the samples irradiated to 10 and 30 kGy is quite large, small dose of irradiation is judged to be enough to cause a significant enhancement of the pyrolysis activity. The samples irradiated to small doses, 10 and 30 kGy, seem to show a pyrolysis behavior different from the other irradiated samples. At a small heating rate of 3 K/min, the TG curves of 10 and 30 kGy samples are close to the TG curve of 60 kGy sample, whereas the former TG curves are distinctly different from the latter TG curve at 10 K/min. These results may suggest that the mechanism of the increase in pyrolysis activity is different among the irradiated samples. A further examination of the influence of irradiation was performed by pyrolyzing the samples at a constant temperature. Similar to the case of dynamic heating rate, the difference in pyrolysis reactivity between the unirradiated and the 30 kGy irradiated sample is quite large, while the difference between the irradiated samples is small. This supports the suggestion that a small radiation dose is enough to cause a significant enhancement on the pyrolysis activity of PP.

3.3 Co-pyrolysis

Assumpcao et al., 2011, considered co-pyrolysis of PP with Brazilian crude oil by varying the temperature (400°C to 500°C) and the amount of PP fed to the reactor. The co-pyrolysis of plastic waste in an inert atmosphere provided around 80% of oil pyrolytic, and of these, half represent the fraction of diesel oil. this technique is a promise for PP waste recycling as it not only minimizes the environmental impact caused by inadequate disposal of this residues, but it also allows the reuse of a non-renewable natural resource (petroleum) through the use of diesel oil fractions obtained in this process. According to the results, the temperature increase has favored the increase of pyrolytic liquid generation and the reduction of the solid formed (Table 1). On the other hand, a huge increase in the PP amount has caused a decrease in total yield (liquid product) (Table 2). In general, it was observed that with temperature increase, there was a small reduction in yield in the diesel distillation range. Moreover, most part of these liquid distillates in a range higher than diesel, corresponding to heavy vacuum gas oil (GOP). This product (GOP) can still be cracked in an FCC generating more profitable products (naphtha and LPG), or can be used as fuel oil. The increase of PP in the reaction favors a yield increase in the diesel distillation range compared to pyrolysis of pure heavy oil, also forming a significant amount of compounds with distillation range lower than diesel.

Pyrolysis temperature (^{o}C)	Amount of PP (g)	Yield of pyrolytic oil present at the liquid boiling point (%)		
		In the Diesel distillation range	Below the Diesel distillation	Above the Diesel distillation
400	0.0	39	n.d.	61
	0.2	40	n.d.	60
	0.4	52	n.d.	48
	0.6	48	1.0	52
	0.8	62	n.d.	38
	1.0	59	n.d.	41
450	0.0	35	n.d.	65
	0.2	30	1.0	69
	0.4	32	n.d.	68
	0.6	37	2.0	61
	0.8	51	1.0	48
	1.0	n.d.	n.d.	n.d.
500	0.0	31	n.d.	69
	0.2	36	1.0	63
	0.4	33	n.d.	67
	0.6	34	6.0	60
	0.8	40	2.0	58
	1.0	n.d.	n.d.	n.d.

Table 1. Yield of pyrolytic oil present at the liquid boiling point during PP co-pyrolysis with Brazilian crude oil (Assumpcao et al., 2011).

Amount of PP (g)	Pyrolysis temperature (^{o}C)	Yield of pyrolytic products (%)		
		Liquid	Solid	Gas
0.0	400	59	30	11
	450	65	26	9
	500	88	10	2
0.2	400	68	28	4
	450	86	11	3
	500	95	4	1
0.4	400	79	13	4
	450	83	10	7
	500	90	3	7
0.6	400	83	14	3
	450	91	5	4
	500	97	2	1
0.8	400	17	81	2
	450	23	74	3
	500	50	49	1
1.0	400	15	84	1
	450	17	82	1
	500	25	73	3

Table 2. Yield of pyrolytic products in mixtures of PP with Brazilian crude oil. (Assumpcao et al., 2011).

Ballice et al**.,** 2002 investigated the temperature-programmed co-pyrolysis of Soma-lignites form Turkey with PP. A series co-pyrolysis operation was performed with lignites and PP using a 1:3, 1:1, 3:1 total carbon ratio of lignites to plastic. A fixed bed reactor was used to pyrolyse small sample of lignites and PP mixture under an inert gas flow (argon). In addition, the performance of the experimental apparatus was investigated by establishing a carbon balance and the degree of recovery of total organic carbon of the samples as aliphatic hydrocarbons and in solid residue was determined. Conversion into volatile hydrocarbons was found higher with increasing PP ratio in lignites–PP system while C16+ hydrocarbons and the amount of coke deposit were lower in the presence of PP. The maximum product release temperature was found to be approximately 440 °C for co-pyrolysis of lignite–PP. Straight- and branched-chain paraffins and olefins from methane to C26, diene and simple aromatic hydrocarbons were determined in co-pyrolysis products. The fraction of *n*-paraffins was higher than that of 1-olefins at a high proportion of lignite in the mixture.

Co-pyrolysis of lignite with PP has been found to give less C16+ *n*-paraffins and 1-olefins than pyrolysis of lignite by increasing PP ratios. Coke deposit in co-processing decreased also by increasing PP ratios. The *n*-paraffins were found to consist of mainly C1–C9, and relatively small amount of C10–C15 and C16+ fractions. The evolution of 1-olefins decreased in co-pyrolysis operation because of the higher hydrogen content in feed by increasing ratios of PP. A slightly synergistic effect were determined in the co-pyrolysis operation and the experimental results indicated that the pyrolysis products of PP are in highly aliphatic character, and during the initial stages of pyrolysis, these pyrolysis products of PP is expected to be a relative poor solvent for the structures of lignite. In addition, relative to liquefaction sources materials such as coals, the dominant components of municipal solid wastes (mainly PE, PS, PET and PP) are hydrogen rich so that co-processing of coal with waste plastics could be a good way to recycle waste plastics into useful products (Table 3).

Hydrocarbon fraction	Lignite	PP	Lignite-PP (1:3)	Lignite-PP (1:1)	Lignite-PP (3:1)
wt.% relative to the 1-olefins					
$C_2 – C_4$	57.8	81.0	58.3	58.2	59.7
C_5-C_9	15.6	19.0	32.6	30.1	26.8
C_{10}-C_{15}	14.7	-	4.2	4.0	3.7
C_{16+}	11.9	-	4.9	8.0	9.8
wt.% relative to all the aliphatic hydrocarbons					
1-Olefins	10.2	10.0	14.4	13.8	13.4

Table 3. 1-Olefins distribution in co-pyrolysis of lignite with PP (Ballice et al.**,** 2002).

Hajekova and Bajus, 2005 investigated the thermal decomposition of polyalkenes as a recycling route for the production of petrochemical feedstock. Polypropylene was thermally decomposed individually in a batch reactor at 450º C, thus forming oil/wax products. Then the product was dissolved in primary heavy naphtha to obtain steam cracking feedstock. The selectivity and kinetics of copyrolysis for 10 mass% solutions of oil/waxes from PP with naphtha in the temperature range from 740 to 820 ºC at residence times from 0.09 to 0.54 s were studied.

The decomposition of polyalkene oil/waxes during copyrolysis was confirmed. It was shown that the yields of the desired alkenes propene increased or slightly decreased compared to the yields from naphtha. In addition to the primary reactions, the secondary reactions leading to coke formation have also been studied. Slightly higher formation of coke was obtained at PP wax solution at the beginning of the measurements, on the clean surface of the reactor. After a thin layer of coke covered the walls, the production was the same as that from naphtha. The results confirm the possibility of polyalkenes recycling via the copyrolysis of polyalkene oils and waxes with conventional liquid steam cracking feedstocks on already existing industrial ethylene units.

3.4 Catalyting cracking

A large number of laboratory studies have been conducted for the direct catalytic cracking of different type of plastics. A large variety of catalysts have been used that even if performing well, they can be unrealistic from the point of view of practical use due to the cost of manufacturing and the high sensitivity of the process to the cost of the catalyst. Some of the studies reported in the literature will be reviewed below.

Zhao et al., 1996 have studied the effects of different zeolites as H-Y, Na-Y, L, H-mordenite and Na-mordenite on the catalytic degradation of PP by thermogravimetry under nitrogen flow. It was found that the degradation temperature of PP strongly depended on the type of zeolite used and the amount added. One type of HY zeolite (320HOA) was shown to be a very effective catalyst. Pyrolysis products, which were identified by using a coupled gas-chromatograph-mass-spectrometer, were also affected by the addition of zeolites. Some zeolites did not change the structure of the products but narrowed the product distribution to a smaller molecule region, while the HYzeolite led to hydrocarbons concentrated at those containing 4-9 carbons. Furthermore, some new compounds with cyclic structures were found in the presence of the HY zeolite.

Also, Zhao studied the effect of irradiation on pyrolysis of polypropylene in the presence of zeolites the results revealed that thermal degradation temperature of PP was significantly reduced when PP was irradiated in the presence of a zeolite. The irradiation-induced temperature reduction depended on the zeolite structure and composition, as well as on the morphology of the mixture. Identification of pyrolysis products indicated that, in the absence of zeolite, irradiation resulted only in a change of the product distribution but no formation of new compounds. In the presence of zeolite, however, a series of oxidized products were formed. In addition, the pyrolysis could be performed at a much lower temperature**.** Irradiation is able to render PP much moresusceptible to thermal degradation when carried out in the presence of zeolite. However, this effect was closely related to the type of zeolites, mixing methods and irradiation conditions.Furthermore, in pyrolysis of properly irradiated PP-zeolite mixtures, new chemicals such as acetone, acetic acid and so on, could possibly be obtained in addition to traditional hydrocarbons.

Ishihara et al., 1993 investigated the catalytic degradation of PP by silica–alumina at temperatures between 180 and 300°C in a semibatch reactor under a nitrogen flow. The production of gas precursors was found essential to decomposition. The most important elementary reaction is the intramolecular rearrangement of chain-end secondary carbonium ions in the liquid fraction to inner tertiary carbon atoms. The catalytic decomposition of

polypropylene proceeds as follows: polymer -degraded polymer +oligomer+ liquid+gas. Gas is produced from the chain-ends of the liquid fraction and its components are primarily isobutene and isopentane. The most important elementary reaction in the decomposition is intramolecular rearrangement taking place via a six-membered transition state to inner tertiary carbon atoms (back-biting reactions). The main gas components are produced by the decomposition of the C, fraction formed by the back-biting reaction.

Durmus et al., 2005 studied thermal-catalytic degradation kinetics of polypropylene over BEA, ZSM-5 and MOR zeolites. Degradation rate of the PP over zeolites was studied by thermogravimetric analysis (TGA) employing four different heating rates and apparent activation energies of the processes were determined by the Kissinger equation. The catalytic activity of zeolites decreases as BEA > ZSM-5a (Si/Al = 12.5) > ZSM-5b (Si/Al = 25) > MOR depending on pore size and acidity of the catalysts. On the other hand, initial degradation is relatively faster over MOR and BEA than that over both ZSM-5 catalysts depending on the apparent activation energy. It can be concluded that acidity of the catalyst is the most important parameter in determining the activity for polymer degradation process as well as other structural parameters, such as pore structure and size.

Lin et al., 2005 have investigated the catalytic cracking of PP in a fluidized bed reactor using H-ZSM-5, H-USY, H-mordenite, silica–alumina and MCM-41, with nitrogen as fluidizing gas (Figure 1). PP was pyrolysed over various catalysts using a laboratory fluidised-bed reactor operating isothermally at ambient pressure. The yield of volatile hydrocarbons for zeolite catalysts was higher than that for non-zeolite catalysts. Product distributions with HZSM-5 contained more olefinic materials with about 60 wt% in the range of C3 - C5. However, both HMOR and HUSY produced more paraffin streams with large amounts of isobutene (i-C4) and both catalysts were deactivated during the course of the degradation. SAHA and MCM-41 showed the lowest conversion and generated an olefin-rich product with a rise to the broadest carbon range of C3 - C7.
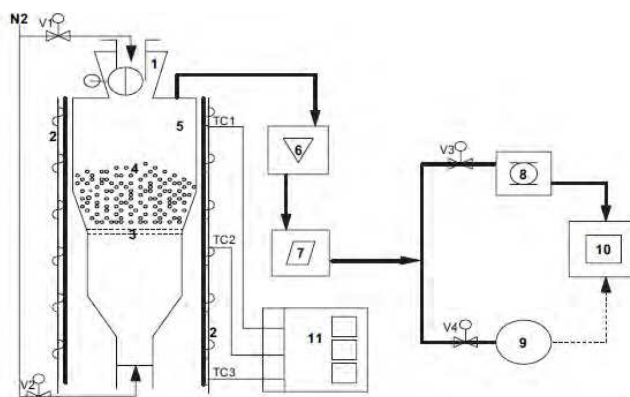
Schematic diagram of a catalytic fluidised-bed reactor system: 1. Feeder; 2. Furnace; 3. Sintered distributor; 4. Fluidised catalyst; 5. Reactor; Condenser; 7. Flow meter; 8. 16-loop automated sample system; 9. Gas bag; 10. GC; 11. Digital controller for three-zone furnace.

Fig. 1. Schematic diagram of catalytic fluidized-bed reactor system (Lin and Yen 2005).

Greater product selectivity was observed with HZSM-5 and HMOR as catalysts with about 60% of the product in the C3-C5 range and HMOR generating the highest yield of i-C4 for all catalysts studied (Table 4).

Degradation results	Catalyst type				
	HUSY	HZSM-5	HMOR	SAHA	MCM-41
Yield (wt.% feed)					
Gas	89.49	94.77	88.29	86.44	86.19
Liquid	3.75	2.31	4.54	4.73	5.07
Residue	6.76	3.92	7.17	9.83	8.74
Involatile residue	3.32	2.27	4.96	7.49	6.83
Coke	3.44	1.25	3.21	2.34	1.91
Mass balance (%)	93.71	95.32	93.24	89.68	88.46
Distribution of gaseous products (wt % feed)					
Hydrocarbon gases (C_1-C_4)	36.73	67.41	59.86	22.54	25.47
Gasoline (C_5-C_9)	51.83	25.54	27.95	63.65	60.56
BTX	0.93	1.82	0.48	0.25	0.16

Table 4. PP degradation products depending on catalysts type (Lin and Yen, 2005).

The larger pore zeolites (HUSY and HMOR) showed deactivation in contrast to the more restrictive HZSM-5. Observed differences in product yields and product distributions under identical reaction conditions can be attributed to the microstructure of catalysts.Valuable hydrocarbons of olefins and iso-olefins were produced by low temperatures and short contact times.

Lin and Yang, 2007 pyrolysed PP over spent FCC commercial catalyst (FCC-s1) using a laboratory fluidised-bed reactor operating isothermally at ambient pressure. The yield of gaseous and liquid hydrocarbon products at 390oC for spent FCC commercial catalyst (87.8 wt%) gave much higher yield than silicate (only 17.1 wt%). Greater product selectivity was observed with FCC-s1 as a post-use catalyst with about 61 wt% olefins products in the C3 - C7 range.

The use of fluidised-bed reaction system coped with a spent FCC equilibrium catalyst can be a better option from economical point of view since it can gives a good conversion with comparable short reaction time, and even its activity is lower than that of the zeolites (ZSM-5 and HUSY) and silica-aluminas (SAHA), this can be compensated by increasing the catalyst to PP ratio. Product distributions with FCC-s1 catalyst contained more olefinic materials in the range of C3-C7 (about 56 wt% at 390 oC). It was concluded that the use of spent FCC commercial catalyst and under appropriate reaction conditions can have the ability to control both the product yield and product distribution from polymer degradation, potentially leading to a cheaper process with more valuable products (Tables 5 and 6).

Degradation results	Ratio of polymer to catalyst (wt.%)				
	10	20	30	40	60
Yield (wt.% feed)					
Gas	26.7	27.8	26.9	27.6	28.2
Liquid	63.2	61.7	60.9	60.3	59.2
Gasoline (C_5-C_9)	57.4	55.4	54.3	52.9	51.4
Condensate liquid	4.9	5.3	5.4	5.8	6.0
BTX	0.9	1.0	1.2	1.6	1.8
Residue	10.1	10.5	12.2	12.1	12.6
Involatile residue	7.6	8.3	9.9	10.4	10.7
Coke	2.5	2.2	2.3	1.7	1.9
Mass balance (%)	89.5	90.6	91.8	92.5	90.4

Table 5. Products of PP pyrolysis with FCC catalyst (Lin and Yang, 2007).

Degradation results	Fluidizing N_2 rates (mL/min)				
	900	750	600	450	300
Yield (wt.% feed)					
Gas	29.6	28.8	26.9	26.3	26.1
Liquid	60.5	60.4	60.9	60.7	60.1
Gasoline (C_5-C_9)	55.1	54.7	54.3	54.6	53.7
Condensate liquid	4.9	4.9	5.4	4.5	4.3
BTX	0.5	0.8	1.2	1.6	2.1
Residue	9.9	10.8	12.2	13.0	13.8
Involatile residue	7.7	8.5	9.9	10.5	11.2
Coke	2.2	2.3	2.3	2.5	2.6
Mass balance (%)	89.2	89.6	91.8	90.3	94.1

Table 6. Effect of fluidizing N_2 rates on the product yield in PP pyrolysis (Lin and Yang, 2007).

Dawood and Miura, 2002 have studied the effect of exposing PP to γ-irradiation prior to the catalytic pyrolysis over a HY-zeolite using a thermobalance and a semi-batch reactor. A significant increase in the rate of the catalytic pyrolysis was realized when PP was exposed to a small irradiation dose of 10 kGy. The high reactivity of the irradiated PP was conjugated with low yields of residue and coke in addition to enhanced selectivity for light distillate (C7–C10). Examining the effect of pyrolysis temperature revealed that the catalytic pyrolysis preferred high temperature among the investigated temperature range of 325–375 ºC. The results presented above clarified that a significant increase in the rate of the catalytic pyrolysis with enhanced selectivity of C7–C10 compounds can be obtained by exposing PP to the ionizing irradiation prior to the catalytic pyrolysis. The results suggested the applicability of the proposed pyrolysis method for enhancing the catalytic conversion of plastic waste into useful hydrocarbons.

Uemichi et al, 1989 investigated the degradation of polypropylene to aromatic hydrocarbons over activated carbon catalysts containing Pt and Fe. The results obtained were compared with those for the degradation of polyethylene. The addition of Pt or Fe to activated carbon resulted in an increase in the yield of aromatics from polypropylene. However, the increase was less

than that from polyethylene. Pt metal was more effective than Fe only when the reaction conditions involved a longer contact time. The formation of aromatics was explained by essentially the same mechanism as the case of polyethylene, in which an influence of methyl branching of polypropylene on the aromatization yield and a difference in catalytic activity of the catalysts containing Pt and Fe for a ring expansion reaction were considered.

Park et al., 2008 reported pyrolysis of polypropylene over mesoporous MCM-48 material. Mesoporous MCM-48 materials were employed as catalysts for the degradation of PP. The catalytic activity of Al-MCM-48 was much higher than that of Si-MCM-48. Al-MCM-48 mainly generated C7–C10 hydrocarbons, while Si-MCM-48 exhibited a relatively broader distribution of oil products (C7–C14). Al-MCM-48 showed high catalytic stability for the degradation of PP. In view of these facts, Al-MCM-48 can be considered a promising catalyst for the degradation of other waste plastics (Tables 7 and 8).

	Without catalyst	Catalyst type		
		Si-MCM-48	Al-MCM-48 (Si/Al=60)	Al-MCM-48 (Si/Al=30)
Conversion (%)	3.3	75.3	90.2	95.7
Yield (wt.%)				
Oil	2.1	58.3	72.2	76.5
Gas	1.2	17.0	18.0	19.2

Table 7. Effect of catalyst type on product yield obtained from PP pyrolysis at 380oC for 1 h and PP:catalyst=5:1 (Park et al., 2008).

Catalyst	Product distribution (wt.%)					
	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_{4s}
Without catalyst	0.9	3.6	1.0	2.3	20.4	71.8
Si-MCM-48	0.1	0.1	0.1	0.4	14.0	85.3
Al-MCM-48 (Si/Al=60)	0.1	0.1	0.2	0.4	12.3	86.9
Al-MCM-48 (Si/Al=60)	0.1	0.1	0.2	0.5	13.4	85.7

Table 8. Effect of catalyst type on the product distribution of the gas fraction during PP pyrolysis at 380oC for 1 h and PP:catalyst=5:1 (Park et al., 2008).

Cardona and Corma, 2000 studied the tertiary recycling of polypropylene by catalytic cracking in a semibatch stirred reactor semicontinuous reactor has been presented that allows carrying out efficiently the catalytic cracking of PP. By working with USY zeolites with different unit cell sizes, it has been proven that neither the total amount nor the strength of the acid sites are the most determinant factors for cracking PP. the first cracking event of PP occurs at or close to the external surface. Then the formation of mesopores in the zeolite strongly improves the cracking activity. This has been supported by the results obtained with a Y zeolite synthesized with smaller crystallite sizes (Table 9). Finally it has been shown that amorphous or ordered silica–aluminas are very active catalysts. However, a FCC equilibrium catalyst can be a better option from an economical point of view since it

gives a very good selectivity, and even if its activity is lower than that of the silica–aluminas, this can be compensated by increasing the catalyst to PP ratio.

Catalyst	Cumulative selectivity (%)								
	Reaction time = 12 min			Reaction time = 24 min			Reaction time = 72 min		
	Gases	Gasoline	Diesel + gas oil	Gases	Gasoline	Diesel + gas oil	Gases	Gasoline	Diesel + gas oil
Si–Al 13%	5.2	78.6	16.2	4.9	72.2	22.9	6.7	70.3	23.0
Resoc-g	10.5	77.5	12.0	8.1	75.7	16.2	7.4	74.7	17.9
H-USY 500	13.2	81.4	5.4	11.2	81.5	7.3	10.2	82.7	7.1
H-USY 712	6.1	77.8	16.1	5.8	75.8	18.4	6.7	76.2	17.1
H-USY 760	8.9	81.0	10.1	8.6	78.1	13.3	9.5	78.8	11.7

Table 9. Effect of the catalyst type on the product distribution during PP pyrolysis at 380 °C (Cardona and Corma, 2000).

Xie et al., 2008 have reported catalytic cracking of polypropylene (PP) over MCM-41 modified by Zr and Mo. The relationship among structure, acidity and catalytic activity of Zr–Mo-MCM-41 was studied. The results showed that Zr–Mo-MCM-41 exhibited high activity for the cracking of PP and good selectivity for producing liquid hydrocarbons of higher carbon numbers. The results were compared with those obtained over HZSM-5, SiO_2–Al_2O_3 and other MCM-41 mesoporous molecular sieves. For the catalytic cracking of PP, Mo enhances the selectivity to high carbon number hydrocarbons and Zr enhances the acidity of catalyst and results in the increasing cracking conversion of PP. Zr–Mo-MCM-41 using $Zr(SO_4)_2$ as Zr source is of the best catalytic activity and selectivity to high carbon number hydrocarbon, which means that Zr–Mo-MCM-41 will probably become good potential catalysts for the cracking of PP (Table 10).

Catalyst	Temperature (°C)	Conversion (%)	Liquid yield (%)	Gas yield (%)
HZSM-5	400	27.1	50.2	49.8
SiO_2-Al_2O_3	400	25.8	60.3	39.7
Thermal cracking	400	30.4	76.2	23.8
Si-MCM-41	400	39.6	81.4	18.9
Mo-MCM-41	400	57.5	90.0	10.0
Zr-Mo-MCM-41	400	98.6	92.0	8.0
Zr-Mo-MCM-41	380	65.4	81.9	18.1
Zr-Mo-MCM-41	390	84.3	87.7	12.3
Zr-Mo-MCM-41	410	99.6	89.0	11.0

Table 10. Catalytic activities of different catalyst in PP pyrolysis for 30 min at catalyst/ PP = 0.01 (Xie et al., 2008).

Panda et al., 2011 investigated catalytic performances of kaoline and silica alumina in the thermal degradation of polypropylene. Polypropylene was cracked thermally and catalytically in the presence of kaoline and silica alumina in a semi batch reactor in the temperature range 400–550ºC in order to obtain suitable liquid fuels. It was observed that up to 450ºC thermal cracking temperature, the major product of pyrolysis was liquid oil and the major product at other higher temperatures (475–550ºC) are viscous liquid or wax and the highest yield of pyrolysis product is 82.85% by weight at 500ºC. Use of kaoline and silica alumina decreased the reaction time and increased the yield of liquid fraction. Again the major pyrolysis product in catalytic pyrolysis at all temperatures was low viscous liquid oil. Silica alumina was found better as compared to kaoline in liquid yield and in reducing the reaction temperature. The maximum oil yield using silica alumina and kaoline catalyst are 91% and 89.5% respectively. On the basis of the obtained results hypothetical continuous process of waste polypropylene plastics processing for engine fuel production can be presented (Table 11).

In conclusion, catalytic pyrolysis of PP reduces environmental impacts, also the time of recycling and results in very useful products, with potential use as fuel replacements.

	Type of catalyst		
	None (thermal cracking)	Kaoline (PP:cat=3:1)	Silica-alumina (PP:cat=3:1)
	T = 500ºC	T = 450ºC	T = 500 ºC
Liquid product (wt.%)	82.85	89.50	91.0
Gaseous product (wt.%)	16.25	9.75	8.0
Solid residue (wt.%)	0.90	0.75	1.0
Density of oil at 15 ºC (g/mL)	0.84	0.745	0.770
Viscosity of oil at 30 ºC (cSt)	4.31	2.18	2.21

Table 11. Pyrolysis of PP in optimum conditions (Panda and Singh, 2011).

4. Chemical recycling of polystyrene

4.1 Introduction

Polystyrene (PS) is widely used in the manufacture of many products due to its favorable properties such as good strength, light weight, and durability and is the material of choice for packaging various electronics and other fragile items. In general, PS accounts for about 9-10% of the plastic waste in municipal solid waste (MSW). In the past several years, PS has received much public and media attention. Polystyrene has been described by various environmental groups as being nondegradable, nonrecyclable, toxic when burned, landfill-choking, ozone-depleting, wildlife-killing, and even carcinogenic. These misconceptions regarding PS have resulted in boycotts and bans in various localities. Actually, PS comprises less than 0.5% of the solid waste going to landfills.

Polystyrene is used in solid and expanded forms both of which can be recycled. Solid PS components such as coffee cups, trays, etc. can be recycled back into alternative applications such as videocassette cases, office equipments, etc. Expanded PS (EPS) foam waste loses its foam characteristics as part of the recovery process. The recovered material can be re-gassed but the product becomes more expensive than virgin material. Instead it is used in solid form in standard molding applications. Both expanded and solid PS wastes have been successfully recycled in extruded plastic timber-lumber. Recycled PS is used to produce plant pots and desk items such as pen, pencils, etc. As with other types of plastic materials, PS recycling takes place after consideration by the industry of a number of issues including eco-efficiency, availability, corporate social responsibility, product quality=hygiene aspects, and traceability.

More than a thousand tones of PS foam worldwide is being disposed off into environment as MSW. The amount is increasing every year. The booming development of electronic products has sharply increased the quantities of Waste from Electrical and Electronic Equipment (WEEE), amplifying the problem of their disposal. The solution can be found only through a modern Design For Environment (DFE) with a big attention to recycling and disassembly.

4.2 Types of polystyrene accepted for recycling

Expanded polystyrene (EPS) foam packaging, which is the familiar white material, custom molded to cushion, insulate and protect all types of products during transportation, can be recycled. EPS insulation boards used for housing and commercial construction, foodservice products like cups, plates, trays, etc. that are made of PS resin foamed to provide a unique insulating quality and loosefill packaging are accepted for recycling. Non-Foam Polystyrene products also called high impact polystyrene (HIPS), oriented polystyrene (OPS), post consumer products, post industrial products, and styrofoam (A Dow Chemical Company brand trademark for a PS foam thermal insulation product) have also been accepted for recycling (Vilaplana et al., 2006).

4.3 Recycling methods for polystyrene products

Before recycling, the recyclable materials should be rinsed off for the removal of any food or dirt particles, the caps of the plastic bottles and glass jars should be thrown away and the oversized materials like cartons, milk jugs, etc. should be crushed so that they can fit into the bin and into the truck more easily. The volume of EPS is reduced by methods such as solvent volume reduction (dissolved using solvent), heating volume reduction, and pulverizing volume reduction (pulverized).

The processed EPS is used in its reduced state as an ingredient for recycled products or it is burnt to generate heat energy. A large amount of expanded PS is discharged after use at wholesale markets, supermarkets, department stores, restaurants and shops, such as electrical appliances stores, as well as at factories of machinery manufacturers. It is collected through the in-house collection of companies or by resource recycling agents and becomes a recycled resource.

4.3.1 Recycling using the dissolution technique

A rather easy way of recovering polymers from a mixture of different plastics is by using an appropriate solvent to selectively dissolve the polymer and then recovering it by removal of

that solvent. In this sense a naturally occurring compound, i.e. limonene (occurring in citrus fruits) has been successfully used to dissolve EPS (Achilias et al., 2009). This solvent has the ability to dissolve EPS in large amounts safely and with negligible degradation of the polymer's performance properties. Conventional melt separation methods cause a large drop in the polymer's molecular weight due to thermal degradation. Consequently dissolved PS can be precipitated through the addition of a non-solvent in the mixture. The solvent is vacuum-evaporated and re-used.

4.3.2 Chemical recycling of PS

One of the attractive chemical recycling processes is the catalytic degradation [Kim et al., 2003] of polystyrene. This process enables to get styrene monomer (S) at relatively low temperature with a high selectivity. Modified Fe-based catalysts were employed for the catalytic degradation of EPS waste, where carbanion may lead to high selectivity of S in the catalytic degradation of PS. The yield of oil (Y_{Oil}) and S (Y_S) were increased in the presence of Fe-based catalysts and with increasing reaction temperature. Y_{Oil} and Y_S were obtained over Fe–K/Al$_2$O$_3$ at the relative low reaction temperature (400°C) 92.2 and 65.8 wt. %, respectively. The value of Ea (activation energy) is obtained as 194 kJ/mol for the thermal degradation of EPS. However, the Ea was decreased considerably to 138 kJ/mol in the presence of the catalysts (Fe–K/Al$_2$O$_3$).

Bajdur et al., 2002 have synthesized sulfonated derivatives of expanded PS wastes, which may be used as polyelectrolytes. Modification was conducted by means of known methods and products having various contents of sulfogroups in polymer chain were obtained. They have found that the polyelectrolytes have good flocculation properties similar to those of anionic commercial polyelectrolytes. The effect of a base catalyst, MgO, on the decomposition of PS was studied through degradation of both a monodisperse polymer and a PS mimic, 1,3,5-triphenylhexane (TPH), to determine the potential of applying base catalysts as an effective means of polymer recycling [Woo et al., 2000]. The presence of the catalyst increased the decomposition rate of the model compound but decreased the degradation rate of PS as measured by evolution of low molecular weight products. Although the model compound results suggest that the rate of initiation was enhanced in both cases by the addition of catalyst, this effect is overshadowed for the polymer by a decrease in the 'zip length' during depropagation due to termination reactions facilitated by the catalyst. Due to the small size of the model compound, this effect does not impact its observed conversion since premature termination still affords a quantifiable low molecular weight product. A decrease in the selectivity to styrene monomer in the presence of MgO was observed for both PS and TPH. They have discussed the reconciliation of their results with those of Zhang et al., 1995 based on differences in the reactor configuration used.

Degradation of PS into styrene, including monomer and dimer, was studied by Ukei et al., 2000 using solid acids and bases viz. MgO, CaO, BaO, K$_2$O, SiO$_2$/Al$_2$O$_3$, HZSM5 and active carbonas catalysts. They have found that solid bases were more effective catalysts than solid acids for the degradation of PS into styrene. This was attributed to differences in the degradation mechanisms of PS over solid acids and bases. Among the solid bases employed, BaO was found to be the most effective catalyst and about 90 wt. % of PS was converted into styrene when thermally degraded PS was admitted to BaO powder at 350°C.

Koji et al., 1998 have succeded to obtain PS foam, which can be recycled into styrene by mixing a PS with a basic metal oxide being a catalytic decomposition catalyst and foaming the mixture with an inert blowing agent. When it is wasted, it can be recycled into styrene by decomposing it by heating to 300–450°C in a nonoxidizing atmosphere. The basic oxide is Na_2O, MgO, CaO or the like and among them CaO is desirable. When the basic metal oxide carried by porous inorganic filler is used, it can exhibit improved effectiveness desirably. The blowing agent used is a nitrogen gas, a chlorofluorocarbon, propane or the like.

Lee et al., 2002, have studied several solid acids, such as silica-alumina, HZSM-5, HY, mordenite, and clinoptilolite as catalysts and screened their performances in the catalytic degradation of PS. The clinoptilolite catalysts (HNZ, HSCLZ) showed good catalytic performance for the degradation of PS with selectivity to aromatics more than 99%. Styrene is the major product and ethylbenzene is the second most abundant one in the liquid product. The increase of acidity favored the production of ethylbenzene by promoting the hydrogenation reaction of styrene. Higher selectivity to styrene is observed at higher temperatures. An increase of contact time by reducing nitrogen gas flow rate enhanced the selectivity to ethylbenzene. Thus a designed operation including acidity of catalyst, reaction temperature, and contact time will be necessary to control the product distribution between styrene monomer and ethylbenzene.

Ke et al., 2005 studied the degradation of PS in various supercritical solvents like benzene, toluene, xylene, etc. at 310–370°C and 6.0MPa pressure. It was found that PS has been successfully depolymerized into monomer, dimmer, and other products in a very short reaction time with high conversion. Toluene used as supercritical solvent was more effective than other solvents such as benzene, ethylbenzene, and p-xylene for the recovery of styrene from PS, though the conversions of PS were similar in all the above solvents. The highest yield of styrene (77 wt%) obtained from PS in supercritical toluene at 360°C for 20 min.

Subcritical water is a benign and effective media for polymer degradation. Suyama et al., 2010 have found that on subcritical water treatment in the presence of an aminoalcohol, unsaturated polyesters crosslinked with styrene were decrosslinked, and a linear polystyrene derivative bearing hydroxy-terminated side-chains was recovered. After modification of the hydroxy groups with maleic anhydride, the polystyrene derivative was re-crosslinked with styrene to form a networked structure again. The resulting solid was degradable by subcritical water treatment in the presence of the aminoalcohol to give another polystyrene derivative bearing hydroxy groups. These processes could be repeated successfully, demonstrating the applicability as a novel recycling system of thermosetting resins. The polystyrene derivative was also re-crosslinked again on heating with an alternative copolymer of styrene and maleic anhydride due to the formation of linkage between the hydroxy groups and carboxylic anhydride moieties.

In order to reduce the consumption of energy and get oligostyrene of several thousands of molecular weight, which can be used as a kind of fuel oil, the thermal decomposition of EPS with a-methylstyrene as a chain-transfer agent was studied by Xue et al., 2004, at a temperature about 200°C. Three kinds of organic peroxides were used as radical accelerators. They found that the addition of dicumyl peroxide (DCP) enhanced the thermal decomposition of EPS even at lower temperature, about 140 ^{o}C, but the addition of tert-

butylcumyl peroxide was less effective than DCP. On the other hand, di-tert-butyl peroxide had almost no effect on the thermal decomposition of EPS.

4.3.3 Mechanism of polystyrene cracking

Radical depolymerization of neat PS samples produces large quantities of monomer (styrene) and chain-end backbiting yields substantial amounts of dimer and trimer. Polymer decomposition proceeds by entirely different processes when a catalyst is present. The formation of the primary PS catalytic cracking volatile products can be explained by initial electrophilic attack on polymer aromatic rings by protons. Protons preferentially attack the *ortho* and *para* ring positions because the aliphatic polymer backbone is an electron-releasing group for the aromatic rings. Most volatile products can be derived from mechanisms beginning with ring protonation. Thermal decomposition of *ortho*-protonated aromatic rings in the polymer chain (1) can lead directly to the liberation of benzene, the primary catalytic cracking product, or may result in chain shortening. Benzene cannot be obtained directly from *para*-protonated aromatic rings in the polymer. However, *para*-protonated rings can react with neighboring polymer chains to yield the same chain scission products that are formed by *ortho*-protonation. The macro cation remaining after benzene evolution (2) may undergo chain shortening β-scission to produce (3) and an unsaturated chain end, rearrange to form an internal double bond and protonate a neighboring aromatic ring (either by intra- or intermolecular proton transfer), cyclize to form an indane structure, or abstract a hydride to produce a saturated chain segment. The substantial quantities of indanes obtained by PS catalytic cracking suggests that cyclization of (2) to form indane structures is a favored process. A consequence of chain unsaturation resulting from (2) might be the formation of conjugated polyene segments that may subsequently cyclize to form naphthalenes. Decomposition of (3), which might be formed from (1) or (2), can result in the formation of styrene or may lead to chain end unsaturation and neighboring ring protonation (Figure 2).
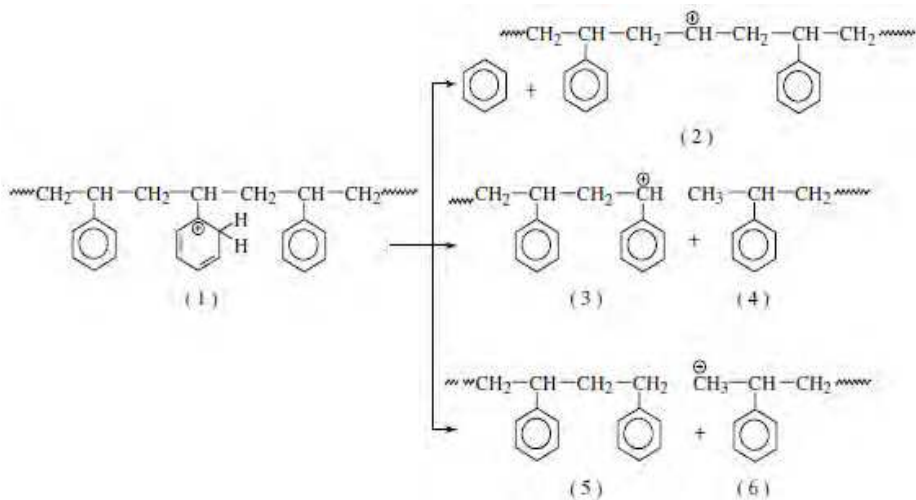
Fig. 2. Mechanism of PS cracking.

Hydride abstraction by (3) would result in a saturated chain end. The lack of significant styrene production from any of the PS-catalyst samples suggests that β-scission of (3) to form styrene is not a dominant decomposition pathway at low temperatures. Chain end unsaturation derived from (3) may result in formation of indenes, which were detected in substantial amounts only when HZSM-5 catalyst was present. The restricted volume of the HZSM-5 channels apparently inhibits hydride abstraction pathways for (3), which results in increased production of indenes and styrene for PS-HZSM-5. Protonation of aromatic rings adjacent to methyl-terminated chain ends (4) can result in the formation of alkyl benzenes, propene, and benzene, depending on how the macro cation decomposes.

4.3.4 Thermo-chemical recycling of PS

Thermochemical recycling techniques such as pyrolysis are usually applied. Thus, PS can be thermally depolymerized at relatively low temperatures in order to obtain the monomer styrene with a high selectivity.

Arandes et al., 2003 have studied the thermal cracking of PS and polystyrene-butadiene (PS-BD) on mesoporous silica which has no measurable acidity. Although the content of PS in domestic plastic wastes is approximately 10wt. %, less attention has been paid to the cracking of dissolved PS than to the cracking of dissolved polyolefins. The kinetic characteristics of PS cracking described by Arandes et al. are different to those of polyolefins and the ideal aim of its valorization is the recovery of the styrene monomer. Bockhorn et al., 1999 and Kruse et al., 2001 made an analysis of the reactions involved in the mechanism of PS cracking and developed a detailed mechanistic model for the polymer degradation. Faravelli et al., 2003 presented a detailed kinetic model for the thermal degradation of PE – PS mixtures.

The technology for thermal cracking that has been more widely studied and that has been tested at larger scale is that based on a fluidized bed, in which the plastics are fed in the solid state and sand is used for helping fluidization [Scheirs and Kaminsky, 2006; Milne et al., 1999; Westerhourt, 1997]. The design of fluidized beds used at laboratory or pilot plant scale has been carried out on the basis, that the kinetics of pyrolysis of plastics is subjected to great uncertainty caused by factors such as heterogeneity of the material, synergy in the cracking of different constituents, and limitations to heat and mass transfer. These factors prevent obtaining kinetics that is reliable for the design of the reactor at temperatures of industrial interest (above 450ºC) [Mehta et al., 1995]. Furthermore, this strategy is suitable for its development in a refinery by using the existing equipment and by optimizing the possibilities of incorporating the products either into the market (subsequent to fuel reformulation) or into the production process itself (subsequent to monomer purification). An additional problem in the cracking of PS is the rapid deactivation of the catalyst caused by the coke formed on the acid sites, which is favored by the aromatic nature of styrene and its high C/H ratio.

A conical spouted bed reactor (CSBR) has been used for the kinetic study of PS pyrolysis in the 450–550ºC range [Aguado et al., 2003] and the results have been compared with those obtained by thermogravimetry (TGA) and in a microreactor (MR) of very high sample heating rate. The comparison proves the advantages of the gas–solid contact of this new reactor for the kinetic study of pyrolysis of plastics at high temperature, which stem from the high heat transfer rate between gas and solid and from the fact that particle agglomeration is avoided.

A swirling fluidized-bed reactor (0.0508m ID and 1.5m in height) has been developed to recover the styrene monomer [Lee et al., 2003] and valuable chemicals effectively from the PS waste, since it can control the residence time of the feed materials and enhance the uniformity of the temperature distribution. To increase the selectivity and yield of styrene monomer in the product, catalyst such as Fe_2O_3, BaO, or HZSM-5 have been used. It has been found that the reaction time and temperature can be reduced profoundly by adding the solid catalyst. The swirling fluidization mode makes the temperature fluctuations more periodic and persistent, which can increase the uniformity of temperature distribution by reducing the temperature gradient in the reactor. The yields of styrene monomer as well as oil products have increased with increasing the ratio of swirling gas, but exhibited their maximum values with increasing the total volume flow rate of gas.

The thermal degradation of real municipal waste plastics (MWP) obtained from Sapporo, Japan and model mixed plastics was carried out at 430°C in atmospheric pressure by batch operation (Bhaskar et al., 2003). The resources and environmental effects assessed over the life of each of the packaging, includes fossil fuel consumption, greenhouse gas emissions, and photochemical oxidant precursors.

Achilias et al. 2007 investigated catalytic and non-catalytic pyrolysis experiments in a fixed bed reactor using either model polymer or commercial waste products as the feedstock. The liquid fraction produced from all the pyrolysis experiments consisted mainly of the styrene monomer and this was subjected to repolymerization without any further purification in a DSC with AIBN initiator. A basic (BaO) and an acidic commercial FCC catalyst were examined in relation to the yield and composition of gaseous and liquid products. Aromatic compounds identified in the liquid fraction of the thermal and catalytic pyrolysis of model PS and commercial products appear in Table 12.

Results show that this product can be polymerized to produce a polymer similar to the original PS. However, it was found that other aromatic compounds included in this fraction could act as chain transfer agents, lowering the average molecular weight of the polymer produced and contributing to a lower Tg polymer. Therefore, it seems that the polymer can be reproduced but with inferior properties compared to a polymer prepared from neat styrene.

A general model for polymer degradation by concurrent random and chain-end processes was developed by Sterling et al., 2001 using continuous distribution kinetics. Population balance equations based on fundamental, mechanistic free radical reactions were solved analytically by the moment method. The model, applicable to any molecular weight distribution (MWD), reduces to the cases of independent random or chain-end scission. Polystyrene degradation experiments in mineral oil solution at 275–350 °C supported the model and determined reaction rate parameters. The degradation proceeded to moderate extents requiring a MW-dependent random scission rate coefficient. Polystyrene random scission activation energy was 7.0 kcal/mol, which agrees well with other thermolysis investigations, but is lower than that found by pyrolysis due to fundamental differences between the processes. Magnesium oxide, added as a heterogeneous catalyst in solution, was found to have no effect on PS degradation rate.

Thermal and thermo-oxidative degradation of PS in the presence of ammonium sulfate [Zhu et al., 1998] was studied with thermogravimetry and FTIR. TGA results indicated that

ammonium sulfate accelerated thermal degradation in nitrogen but delayed thermo-oxidative degradation of PS in air. IR analysis of tetrahydrofuran extracts, from the samples degraded at 340°C and of residues after thermal treatment at 340°C in a furnace, showed that the acceleration of thermal degradation and the suppression of thermo-oxidative degradation were due to sulfonation and oxidation of ammonium sulfate and its decomposition products, and formation of unsaturated structures in the PS chain.
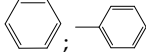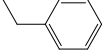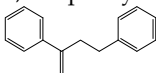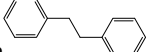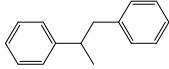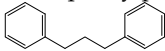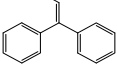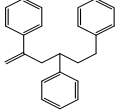
Compounds, chemical formula	Thermal	Catalytic BaO	Catalytic FCC	Plastic container	Plastic glass (EPS)
Styrene (**monomer**)	63.9	69.6	45.1	53.3	70.0
Benzene, Toluene	2.0	2.4	5.0	5.6	2.5
Ethylbenzene	0.5	1.1	-	1.9	1.5
a-Methylstyrene	2.1	2.6	6.3	5.9	2.3
Xylene	-	-	16.8	-	-
Cumene	-	-	1.7	0.2	0.3
2,4-Diphenyl-1-butene (**dimer**)	14.0	18.4	1.9	11.9	9.0
Indane, Indene, etc.	2.0	0.3	5.0	2.5	0.2
1,2-Diphenylethane	2.2	0.7	0.9	2.1	0.8
1-methyl-1,2Diphenylethan	1.1	0.4	0.5	1.4	0.4
1,3-Diphenylpropane	0.6	0.6	0.5	2.8	0.8
1,1'-Diphenylpropene	0.7	0.4	1.1	-	0.7
2,4,6-Triphenyl-1-hexene(**trimer**)	2.2	1.8	0.3	3.5	5.0
Other aromatic compounds	8.7	1.7	14.9	8.9	6.4

Table 12. Aromatic compounds identified in the liquid fraction of the thermal and catalytic pyrolysis of model polystyrene and commercial products based on polystyrene (wt.-% on liquid produced) (Achilias et al., 2007).

Thermal degradation of PS has been investigated in the presence of water [Beltrame et al., 1997] under subcritical conditions (hydrous pyrolysis). The experiments were carried out in closed systems under inert atmosphere, in the temperature range 300–350 ºC, at pressures up to 18 MPa, for 1–120 h. The products obtained, separated as gases, volatiles, and heavy compounds. The results showed that the presence of water increases the yields of the volatile products, mainly in the first steps of the pyrolytic process, and leads to higher yields of monomer. This latter observation suggests a lowering of the secondary reactions extent.

The catalytic degradation of waste plastics such as HDPE, LDPE, PP and PS over spent fluid catalytic cracking (FCC) catalyst was also carried out at atmospheric pressure with a stirred semi-batch operation at 400 ºC [Lee et al., 2002]. The objective was to investigate the influence of plastic types on the yield, liquid product rate, and liquid product distribution for catalytic degradation. The catalytic degradation of waste PE and PP with polyolefinic structure exhibited the liquid yield of 80–85% and the solid yield of below 1%, whereas that of waste PS with polycyclic structure produced much more liquid, solid products, and much less gas products. Accumulative liquid product weight by catalytic degradation strongly depended on the degradation temperature of the plastics.

In accordance with the option of recycling plastics into fuels by dissolving them in standard feedstocks [Puente et al., 1998] for the process of catalytic cracking of hydrocarbons, FCC, and various acidic catalysts (zeolites ZSM-5, mordenite, Y, and a sulfur-promoted zirconia) were tested in the conversion of PS dissolved into inert benzene at 550 ºC in a fluidized- bed batch reactor. Experiments were performed with very short contact times of up to 12 sec. Main products were in the gasoline range, including benzene, toluene, ethylbenzene, styrene, and minor amounts of C9–12 aromatics and light C5– compounds. Coke was always produced in very significant amounts. Even though sulphur promoted zirconia is highly acidic, the low proportion of Brönsted-type acid sites does not allow the occurrence of secondary styrene reactions. It was shown that most favorable product distributions (higher yields of desirable products) are obtained on equilibrium commercial FCC catalysts.

PS can be recycled into styrene monomer in association with some other aromatics, from which styrene can be converted to biodegradable plastic such as polyhydroxyalkanoates (PHA). Recently scientists have achieved 10% yield of PHA from PS [Ward et al., 2006]. The chain length of PHA produced was 10. The yield and composition of oils and gases derived from the pyrolysis and catalytic pyrolysis of PS has been investigated. The pyrolysis and catalytic pyrolysis was carried out in a fixed bed reactor. Two catalysts were used, zeolite ZSM-5 and Y-zeolite and the influence of the temperature of the catalyst, the amount of catalyst loading, and the use of a mixture of the two catalysts was investigated. The main product from the uncatalyzed pyrolysis of PS was oil consisting mostly of styrene and other aromatic hydrocarbons like toluene and ethylbenzene. In the presence of either catalyst an increase in the yield of gas and decrease in the amount of oil production was found, but there was significant formation of carbonaceous coke on the catalyst. Increasing the temperature of the Y-zeolite catalyst and also the amount of catalyst in the catalyst bed resulted in a decrease in the yield of oil and increase in the yield of gas. Oil derived from the catalytic pyrolysis of PS contain aromatic compounds such as single ring compounds like benzene, toluene, styrene, m-xylene, o-xylene, p-xylene, ethylmethylbenzene, propenyl-benzene, methylstyrene; two ring compounds like indene, methylindene, naphthalene, 2-

methylnaphthalene, 1-methylnaphthalene, biphenyl, methylbiphenyl, dimethylnaphthalene, trimethylnaphthalene, tetramethylnaphthalene, ethylbiphenyl; three ring compounds like phenanthrenes and four ring compounds like pyrenes and chrysenes.

4.4 Future prospectus

Some future prospectus of PS recycling include (Maharana et al., 2007).

1. Thermal recycling of PS yields higher percentage of styrene monomer, which can be fermented by bacteria to produce polyhydroxyalkanoates (PHA) — the starting material for the synthesis of biodegradable polymers.
2. The waste PS can be blended with biodegradable polymers to produce biodegradable polymers.
3. Styrene monomer produced by recycling can be grafted onto biodegradable polymers to give biodegradable polymers.

5. Chemical recycling of polyethylene (LDPE and HDPE)

5.1 Introduction

Under the category of chemical recycling of polyethylenes, advanced process (similar to those employed in the petrochemical industry) appear e.g. pyrolysis, gasification, liquid–gas hydrogenation, viscosity breaking, steam or catalytic cracking (Al-Salem *et al*, 2009). Catalytic cracking and reforming facilitate the selective degradation of waste plastics. The use of solid catalysts such as silica alumina, ZSM-5, zeolites, and mesoporous materials for these purposes has been reported. These materials effectively convert polyolefins into liquid fuel, giving lighter fractions as compared to thermal cracking (Al-Salem *et al*, 2009).

In particular, polyethylene has been targeted as a potential feedstock for fuel (gasoline) producing technologies. PE thermally cracks into gases, liquids, waxes, aromatics and char. The relative amounts of gas and liquid fraction are very much dependent on the type of polymer used. Thus, higher decomposition was observed in PP, followed by LDPE and finally HDPE. It seems that less crystalline or more branched polymers are less stable in thermal degradation (Achilias et al., 2007). Many papers have been published recently on this subject and excellent reviews can be found in the book by Scheirs and Kaminsky, 2006 and Achilias et al., 2006.

Polyethylene (as well as other vinyl polymers) degrade via a four step free radical mechanism: radical initiation, de-propagation (as opposed to propagation in the case of polymerization), intermolecular and intramolecular hydrogen transfer followed by β-scission (initial step in the chemistry of thermal cracking of hydrocarbons and the formation of free radicals) and, lastly, radical termination. β-Scission and hydrogen abstraction steps often occur together in a chain propagation sequence. That is, a radical abstracts a hydrogen atom from the reactant to form a molecule and a new radical. A bond β is then broken to the

radical centre (β-scission) to regenerate an abstracting radical and to produce a molecule with a double bond (a molecule with a double bond involving the carbon atom that had been the radical centre). Sample size and surface area to volume ratio of the melt have a significant influence on the rate and relative importance of the various mechanisms of polymer degradation. In pyrolysis, which is normally done on micro-scale, only random initiation and intermolecular transfer were reported to be important. Conversely, on milligram scale of polyethylene charges and samples, intermolecular transfer of hydrogen atoms via abstraction by free radicals was considered to be the predominant transfer mechanism to produce volatiles. There is also a growing interest in developing value added products such as synthetic lubricants via PE thermal degradation.

The development of value added recycling technologies is highly desirable as it would increase the economic incentive to recycle polymers. Several methods for chemical recycling are presently in use, such as direct chemical treatment involving gasification, smelting by blast furnace or coke oven, and degradation by liquefaction. The main advantage of chemical recycling is the possibility of treating heterogeneous and contaminated polymers with limited use of pre-treatment. Petrochemical plants are much greater in size (6–10 times) than plastic manufacturing plants. It is essential to utilize petrochemical plants in supplementing their usual feedstock by using plastic solid wastes (PSW) derived feedstock (Al-Salem *et al,* 2009).

5.2 Thermolysis schemes and technologies

5.2.1 Pyrolysis

Thermolysis is the treatment in the presence of heat under controlled temperatures without catalysts. Thermolysis processes can be divided into advanced thermo-chemical or pyrolysis (thermal cracking in an inert atmosphere), gasification (in the sub-stoichiometric presence of air usually leading to CO and CO_2 production) and hydrogenation (hydrocracking).

Thermal degradation processes allow obtaining a number of constituting molecules, combustible gases and/or energy, with the reduction of landfilling as an added advantage. The pyrolysis process is an advanced conversion technology that has the ability to produce a clean, high calorific value gas from a wide variety of waste and biomass streams. The hydrocarbon content of the waste is converted into a gas, which is suitable for utilisation in either gas engines, with associated electricity generation, or in boiler applications without the need for flue gas treatment. This process is capable of treating many different solid hydrocarbon based wastes whilst producing a clean fuel gas with a high calorific value. This gas will typically have a calorific value of 22–30 MJ/m^3 depending on the waste material being processed. Solid char is also produced from the process, which contains both carbon and the mineral content of the original feed material. The char can either be further processed onsite to release the energy content of the carbon, or utilized offsite in other thermal processes (Al-Salem *et al*, 2009).

The main pyrolysis units and technologies on an industrial scale include PYROPLEQ (rotary drum), Akzo (circulating fluidized bed), NRC (melt furnace), ConTherm technology (rotary drum), PKA pyrolysis (rotary drum), PyroMelt (melt furnace), BP (circulating fluidized

bed), BASF (furnace) and NKT (circulating fluidized bed). Detailes can be found in Al-Salem *et al*, 2010.

Pyrolysis provides a number of other advantages, such as (i) operational advantages, (ii) environmental advantages and (iii) financial benefits. Operational advantages could be described by the utilisation of residual output of char used as a fuel or as a feedstock for other petrochemical processes. An additional operational benefit is that pyrolysis requires no flue gas clean up as flue gas produced is mostly treated prior to utilisation. Environmentally, pyrolysis provides an alternative solution to landfilling and reduces greenhouse gas (GHGs) and CO_2 emissions. Financially, pyrolysis produces a high calorific value fuel that could be easily marketed and used in gas engines to produce electricity and heat. Several obstacles and disadvantages do exist for pyrolysis, mainly the handling of char produced and treatment of the final fuel produced if specific products are desired. In addition, there is not a sufficient understanding of the underlying reaction pathways, which has prevented a quantitative prediction of the full product distribution (Al-Salem *et al.,* 2009).

5.2.2 Gasification

Air in this process is used as a gasification agent, which demonstrates a number of advantages. The main advantage of using air instead of O_2 alone is to simplify the process and reduce the cost. But a disadvantage is the presence of (inert) N_2 in air which causes a reduction in the calorific value of resulting fuels due to the dilution effect on fuel gases. Hence, steam is introduced in a stoichiometric ratio to reduce the N_2 presence. A significant amount of char is always produced in gasification which needs to be further processed and/or burnt. An ideal gasification process for PSW should produce a high calorific value gas, completely combusted char, produce an easy metal product to separate ash from and should not require any additional installations for air/water pollution abatement (Al-Salem et al, 2009).

Early gasification attempts of plastics, have been reported since the 1970s. The gasification into high calorific value fuel gas obtained from PSW was demonstrated in research stages and results were reported and published in literature for PVC, PP and PET. The need for alternative fuels has lead for the co-gasification of PSW with other types of waste, mainly biomass. Pinto *et al.* (2002, 2003) studied the fluidized bed co-gasification of PE, pine and coal and biomass mixed with PE. Xiao *et al.* (2009) co-gasified five typical kinds of organic components (wood, paper, kitchen garbage, plastic (namely PE), and textile) and three representative types of simulated MSW in a fluidized-bed (400–800 ^{0}C). It was determined that plastic should be gasified at temperatures more than 500 ^{0}C to reach a lower heating value (LHV) of 10,000 kJ/N (Al-Salem *et al*, 2009).

5.2.3 Hydrogenation (hydrocracking)

Hydrogenation by definition means the addition of hydrogen by chemical reaction through unit operation. The main technology applied in PSW recycling via hydrogenation technology is the Veba process. Based upon the coal liquefaction technology, Veba Oel AG converted coal by this process into naphtha and gas oil. Major technologies are summarized in Al-Salem *et al*, 2009.

5.2.4 Other chemical recycling schemes

Degradative extrusion provides an optimum engineering solution especially on a small-industrial scale (10 kg/h). The advantages of degradative extrusion as (i) achieving molecular breakdown of thermoplastics and hence low viscosity polymer melts, (ii) applying a combination of mechanical and chemical recycling scheme prompts the degradation process by introducing steam, gas, oxygen or catalysts, if needed. Another advantageous technology for chemical treatment is catalytic and steam cracking. The concept for both processes is the employment of either steam or a catalyst in a unit operation (Al-Salem *et al,* 2009).

5.3 Polyolefins thermal cracking

Appropriate design and scale (of operation and economy) are of paramount importance when it comes to thermal treatment plants. Thermal degradation behaviour in laboratory scale enables the assessment of a number of important parameters, such as thermal kinetics, activation energy assessment (energy required to degrade materials treated and product formation) and determining reference temperatures of the half life of polymers and maximum degradation point achievable. It is also important to perform pilot scale experiments utilizing a number of rectors and unit operation before commencing with an alteration on a performance scale This will also aid in the determination of the mode of the material processing of the thermal plant (i.e. pulsating, continuous, batch, etc.). Pyrolysis (depolymerization in inert atmospheres) is usually the first process in a thermal plant, and is in need of appropriate end-product design.

A number of studies have been carried out (Achilias et al., 2006) on polyolefins thermal cracking in inert (pyrolysis) and/or partially oxidized atmospheres (e.g. step pyrolysis, gasification). Previous reports focused on kinetic parameters estimations by means of different techniques and experimental conditions. Thermogravimetry is the most commonly used technique for the determination of kinetic parameters, although the experimental conditions utilized are very different, involving broad ranges of temperature, sample amount, heating rates (in the case of dynamic runs), reaction atmospheres and pressures. Almost all of previously published literature shows a power law equation to describe the thermal cracking of polymers and perform isothermal and/or dynamic experiments (Al-Salem *et al*., 2010).

5.4 Catalytic degradation

Studies concerning the use of different catalysts in the pyrolysis of polyolefins have been conducted by many authors (Achilias et al., 2006). Thus, TG and micro-reactors have been widely used to pyrolyse plastics with zeolite-based acid catalysts (Marcilla et al., 2001; 2004). Catalytic pyrolysis of polyethylene samples has also been carried out in the laboratory scale reactors, such as batch reactors (Seo et al., 2003, Van Grieken et al., 2001), semi-batch reactors (with evacuation of volatile products) (Akpanudoh et al.2005, Cardona and Corma, 2002) and fixed beds (Achilias et al., 2007).

The catalytic degradation of polymeric materials has been reported for a large range of model catalysts, including amorphous silica–alumina, zeolites Y, mordenite and ZSM-5, the

family of mesoporous MCM-41 materials (Marcilla *et al.,* 2002; 2003) and a few silico-aluminophosphate molecular sieves (Araujo *et al.,* 2002, Fernandes et al., 2002). Catalytic activity is closely related to the amount of acid sites, pore size and also shape of the catalyst (Park *et al.*, 2008, Serrano *et al.,* 2003). Silicoaluminophosphate (SAPO) molecular sieves represent an important class of adsorbents and catalytic materials generated by the introduction of silicon into its aluminophosphate framework. The medium pore SAPOs are attractive for catalytic applications due to the presence of specific acid sites in its structure which can convert the polymer into useful hydrocarbons (Elordi *et al.*, 2009, Singhal *et al.*, 2010, Park *et al*. 2008). The use of $BaCO_3$ as a catalyst for the thermal and catalytic degradation of waste HDPE was also reported (Rasul Jan *et al.*, 2010).

The catalysts more frequently employed for the cracking of polyolefins are shape-selective zeolites and mesoporous materials, such as HY, HZSM-5, Hβ or MCM-41 (Huang et al., 2009), which undergo inevitable deactivation by coke deposition. Indeed, this deactivation is a major hurdle in the implementation and scale-up of the valorization of plastics by cracking (Marcilla et al. 2007). Microporous zeolites have very high thermal stability and customized acid sites. Thus, the selection of the zeolite should be based on a target selectivity: HZSM-5 zeolite promotes the production of olefins (original monomers), while Hβ and HY zeolites maximize the production of middle distillates (Elordi et al., 2009).

The relevant literature reports well-founded mechanisms for coke formation and protocols for characterizing the coke deposited on zeolites. These studies assay reactions such as the cracking of hydrocarbons (Cerqueira et al., 2005; 2008, Guisnet et al., 2009). Marcilla et al. studied the deactivation of zeolites during the cracking of high-density polyethylene (HDPE), by using mainly a thermobalance as reactor. It should be pointed out that coke formation is strongly affected by the following factors, amongst others: catalyst properties (e.g. shape selectivity, acidity, and concentration of acid sites) (Huang et al, 2009), reactor medium (Aguayo et al., 1997), operating conditions or feedstock properties.

5.5 Reactor types

5.5.1 Pyrolysis in a fluidized bed reactors

Pyrolysis in a fluidized bed reactor and similar devices is the one with most possibilities for large-scale implementation for continuous waste plastic upgrading. The thermal degradation of plastic polymers has been studied first (Predel and Kaminsky, 2000, Berrueco et al. 2002, Mastellone et al., 2002, Mastral et al., 2002), but in situ catalytic pyrolysis has become a relevant research topic (Mastral et al., 2006, Hernández et al., 2007). The conical spouted bed reactor (CSBR) presents interesting conditions for catalytic pyrolysis because of the low bed segregation and lower attrition than the bubbling fluidized bed. The good performance of the CSBR has been proven for the selective production of waxes (Aguado et al., 2002), fuel-like hydrocarbons (Elordi et al., 2007) and monomers (Elordi et al., 2007). This good performance is a consequence of the solid flow pattern, high heat transfer between phases and the smaller defluidization problems when sticky solids are handled. Defluidization is due to the agglomeration of soid particles (sand) coated with melted plastic, constituting a severe problem in fluidized bed reactors. In the CSBR, polyolefins melt as they are fed into the reactor and they uniformly coat the sand and catalyst particles

due to their cyclic movement. Vigorous solid flow and the action of the spout avoid the formation of agglomerates. Furthermore, the CSBR has great versatility in terms of gas residence time, which may be reduced to values near 20 ms (Olazar et al., 1999) and, consequently, the yield of polyaromatic compounds is minimized. Besides, the smaller attrition of catalyst particles, due to the absence of a distributor plate, is another advantage over the fluidized bed for its use in catalytic processes. This excellent behaviour of the CSBR has already been recorded in other processes carried out prior to catalytic pyrolysis, such as catalytic polymerization, where a similar problem of fusion of catalyst particles coated with polymer occurs (Olazar et al., 1994). The simple design of a CSBR makes its scaling up straightforward. Furthermore, its throughput by reactor volume unit is higher than that of a bubbling fluidized bed due to the lower amount of sand required for fluidization enhancement.

5.5.2 Batch reactors

Thermal and catalytic degradation of polyethylene was conducted by Seo et al. 2003 at atmospheric pressure in a batch type reactor as is illustrated in Fig. 4. The reactor was a 1.1-liter round shape stainless steel bottle placed in a thermostatic furnace. Experimental procedure is as follows. The reactor system was connected to a nitrogen supply to eliminate air before premixed plastics and catalysts were fed into the reactor. Temperature of the reactor was increased to 450 ^{0}C and held for 30 min until the reaction was completely finished.
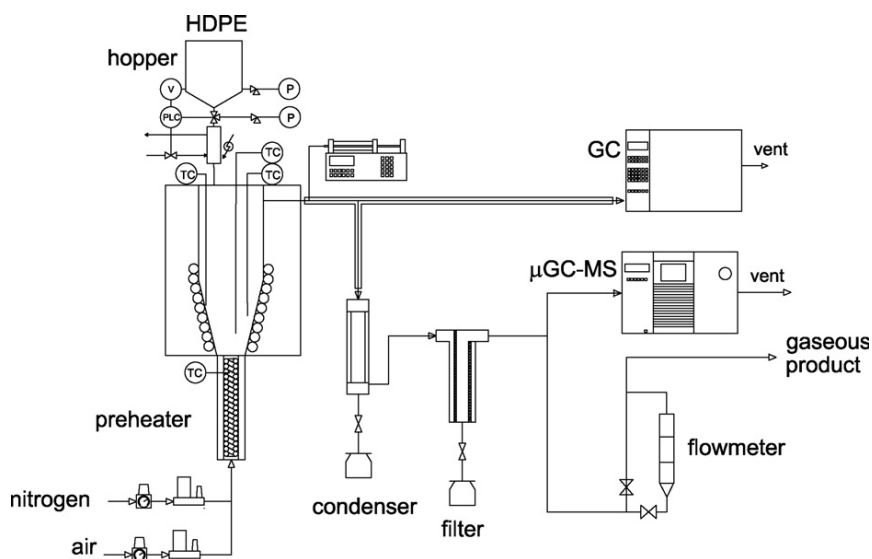

Fig. 3. Schematic representation of the continuous pyrolysis unit (Elordi et al. 2009).

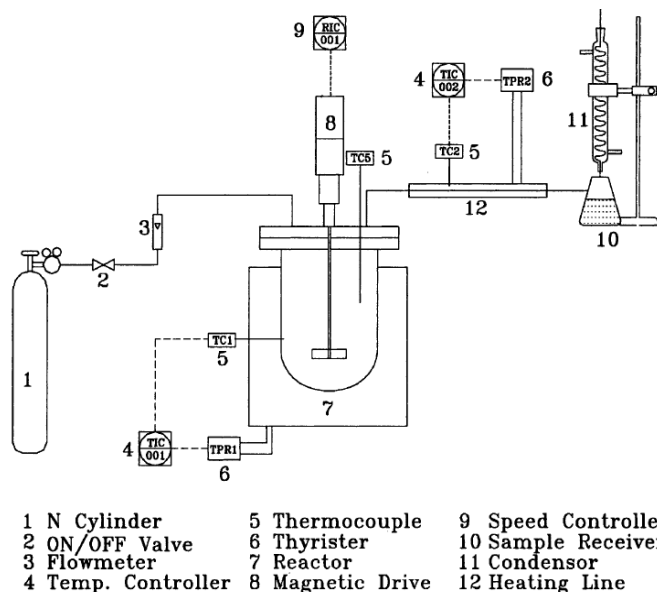|		
1 N Cylinder	5 Thermocouple	9 Speed Controller
2 ON/OFF Valve	6 Thyrister	10 Sample Receiver
3 Flowmeter	7 Reactor	11 Condensor
4 Temp. Controller	8 Magnetic Drive	12 Heating Line

Fig. 4. Schematic diagram of a batch pyrolysis system (Seo et al., 2003).

Another type of laboratory scale batch reactor was used for the catalytic degradation of polyethylene by Van Grieken et al. (2001). The experiments were carried out in a batch reactor provided with a helicoidal stirrer at 120 rpm (Fig. 5). Three temperatures (380, 400 and 420°C) and different reaction times (0–360 min) under nitrogen flow were studied. The effluent from the reactor was connected to a water-cooled trap in order to condense the liquid products, whereas the effluent gas was finally collected in a teflon bag.
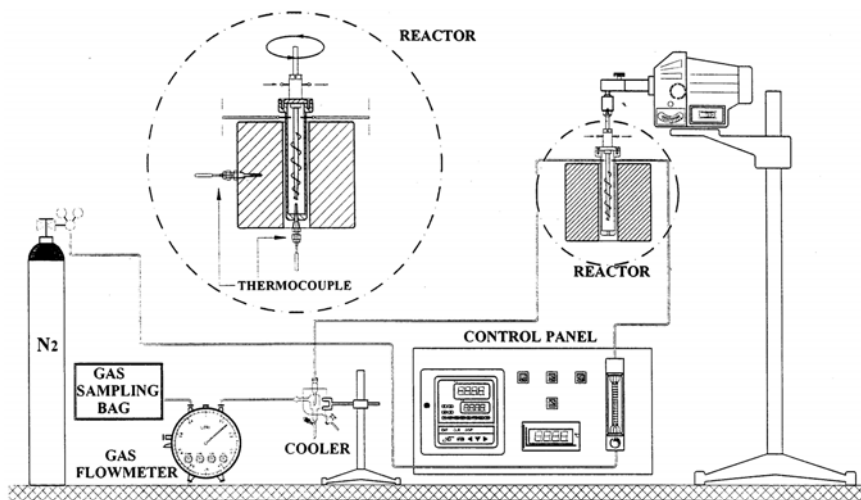
Fig. 5. Scheme of the experimental cracking reaction system (Van Grieken et al., 2001).

5.5.3 Fixed bed reactor

Achilias et al. (2007) used a laboratory-scale fixed bed reactor (Fig. 6) to study the thermal and catalytic degradation of polyethylene. The reactor was filled with the FCC catalyst and the piston was filled with the polymer. The time of the experiment was 17 min and the reaction temperature 450 ^{0}C. Experimental conditions and product yield from the thermal and catalytic pyrolysis of LDPE, HDPE and PP appear in Table 13.

Polymer	Temperature (ᵒC)	Catalyst	Gaseous product (wt.%)	Liquid product (wt.%)	Residue (wt.%)
LDPE	450	-	1.4	22.2	76.4
HDPE	450	-	1.7	21.6	76.7
PP	450	-	4.1	49.3	46.6
LDPE	450	FCC	0.5	46.6	52.9
HDPE	450	FCC	0.5	38.5	61.0
PP	450	FCC	6.2	67.3	26.5

Table 13. Experimental conditions and product yield from the thermal and catalytic pyrolysis of LDPE, HDPE and PP (Achilias et al., 2007).
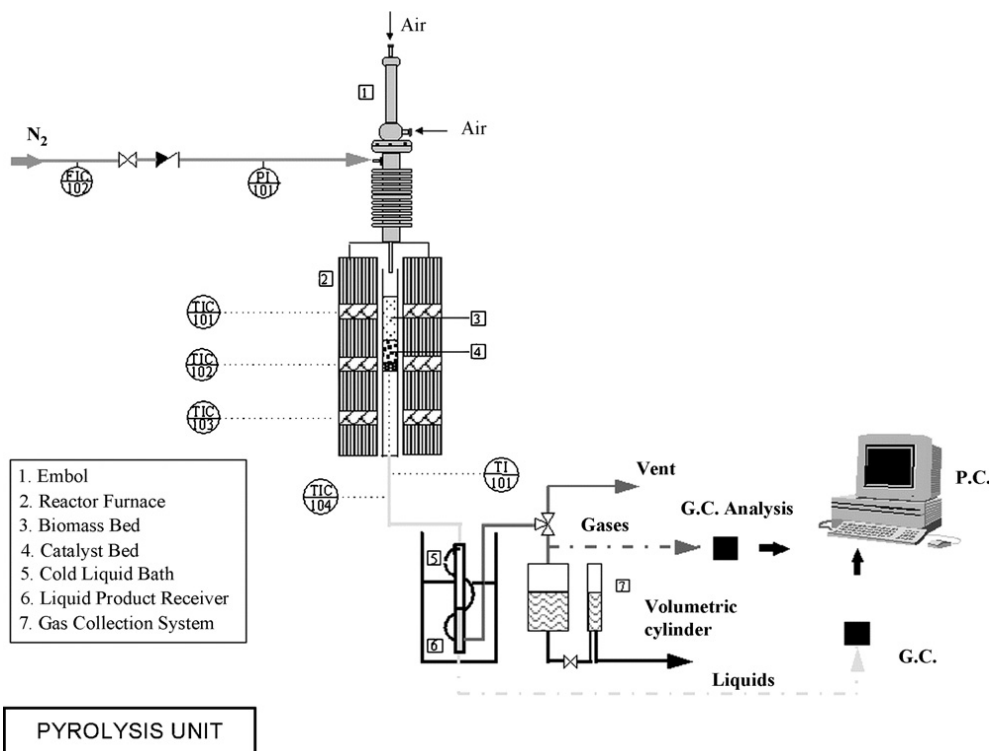
Fig. 6. The fixed bed reactor system (Achilias et al., 2007).

6. Chemical recycling of poly(vinyl chloride)

6.1 Introduction

Poly(vinyl chloride) main applications include food packaging, shoes, flooring ,pipes, clothing (leather-like material), ceiling tiles and multi-layered flooring and windows-windoors frames. It has a lifetime range of 5 years. PVC has the same density as that of PET, a property that made the separation prior to recycling of plastic wastes containing both polymers really difficult. The technique used for the efficient separation is X-ray fluorescence. The chlorine atoms of PVC are detected and the wastes are indicated for separation. Also IR sorting is widely used (Sadat-Shojai and Bakhshandeh, 2011).

In principle, PVC waste can be available in two ways: as a mixed plastic waste (MPW) fraction (with a rather low PVC content), or as a PVC-rich plastics fraction.
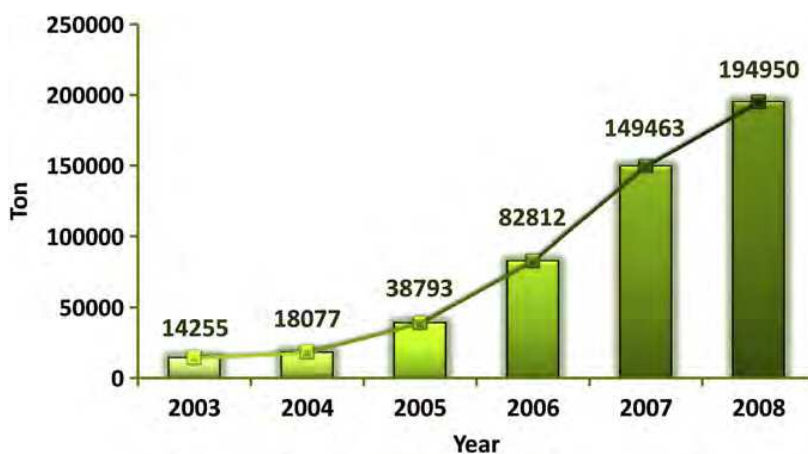
Fig. 7. The tonage of recycled PVC in EUROPE (Sadat-Shojai, Bakhshandeh, 2011).

As it is well-known PVC incineration is connected with problems arising from the high chlorine content of this polymer which yields large amounts of hydrochloric acid (HCl) during thermal decomposition, beside the possibility of formation of persistent and toxic compounds such as toxic dioxines and furans (Garcia et al., 2007; Ulutan, 1998; Ali and Siddiqui, 2005). In addition, when PVC wastes are fired in an incinerator, HCl corrodes the boiler tubes of the incinerator and other equipments. Therefore the steam pressure must be kept relatively low to prevent corrosion of the heat recovery boiler (Yoshioka et al., 1998). One of the best solutions to this problem may be neutralization of HCl with calcium carbonate (lime) and/or sodium hydroxide (caustic soda) to convert the released HCl to the salts. Also special filters can also be used to prevent problems related to atmospheric emissions during the combustion process (Machado et al., 2010).

Beside all above problems, net energy recovered by incineration of PVC-rich waste is not high enough to make it highly economic. As most hydrocarbon polymers, the calorific value from incineration of PVC in an ideal conditions is about 64 MJ/kg, compared to, for example, 17 MJ/kg for paper, or 16 MJ/kg for wood. Moreover, PVC is inherently difficult to combust, so that complete combustion of PVC-rich waste occurs at such high temperatures (>1700 K), that it is economically prohibitive (Xiong, 2010).

Therefore mechanical and/or chemical recycling of PVC plastic wastes seems the logical solution One usual approach for chemical recycling of PVC wastes is currently "thermal cracking" via hydrogenation, pyrolysis or gasification (Ryu et al., 2007; Williams and Williams, 1998; DeMarco et al., 2002; Kaminsky and Kim, 1999; Borgianni et al., 2002).

The main intermediate product of the thermal cracking is a polyene material that continues to degrade by evolution of aromatics and converts to a products which their composition will be strongly determined by processing variable such as type of atmosphere, temperature and residence time. In an inert atmosphere, the degradation products will be hydrochloric acid (HCl), gaseous and liquid hydrocarbons, and char, which among them HCl is a main product and can be reused either in vinyl chloride production, or in other chemical processes (Slapak et al., 1999).

In the case of manufacturing process of vinyl chloride, a gas purification unit must also be added to obtain high purity hydrogen chloride gas.

In a steam atmosphere at high temperatures, the hydrocarbon fraction will be converted into the some other products such as carbon monoxide, carbon dioxide and hydrogen. In a reported process bench-scale bubbling fluidized bed to investigate some processing parameters on the product outcome. The choice of type of bed material is essential for the product outcome, so that the use of catalytic inactive solid quartz as bed material results in the production of large amounts of char and tar, whereas the application of catalytic active material such as porous alumina results in a high conversion of PVC into the syngas. Moreover, according to their results, temperature has a large impact on the composition of the products, so that the carbon to gas conversion improved from about 70% at 1150 K to approximately 100% by increasing the reactor temperature to 1250 K. For chemical recycling of PVC, an increase in efficiency of dehydrochlorination process is usually attributed to the successful recycling (Wu et al., 2009).

It has been also reported that the emission of hydrogen chloride changes significantly with the oxides used indicating the chlorine fixing ability of oxides and also that utilization of poly(ethylene glycol) (PEG) can accelerate dehydrochlorination of PVC, so that at 210 °C for 1 h the dehydrochlorination degree was as high as 74% for PVC/PEG, while for PVC only 50%. Moreover, they demonstrated that for PVC/ PEG the decomposition of PVC shifted to lower temperatures compared with that of pure PVC, suggesting some interactions exist between PEG and PVC that caused the faster dehydrochlorination rate. According to their results, during this process, no waste byproducts such as KCl were produced, and satisfactory recyclability of PEG (10 cycles) can be obtained (Wu et al., 2009).

An alternative method to thermal process of dehydrochlorination is the rather easy process of dehydrochlorination under the influence of alkaline media to recover hydrochloric acid

with a possibility that the degradation of PVC by oxygen oxidation in an aqueous alkaline solution to produce various carboxylic acids (Brown, 2002).

Some researchers demonstrated that dehydrochlorination of flexible-PVC occurred first and followed then by oxidation. They reported that the major products were oxalic acid, a mixture of benzenecarboxylic acids, and CO_2. However, the chlorine content could also be recovered in the form of HCl by adjusting the reaction conditions such as alkali concentration (Yoshioka et al., 1998).

Among various methods of thermal cracking, pyrolysis is a more well-known procedure in the chemical recycling of PVC. The process of pyrolysis, which takes places at 500-900°C without any oxygen, is a very suitable recycling method especially in the case of mixed plastic wastes (PVC recycling, 2005). In a typical process, a PVC-rich waste can be pyrolysed to hydrocarbons (oil), soot, hydrochloric acid, chlorinated hydrocarbons, etc., which hydrochloric acid needs to be removed from the pyrolysis gas although this removal process can result in the formation of toxic dioxins in some stages. The main end product of pyrolysis is, however, oil industry (Sadat-Shojai and Bakhshandeh, 2011).

One main problem connected with pyrolysis of PVC and mixed plastics containing PVC materials is corrosion of the process equipment (e.g., pyrolysis reactor and piping) mainly by the formation of the acid gas (HCl). Moreover, many petrochemical specifications limit the amounts of halogens (appeared in the forms of hydrogen chloride and chloro organic compounds) to a very low range in the gas and oil derived from plastic waste. Therefore in the case of mixed plastic wastes (uneconomic to separate to a single polymer) with a low PVC content, the conventional chemical recycling is frequently used only for a waste stream in which the PVC content is less than 30% (for example, the multiple material products) (Duangchang, 2008).

So far, several solutions to such problems have been proposed which some of them have already been put into practical use. For example, milling of PVC with CaO can be an effective way to extract Cl from the waste (Tongamp et al., 2008).

An attempt has also been made to develop a process for recovering metals from alloy-wastes by using a mechanochemical reaction consisting of a co-grinding alloy and PVC waste, followed by washing with water and filtration (Zhang et al., 2007).

Currently, the NKT-Watech pyrolysis process in Europe uses another two-step pyrolysis of PVC wastes in a stirred vessel. Calcium carbonate and filler are used to react with liberated HCl and produce calcium chloride. Then at the increased temperature, the polymer chains break down which produce a solid coke residue. Finally, the residual calcium chloride can be treated to make it suitable for selling (Scheirs, 2010).

Alternative approach is pre-treatment of mixed plastic waste by removing PVC and other halogenated plastics from the feed. Such pre-treatment consists of a dilution of the wastes having excessive chlorine content with less chlorine-containing or chlorine-free polymer mixture. It is also common to dilute the chlorine-containing hydrocarbon feed with chlorine-free petroleum fractions coming from refineries. Another possibility, as a less expensive and more acceptable process, is thermal dehalogenation which takes place either in a liquid or in a fluidized bed pyrolysis.

A new method consisting of copyrolysis of PVC with nitrogen compounds in biowaste to reduce the corrosive effects of the generated HCl was reported. The researchers studied the pyrolysis conditions between PVC and cattle manure via a statistical method and optimized conditions to provide the highest HCl reduction during PVC pyrolysis. They also applied the optimized conditions to a plastic mixture and then determined the quality of the obtained products. They concluded that the lowest heating rate, the highest reaction temperature (450°C), and the PVC:cattle manure ratio of 1:5 are the suitable conditions which provide the highest HCl reduction. However, according to their results the presence of manure decreases the oil yield of pyrolysis by about 17% (Duangchang, 2008).

PVC can also be chemically modified by nucleophilic substitution of chlorine atoms in its structure as it has been described: reactions of rigid PVC with various nucleophiles (Nu) such as iodide, hydroxide, azide, and thiocyanate in ethylene glycol as solvent. Such reactions lead to the substitution of Cl by Nu and finally elimination of HCl, resulting in the dehydrochlorination of the rigid PVC. According to their results, the dehydrochlorination yield increased with an increasing nucleophiles concentration, resulting in a maximum substitution at high nucleophiles amounts. Moreover, when ethylene glycol was replaced by diethylene glycol the dehydrochlorination was found to be accelerated, which may be due to the higher compatibility of diethylene glycol with PVC, making it easier to penetrate the rigid PVC particles (Kameda et al., 2010).

Several different technologies based on depolymerization and repolymerization processes have been developed for chemical recycling of PVC, which unfortunately the most of them are more expensive than the mechanical recycling (LaMantia, 1996).

PVC waste was used in a research wich carried out for the recycling electric arc furnace dust by heat treatment with PVC. The entire process aimed to recover the zinc, lead, and cadmium from the dust and was adjusted so that the residual dust can be injected into the electric arc furnace (Lee et al., 2007).

There are many reports, where thermoanalytical methods especially coupled methods with gas analysis systems, can deliver suitable information for the recycled PVC that needs to be characterized (Matuschek et al., 2000).

6.2 Mixed plastic recycling processes

Recovinyl-Co (UK) deals with post-consumer PVC to reproduce two grades via mechanical recycling. Due to its structure and composition, PVC can easily be mechanically recycled in order to obtain good quality recycling material. Careful and proper sorting is of crucial importance for the optimal recycling of PVC (Recovinyl, 2008).

A pyrolytic process which has proven to be successful for plastic solid waste rich in PVC, is the Akzo process (Netherlands). With a capacity of 30 kg/h, this fast pyrolysis process is based on a circulating fluidised bed system (two reactors) with subsequent combustion. Input to the process is shredded mixed waste including a high percentage of PVC waste. The main outputs consist of HCl, CO, H_2, CH_4 and, depending on the feedstock composition, other hydrocarbons and fly ash (Tukker et al., 1999).

The NRC process is another successful pyrolysis scheme. This process is based on the pyrolysis with subsequent metal extraction technology. The aim is to produce purified calcium chloride instead of HCl. The input to the process is PVC waste (cables, flooring, profiles, etc.). No other plastic solid waste type is fed to the processing, which results in calcium chloride, coke, organic condensate (for use as fuels) and heavy metals for metal recycling, as products (Al-Salem et al., 2009).

The NTK process, depicted below (fig. 8), is a very successful recycling process. The process is based on an initial pre-treatment step that involves separating light plastics (PP, PE, etc.) and other materials, e.g. wood, sand, iron, steel, brass, copper and other metallic pollutants. The PSW waste is then fed to a reactor at a low pressure (2–3 bars) and a moderate temperature (375°C). The process emits neither dioxins, chlorine, metals nor plasticizers. Also, there are no liquid waste streams in the process since all streams are recycled within the system. There is a small volume of carbon-dioxide gas formed by the reaction between lime/limestone and hydrogen chloride. Mixed PVC building waste containing metals, sand, soil, PE, PP, wood and rubber waste have been successfully treated (Al-Salem et al., 2009).

The gasification into high calorific value fuel gas obtained from PVC was also reported by Borgianni et al., 2002.
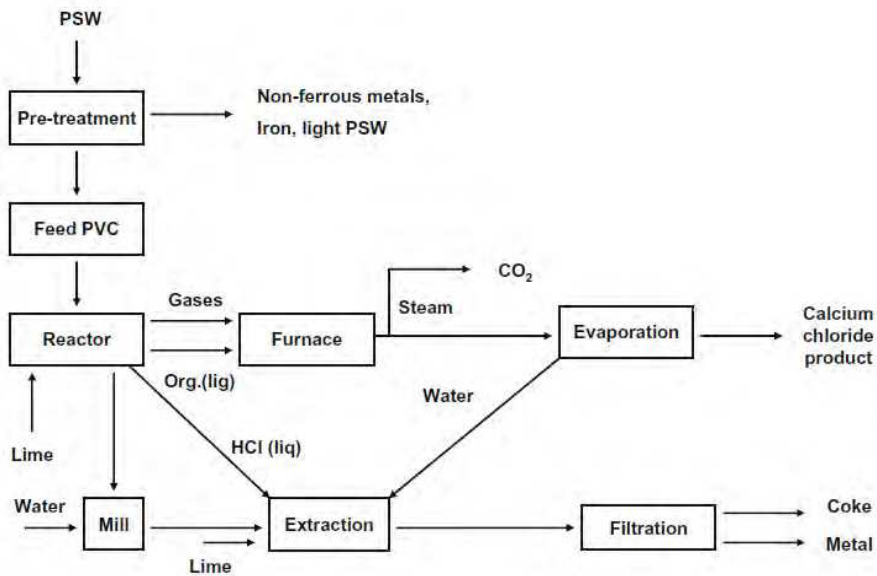
Fig. 8. NTK process diagram (Tukker et al., 1999).

Chemical recycling of PVC has been also attempted. Most of the proposed processes use the rather easy dehydrochlorination of PVC either under the influence of heat of alkaline media. The oxidative degradation of PVC by molecular oxygen in aqueous alkaline solution at temperatures between 150 and 260 $^{\circ}$C with oxygen pressures of 1–10 MPa has been reported. The main products are oxalic acid and carbon dioxide, their yield

depending on the reaction conditions and the alkali concentration. The maximum yield of oxalic acid was 45%and 42% of the chlorine content could be recovered in the form of HCl (Shin et al., 1998).

Oxidative degradation of rigid-PVC pellets (R-PVC) with oxygen was carried out in 1-25 mol/kg-H_2O (m) NaOH solutions, at 150-260°C and P_{O2} of 1-10 MPa in order to investigate the chemical recycling of PVC materials. The apparent rate of oxidative degradation of R-PVC progressed as a zero order reaction, and the apparent activation energy was 38.5 kJ/mol. The major products were oxalic acid, a mixture of benzene-carboxylic acids, and CO_2. The tin in R-PVC was extracted completely. The possibility of converting PVC materials into raw materials such as carboxylic acids by chemical recycling is reported (Yoshioka et al., 2000).

6.3 Mixed PVC wastes World inititives

Regarding the chemical recycling of mixed plastic wastes with a PVC content of up to several percent, the following initiatives seem to be most realistic for the coming 5 years: **Texaco gasification process** (NL, pilot in the US), Polymer cracking process (consortium project, pilot), **BASF conversion process** (D, pilot but on hold) **Use as reduction agent in blast furnaces** (D, operational), **Veba Combi Cracking process** (D, operational but to be closed by 2000**), Pressurized fixed bed gasification of SVZ** (D, operational). A brief report on these initiatives is presented below (Sadat-Shojai and Bakhshandeh, 2011).

BP Chemicals has led promotion of Polymer Cracking technology for feedstock recycling since its beginnings in the early 1990's. Since the challenge of recycling of plastics is industry wide, support has been provided by a Consortium of European companies to develop the
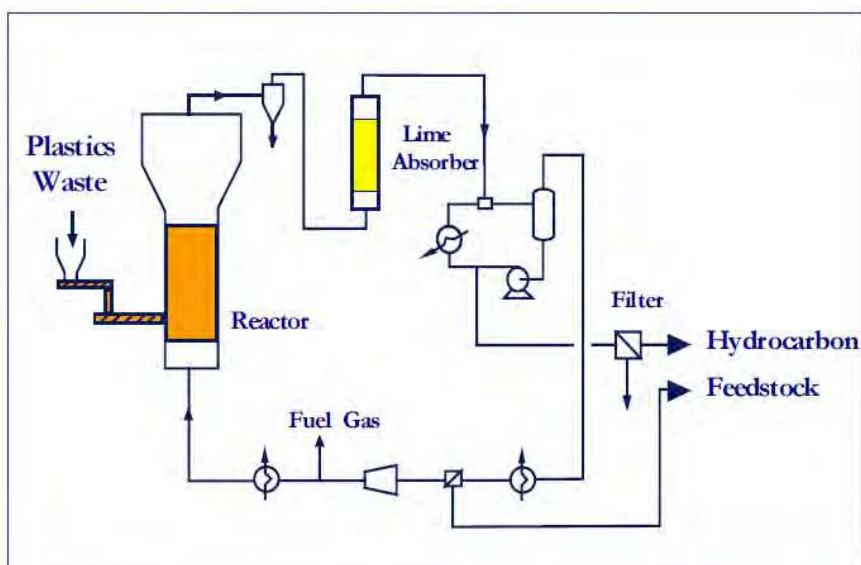

Fig. 9. The BP polymer cracking process (Tukker et al., 1999).

technology – initially including Elf Atochem, DSM, Fina and Enichem. The consortium members at the time of the successful pilot plant trials in 1997 were BP Chemicals, Elf Atochem, EniChem, DSM, CREED and the APME. Some elementary preparation of the waste plastics feed is required, including size reduction and removal of most non-plastics. This prepared feed is fed directly into the heated fluidised bed reactor which forms the heart of the Polymer Cracking process. The reactor operates at approximately 500°C in the absence of air. The plastics crack thermally under these conditions to hydrocarbons which vaporise and leave the bed with the fluidising gas. Solid impurities, including metals from e.g. PVC stabilisers and some coke, are either accumulated in the bed or carried out in the hot gas as fine particles for capture by cyclone. The decomposition of PVC leads to the formation of HCl, which is neutralised by bringing the hot gas into contact with a solid lime absorbent. This results in a $CaCl_2$ fraction that has to be landfilled. The purified gas is cooled, to condense most of the hydrocarbon as valuable distillate feedstock. This is then stored and tested against agreed specifications before transfer to the downstream user plant. The remaining light hydrocarbon gas is compressed, reheated and returned to the reactor as fluidising gas. Part of the stream could be used as fuel gas for heating the cracking reactor, but as it is olefin-rich, recovery options are being considered.

The process shows very good results concerning the removal of elements like chlorine. With an input of 10,000 ppm (or 1%) Cl, the products will contain around 10 ppm Cl. This is somewhat higher than the specifications of 5 ppm typical for refinery use. However, in view of the high dilution likely in any refinery or petrochemical application, BP assumes that this is acceptable. Also, metals like Pb, Cd and Sb can be removed to very low levels in the products. Tests have shown that all the hydrocarbon products can be used for further treatment in refineries (Brophy et al., 1997).

The BASF feedstock recycling process was designed to handle the recycling of mixed plastic waste supplied by the DSD collection system. The process is as follows, before the waste plastics can be fed to the process, a pretreatment is necessary (fig. 10). In this pretreatment the plastics are ground, separated from other materials like metals and agglomerated. The conversion of the pretreated mixed plastic into petrochemical raw materials takes place in a multi-stage melting and eduction process. In the first stage the plastic is melted and dehalogenised to preserve the subsequent plant segments from corrosion. The hydrogen chloride separated out in this process is absorbed and processed in the hydrochloric acid production plant. Hence, the major part of the chlorine present in the input (e.g. from PVC) is converted into saleable HCl. Minor amounts come available as NaCl or $CaCl_2$ effluent (Heyde and Kremer, 1999). Gaseous organic products are compressed and can be used as feedstock in a cracker. In the subsequent stages the liquefied plastic waste is heated to over 400 °C and cracked into components of different chain lengths. About 20-30% of gases and 60-70% of oils are produced and subsequently separated in a distillation column. Naphtha produced by the feedstock process is treated in a steam cracker, and the monomers (e.g. ethylene, propylene) are recovered. These raw materials are used for the production of virgin plastic materials. High boiling oils can be processed into synthesis gas or conversion coke and then be transferred for further use. The residues consist of 5% minerals at most, e.g. pigments or aluminium lids. It seems likely that metals present in PVC-formulations mainly end up in this outlet. The process is carried out under atmospheric pressure in a closed system and, therefore, no other residues or emissions are formed.
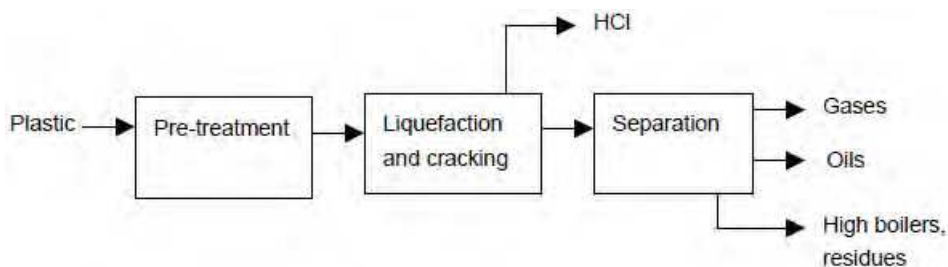
Fig. 10. BASF process [Heyde and Kremer, 1999].

Mixed PVC waste can be used as reduction agent in blast furnaces. For the production of pig iron for steel production, iron ore (Fe_2O_3) has to be reduced to Fe. This process takes place in a blast furnace. Coke, coal and heavy oil are normally used as reducing agents in this process. Iron and steel companies try to lower the consumption of coke, by partly replacing it with coal, gas or fuel oil (30% in weight seems to be the maximum), via coal injection technology. Recently, new developments have started to replace the conventional reducing agents by plastics waste. Though others like British Steel (UK) have done trials as well, the prominent pioneer in this field is Stahlwerke Bremen, Germany. Stahlwerke Bremen is a large German steel manufacturer which operates two blast furnaces to produce over 7000 t/day, or some 3 Million tpa pig iron. Currently, German is the sole country that blast furnace are the only plants using waste this way (DKR/DSD, 1999).

Veba Combi Cracking process. The plant configuration includes a depolymerisation section and the VCC section (fig. 11). Depolymerisation is required to allow further processing in the VCC section. In the depolymerisation section the agglomerated plastic waste is kept between 350-400°C to effect depolymerisation and dechlorination. The overhead product of the depolymerisation is partially condensed. The main part (80 %) of the chlorine introduced with PVC is present as HCl in the light gases. It is washed out in the following gas purification process, yielding technical HCl. The condensate, containing 18 % of the chlorine input, is fed into a hydrotreater. The HCl is eliminated with the formation water. The resulting Cl-free condensate and gas are mixed with the depolymerisate for treatment in the VCC section. The depolymerisate is hydrogenated in the VCC section at 400-450°C under high pressure (about 100 bar) in a liquid phase reactor with no internals. Separation yields a product which after treatment in a fixed-bed hydrotreater is a synthetic crude oil, a valuable product which may be processed in any refinery. From the separation a hydrogenated residue stream also results, which comprises heavy hydrocarbons contaminated with ashes, metals and inert salts. This hydrogenation bitumen is a byproduct which is blended with the coal for coke production (2 wt%). It is most likely that the major part of any metals present in a PVC formulation end up in this residue flow. Light cracking products end up in off-gas (E-gas), which is sent to a treatment section for H_2S and ammonia removal. As indicated above, the main part of the chlorine present in the input (i.e. from PVC) is converted into usable HCl. Some 2% of the chlorine input is bound to $CaCl_2$ in the process by a 4 times leaner than stochiometric amount of CaO.
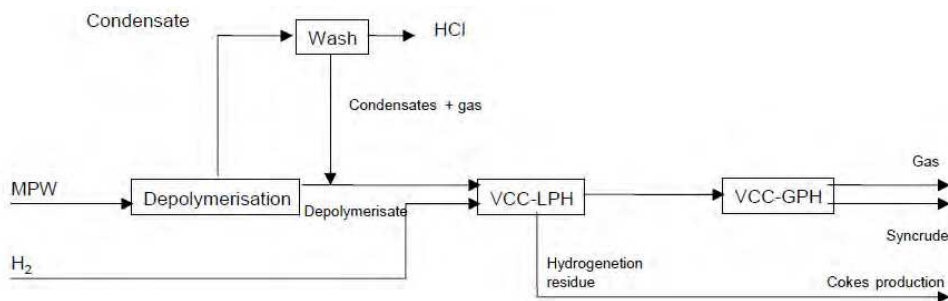
Fig. 11. Veba Combi Cracking process (Sas, 1994).

7. Chemical recycling of polycarbonate

7.1 Introduction

Polycarbonate plastics, $C_{16}H_{14}O_3$ (Fig. 12) are polyesters known for their excellent mechanical properties. Featuring high-impact resistance, UV resistance, and flame retardancy as well as excellent electrical resistance, polycarbonates are used in a wide variety of materials. Polycarbonates do not have their own recycling identification code and therefore fall under the #7 "other" classification. Polycarbonates may be made a variety of ways, the most popular of which from Bisphenol-A (BPA) feedstock. BPA use is highly controversial, and the FDA has recently decided to reopen an inquiry on the safety of BPAs. [Jawad et al., 2009].

This is following an approval in 2008. Nalgene Outdoor Products, the pre-eminent manufacturer of reusable plastic water bottles, is transitioning from polycarbonate bottles to other plastics as well as metal alternatives in the wave of negative consumer perception of BPA.
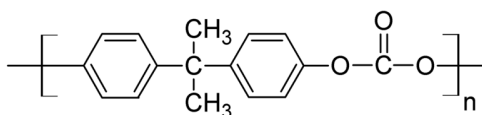
Fig. 12. Structural unit of polycarbonate.

Due to its excellent properties, polycarbonate (PC) is widely used in the manufacture of compact disks, bullet proof windows, food packaging and soft-drink bottles. With the rapid increase in the production and consumption of PC, the chemical recycling of waste PC to obtain valuable products has received greater attention in recent years. Waste PC can be depolymerised through a chemical treatment to produce monomers that can be used to reproduce virgin PC products. Various methods for the chemical recycling of waste PC to recover raw materials have been reported; these methods include thermal pyrolysis [Yoshioka

et al., 2005; Chiu et al., 2006; Achilias et al., 2009], alcoholysis [Oku et al., 2000; Hu et al., 1998] and hydrolysis [Grause et al., 2009; Ikeda et al., 2008]. It is difficult to recover pure BPA using thermal pyrolysis, and it can be only obtained using hydrolysis. [Liu et al., 2011].

For the purpose of recycling of polycarbonate (PC), e.g. poly[2,2-bis(4-hydroxyphenyl) propane carbonate], in the form of an essential monomer bisphenol A, there have been reported a number of depolymerization methods.[Hub et al., 1998] Due to the insolubility of PC in water, the aqueous depolymerizations require severe conditions such as long reaction times, high temperatures and pressures. Therefore, instead of using aqueous systems, organic solvent systems such as methylene chloride in combination with ammonia [Fox et al., 1989], a mixed solvent of phenol and methylene chloride in combination with an alkali catalyst [Buysch et al., 1994; Shafer, 1994] have been reported. With organic solvents, however, a tedious product separation process is generally required.

7.2 Recycling techniques

With the rapid increase of production and consumption of PC, the chemical recycling of waste PC has been gaining greater attention in recent years to obtain valuable products. Methanolysis is one of the most important method to recover pure monomer BPA and dimethyl carbonate (DMC). However, due to the insolubility of PC in methanol, the reported methanolysis methods require high temperature and pressure and in presence of a lot amount of concentrated bases or acids. The acid or base catalysts used in traditional methods cannot be reused and result in other disadvantages such as equipment corrosion, tedious workup procedure and environmental problem. Although supercritical method can overcome some of above-mentioned shortcomings, it has its own disadvantages such as severe conditions, so its application is limited. According to a study polycarbonate could be completely decomposed into its monomer, BPA with high pressure (not atmospheric pressure) high temperature steam (300 °C) in five minutes reaction time. It is known that PC can be decomposed into monomer in alkaline alcohol or aqueous solutions. However, the monomer BPA yield has been reported as to be relatively low due to BPA instability in that condition. To develop a high-effective process of PC recycling, a reactive atmosphere must be provided that preserves the stability of BPA and get has high reactivity for PC. To determine the optimum conditions for recycling PC, it is important to know the stability or reactivity of BPA, as well as the decomposition rate of PC.

Alkali-catalysed depolymerization of polycarbonate wastes by alcoholysis in supercritical or near critical conditions has been also studied by other researchers in order to recover the essential monomer BPA and DMC as a valuable by-product (Liu et al., 2009). Some works aimed to develop continuous process and possible scale-up for decomposition of both PC plastic wastes using methanol as solvent/reagent and NaOH as alkali catalyst. Total depolymerization of PC has been achieved working at a temperature range of 75–180 °C and pressures from 2 to 25 MPa.

However, due to the insolubility of PC in water, the aqueous depolymerizations require severe conditions such as long reaction times, high temperatures and pressures. Therefore, instead of using aqueous systems, organic solvent systems such as methylene chloride in combination with ammonia, a mixed solvent of phenol and methylene chloride in

combination with an alkali catalyst is also used. An environmentally friendly strategy for methanolysis of polycarbonate to recover bisphenol A and dimethyl carbonate was recently developed in which PC could be methanolyzed in an ionic liquid without any acid or base catalyst under moderate conditions (Liu et al., 2011).

7.2.1 Methanolysis in the presence of ionic liquids

The methanolysis of polycarbonate using ionic liquid [Bmim][Ac] as a catalyst was studied recently by Liu et al., 2011. The effects of temperature, time, methanol dosage and [Bmim][Ac] dosage on the methanolysis reaction were examined. They concluded that methanolysis of PC to obtain its starting monomers, BPA and DMC, could occur in the presence of ionic liquid [Bmim][Ac] under moderate conditions without an acid or base catalyst. The methanolysis conversion of PC was nearly 100% and the yield of BPA was over 95% under the following conditions: m([Bmim][Ac]):m(PC) = 0.75:1, m(methanol):m(PC) = 0.75:1, a reaction temperature of 90 ◦C and a total time of 2.5 h. The ionic liquid [Bmim][Ac] could be reused up to 6 times without an apparent decrease in the conversion of PC and yield of BPA. This strategy could overcome the shortcomings associated with the traditional methods, such as the infeasibility of reusing the catalyst, equipment corrosion, tedious workup procedures and environmental problems. Moreover, the investigation on kinetics indicated that the methanolysis of PC in [Bmim][Ac] was a first-order reaction and the activation energy was 167 kJ/mol. The reaction formula was as follows:
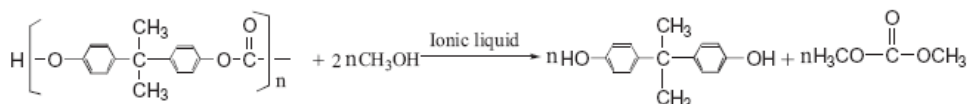

Fig. 13. Methanolysis of PC.

A mechanism for the methanolysis of PC in the presence of ionic liquid [Bmim][Ac] is suggested in Figure 14. After PC was dissolved or swelled in the ionic liquid, it reacted with methanol to form oligomers under ionic liquid catalysis. Then, the resulting oligomers reacted with methanol further to produce the final products, BPA and DMC.

7.2.2 Alkali catalyzed methanolysis

Alkali-catalyzed methanolysis of poly[2,2-bis(4-hydroxyphenyl)propane carbonate] in a mixed solvent of methanol and toluene or dioxane was studied by the team of Oku et al., 2000 at Kyoto Institute of Technology. Treatment of PC pellets in MeOH with a catalytic amount of NaOH at 608C for 330 min yielded only 7% BPA. However, in a mixed solvent of MeOH and toluene, the analogous treatment for 70 min completely depolymerized PC to give free bisphenol A (96%) in a solid form and dimethyl carbonate (DMC) (100%) in solution.

The characteristic feature of the present methanolysis is that PC can be depolymerized to its starting monomer components BPA and DMC by the use of a catalytic amount of alkali-metal hydroxide under mild reaction conditions. The monomers can be obtained almost quantitatively in very pure states and they can be recycled as the monomers of PC and epoxy resins.

The alkali catalysed methanolysis also studied by Liu et al., 2009 but the reaction took place in a reactor with a stirrer and a refluxing condenser. The results did not differ much because of the use of refluxing condenser. The temperature, on the other hand effected the efficiency of methanolysis in both studies with the temperature of 60°C presenting the greater rate of BPA formation.
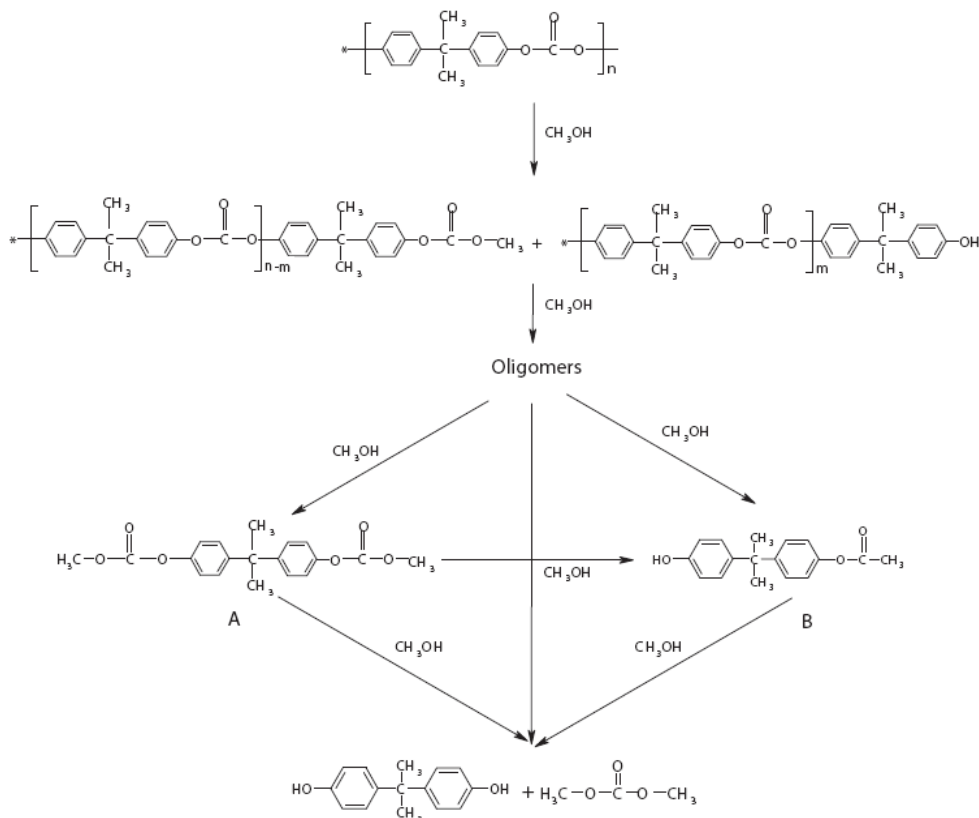

Fig. 14. Methanolysis mechanism for PC in the presence of ionic liquid [Bmim][Ac] [Liu et al., 2011].

7.2.3 Hydrolysis with high temperature steam

Watanabe et al. 2009, found that polycarbonate was rapidly hydrolyzed in high pressure high temperature steam around the saturated pressure of water at 573 K. For 300 s (5 min) reaction time, PC completely decomposed into bisphenol A and the maximum yield of BPA was around 80%. In liquid water phase at 573 K, PC still remained even for 3000 s (50 min). The high yield of bisphenol A in high pressure steam was due to its high stability. The amount of water required for degradation was drastically reduced and thus the high pressure high temperature steam process was energetically and economically preferable.
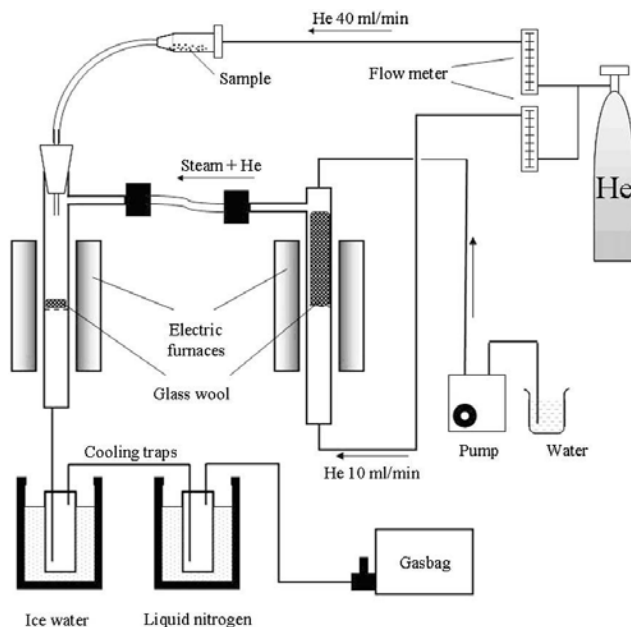
Fig. 15. Apparatus hydrolysis with high temperature steam (Grause et al., 2009).

The reaction mechanism of polycarbonate hydrolysis in high pressure high temperature steam seems to be both surface and bulk erosion.

Another study of polycarbonate hydrolysis has been done by Grause et al., 2009 at Tohoku University. They studied the pyrolytic hydrolysis in the presence of earth-alkali oxides and hydroxides as catalysts. The experiments were carried out in a steam atmosphere in the presence of MgO, CaO, Mg(OH)$_2$ or Ca(OH)$_2$. All of these catalysts accelerated the hydrolysis of PC drastically, with MgO and Mg(OH)$_2$ being more effective than their Ca counterparts. The differences between oxides and hydroxides were negligible indicating the same mechanism for both, oxides and hydroxides. BPA was the main product at 300 ºC, with a yield of 78% obtained in the presence of MgO. At 500 ºC, BPA was mainly degraded to phenol and isopropenyl phenol (IPP). It can be shown that a combined process involving PC hydrolysis at 300 ºC and BPA fission at 500 ºC leads to high yields of phenol and IPP and the drastic decrease of residue. The apparatus of the experimental process is shown in Fig. 15.

7.2.4 Hydrolysis in other solvents but water

Alkali-catalyzed hydrolysis of PC in a solvent in which it can substantially dissolve such as N-methyl-2-pyrrolidone, 1,4-dioxane, tetrahydrofuran or DMF were studied by Liu et al., 2009. The results showed that hydrolysis of PC could take place under moderate conditions. No BPA was detected when hydrolysis of PC was carried out under given conditions in water without co-solvents. However, when the hydrolysis was carried out under the same conditions in presence of such a solvent, the rate of hydrolysis was significantly accelerated.

Also, with the increasing of amount of H_2O, the yield of BPA gradually increased and a maximum yield was obtained when using ratio of $PC:H_2O$ close to 1.5:1. When the amount of water was more than this ratio the BPA yield decreased. Moreover, under the conditions of reaction temperature 100 ^{o}C, $m(PC):m(H_2O)$ = 1:0.7, $m(PC):m(NaOH)$ = 10:1, reaction time 8 h and using 1,4-dioxane as solvent, the hydrolysis conversion of PC was almost 100% and the yield of bisphenol A was over 94%.

7.2.5 Noncatalyzed glycolysis of PC in ethylene glycol

Kim et al. 2009 explored the depolymerization of polycarbonate waste by glycolysis using ethylene glycol without catalyst in order to get the monomer bisphenol A. This process can be considered as a green process from the viewpoint of using neither toxic solvents nor alkali catalyst. The maximum yield of BPA of 95.6% was achieved at reaction temperature 220 °C for 85 min with an EG/PC weight.

This reaction mechanism is illustrated in Fig. 16. Ethylene glycol penetrates into the PC polymer particle so that the particles are swollen. The PC is depolymerized in the solid state
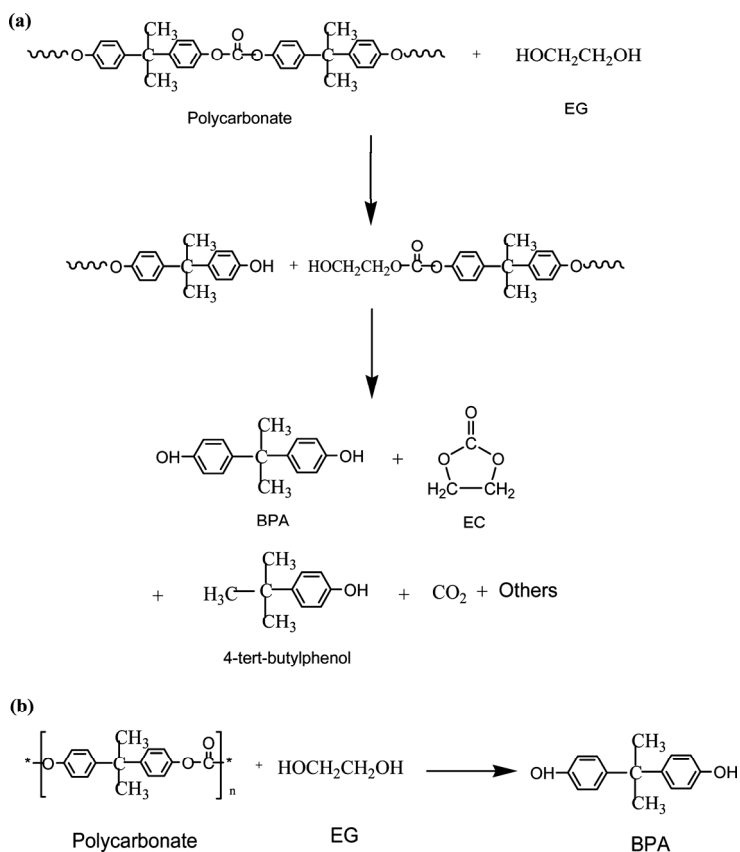

Fig. 16. PC glycolysis reaction pathway (Kim et al., 2009**).**

by the diffused EG. Random scissions of PC take place to lower the average molecular weight until the resulting oligomer can be dissolved in the bulk EG solution but retains solid state. The solid oligomer dissolves in EG solution, and the size of the PC particle shrinks as the dissolution proceeds, which is a heterogeneous reaction. The dissolved oligomer continues to be depolymerized with EG in the bulk solution to produce its monomer, BPA, which is a homogeneous reaction.

7.3 Pyrolysis of PC based polymers

Achilias et al., 2009, investigated pyrolysis of PC and PC based Waste Electric and Electronic Equipment as a means of chemical recycling of this polymer. A laboratory-scale fixed bed reactor was used and the appropriate pyrolysis temperature was selected after measuring the thermal degradation of model PC by Thermogravimetric analysis. After pyrolysis a large amount of oil was measured, together with a smaller amount of gaseous product, leaving also a solid residue. For both samples (model PC and a compact disc based on PC), the gaseous fraction consisted mainly of CO_2 and CO, whereas in the liquid fraction a large amount of different phenolic compounds, including the monomer bisphenol A, was measured. It seems that recycling of used CDs by pyrolysis is a very promising technique having the potential of producing useful high-value chemicals, which may find applications in the petrochemical industry.

7.4 Problems of PC recycling

Recycled polycarbonate is usually less resilient, have decreased impact resistance when compared with newly manufactured polycarbonate. The addition of fillers and pigments can also decrease the plastic's resilience. This problem can be addressed by the use of chemicals to modify impact resistance in recycled polycarbonate. Up to 15% recycled material can safely be added to the virgin resin without significantly altering properties of the virgin material.

The nature of the compact disc (CD) does not allow it to be easily recycled. The disc is a multi-layer product consisting of PC substrate and three coatings. These coatings, aluminium, lacquer and printing, respectively make up only a small portion of the entire disc. These materials should be separated or recovered in order to recycle the polycarbonate. There are a variety of methods for the removal of paint or plating from engineering plastics, ranging from the chemical to physico-mechanical procedures. Such techniques include chemical stripping or chemical recovery (high-temperature alkaline treatment), melt filtration, mechanical abrasion, hydrolysis, liquid cyclone, compressed vibration, cryogenic grinding, dry crushing and roller pressing.

The disadvantages of PC include high melt viscosity and notch sensitivity. Used PC usually suffered from crazing caused by light, radiation and chemicals present in the service environment, which make the problem of notch sensitivity even worse.

As with other thermoplastics, the level of mechanical and physical properties of polycarbonate depends on the molecular weight. However, production waste, recyclates etc. frequently do not, or no longer, possess the required molecular weights. Direct material

recycling of production waste or recyclates is therefore possible only to a very limited extent. When recycling polycarbonate residues, production wastes, remainders, recyclates and similar polycarbonate compositions, it is therefore desirable and essential to increase the molecular weight to a sufficient level for the projected new use. So, for example, low-molecular production scrap from PC production for Compact Discs could be increased to the molecular weight range required for injection molding. Or the average molecular weight of PC recyclate from the de-lamination of Compact Discs should be increased sufficiently to allow the material to be used, as a component in the production of PC/ABS blends.

It was found that, surprisingly, it is possible to condense polycarbonates from waste by simple melting in a vacuum, optionally with bisphenols or suitable oligocarbonates with OH terminal groups, to produce, directly, polycarbonates of higher molecular weights.

8. Chemical recycling of nylon

8.1 Introduction

Nylon is one of the early polymers developed by Wallace Carothers in 1935, at DuPont's research facility. Today, nylon is one of the most commonly used polymers. Nylons, also known as polyamides, can be produced by the reaction of a diamine with a dicarboxylic acid, condensation of the appropriate amino acid, ring opening of a lactam, reaction of a diamine with a diacid chloride, and reaction of a diisocyanate with a dicarboxylic acid. Nylon is a crystalline polymer with high modulus, strength, impact properties, low coefficient of friction, and resistance to abrasion. A variety of commercial nylons are available including nylon 6, nylon 11, nylon 12, nylon 6,6, nylon 6,10, and nylon 6,12. The most widely used nylons are nylon 6,6 and nylon 6. Polyamides are used most often in the form of fibers, primarily nylon 6,6 and nylon 6, although engineering applications are also of importance. Nylon 6,6 is prepared from the polymerization of adipic acid and hexamethylenediamine, while nylon 6 is prepared from caprolactam.

Nylon recycling has increased substantially in the last several years. Most recycling efforts have focused on recovery of carpet. According to the U.S. Department of Energy, about 3.5 billion lb of waste carpet are discarded each year in the United States, with about 30% of them made from nylon 6.

Processing of recyclables is necessary to transform the collected materials into raw materials for the manufacture of new products. In general there are two categories for nylon recycling, chemical and thermal recycling.

- **Chemical recycling.** Involves breaking down the molecular structure of the polymer, using chemical reactions. The products of the reaction then can be purified and used again to produce either the same or a related polymer.
- **Thermal recycling.** Also involves breaking down the chemical structure of the polymer. In this case, instead of relying on chemical reactions, the primary vehicle for reaction is heat. In pyrolysis, for example, the polymer (or mixture of polymers) is subjected to

high heat in the absence of sufficient oxygen for combustion. At these elevated temperatures, the polymeric structure breaks down.

8.2 Depolymerization of nylons

Due to the higher value of nylons in comparison with other polymers used in carpet, nylon carpet has been looked at as a resource for making virgin nylon via depolymerization. Most of polyamides used commercially are nylon 6,6 or nylon 6, and the largest supply of waste for recycling of nylons is obtained from used carpets. The waste carpets are collected, sorted and then subjected to a mechanical shredding process before depolymerization.
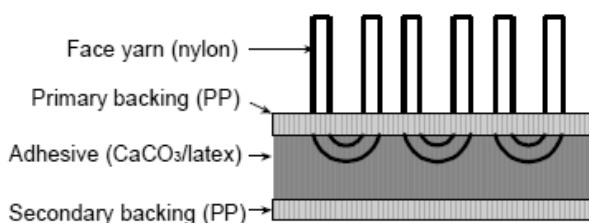
Fig. 17. Typical carpet construction.

Although there are many active recycling operations, they mostly focus their work in the recycling of nylon 6 and nylon 6,6 basically collected from carpet waste. It is obvious the need for further research to develop methods for recycling more commercially used nylons.

8.3 Hydrolysis of nylon 6

A process for depolymerizing nylon 6 scrap using high pressure steam was patented by by AlliedSignal, Inc. (Sifniades et al., 1999]. Ground scrap was dissolved in high-pressure steam at 125-130 psig (963-997 kPa) and 175-180^{0}C for 0.5 hour in a batch process and then continuously hydrolyzed with super-heated steam at 350^{0}C and 100 psig (790 kPa) to form ε-caprolactam at an overall recovery efficiency of 98%. The recovered monomer could be repolymerized without additional purification. Braun et al., 1999 reported the depolymerization of nylon 6 carpet in a small laboratory apparatus with steam at 340^{0}C and 1500 kPa (200 psig) for 3 hours to obtain a 95% yield of crude ε-caprolactam of purity 94.4%. Recently, patents were issued to AlliedSignal for the depolymerization of polyamide-containing carpet (Sifniades et al., 1999).

Acid hydrolysis of nylon 6 wastes [Chaupart, 1998] in the presence of superheated steam has been used to produce aminocaproic acid which under acid conditions is converted to ε-caprolactam, and several patents have been obtained by BASF [Corbin et al., 1999]. Acids used for the depolymerization of nylon 6 include inorganic or organic acids such as nitric acid, formic acid, benzoic acid, and hydrochloric acid [Bajaj and Sharma, 1997]. Orthophosphoric acid and boric acid are typically used as catalysts at temperatures of 250-350^{0}C. In a typical process, superheated steam is passed through the molten nylon 6 waste at 250-300^{0}C in the presence of phosphoric acid. The resulting solution underwent a multistage chemical purification before concentration to 70% liquor, which was fractionally distilled in

the presence of base to recover pure ε-caprolactam. Boric acid (1%) may be used to depolymerize nylon 6 at 400⁰C under ambient pressure. A recovery of 93-95% ε-caprolactam was obtained by passing superheated steam through molten nylon 6 at 250-350⁰C. Sodium hydroxide has been used successfully as a catalyst for the base-catalyzed depolymerization of nylon 6.

8.3.1 Catalytic pyrolysis

Catalytic pyrolysis has been studied as a hybrid process for recovering caprolactam from nylon 6 followed by high temperature pyrolysis of the polypropylene into a synthetic natural gas. Czernik *et al.*, 1998 investigated the catalysis of the thermal degradation of nylon 6 with an α-alumina supported KOH catalyst in a fluidized bed reactor. In the temperature range of 330°C to 360°C the yield of caprolactam exceeded 85%. Bockhorn *et al.*, *2001* use a liquid catalyst composed of a eutectic mixture of 60 mol% NaOH and 40 mol% KOH which melts at 185°C. At 290°C the caprolactam yield exceeded 95%.

8.3.2 Recovery of caprolactam

Approximately 10-12% by weight of oligomers is formed in the synthesis of polycaprolactam (nylon 6). These oligomers are removed by extraction with water or by distillation under vacuum. In the process, two types of liquid wastes are formed: (1) a 4-5% aqueous solution of low-molecular weight compounds, consisting of ca. 75% by weight of caprolactam and ca. 25% by weight of a mixture of cyclic and linear caprolactam oligomers and (2) a caprolactam-oligomer melt, containing up to 98% caprolactam and small amounts of dimer, water, and organic contaminants. The recycle of caprolactam involves two different stages: depolymerization of polymeric waste and purification of the caprolactam and oligomers obtained.

A general recovery of caprolactam from liquid waste generates 20-25% oligomers along with organic and inorganic compounds as impurities. The distillation of caprolactam under reduced pressure produces a residue which consists of inorganic substances such as permanganates, potassium hydrogen sulfate, potassium sulfate, sodium hydrogen phosphate, and sodium phosphate. The larger portion of the residue contains cyclic and linear chain oligomers plus 8-10% of caprolactam. The types and exact amounts of impurities depend on the method used for the purification and distillation of caprolactam.

The cyclic oligomers are only slightly soluble in water and dilute solutions of caprolactam. They tend to separate out from the extracted waste during the process of concentration and chemical purification of the caprolactam. The cyclic oligomers tend to form on the walls of the equipment used in the process equipment. 6-Aminocaproic acid or sodium 6-aminocaproate may also be found in the oligomeric waste especially if sodium hydroxide is used to initiate the caprolactam polymerization.

8.3.3 Applications of depolymerized nylon 6

Chemical recycling of nylon 6 carpet face fibers has been developed into a closed-loop recycling process for waste nylon carpet [Bajaj and Sharma, 1997; Brown, 2001]. The

recovered nylon 6 face fibers are sent to a depolymerization reactor and treated with superheated steam in the presence of a catalyst to produce a distillate containing caprolactam. The crude caprolactam is distilled and repolymerized to form nylon 6. The caprolactam obtained is comparable to virgin caprolactam in purity. The repolymerized nylon 6 is converted into yarn and tufted into carpet. The carpets obtained from this process are very similar in physical properties to those obtained from virgin caprolactam.

The "6ix Again" program of the BASF Corp. has been in operation since 1994. Its process involves collection of used nylon 6 carpet, shredding and separation of face fibers, pelletizing face fiber for depolymerization and chemical distillation to obtain a purified caprolactam monomer, and repolymerization of caprolactam into nylon polymer [BASF, 2001].

Evergreen Nylon Recycling LLC, a joint venture between Honeywell International and DSM Chemicals, was in operation from 1999 to 2001. It used a two-stage selective pyrolysis process. The ground nylon scrap is dissolved with high-pressure steam and then continuously hydrolyzed with super-heated steam to form caprolactam. The program has diverted over one hundred thousand tons of post consumer carpet from the landfill to produced virgin-quality caprolactam [Brown, 2001].

8.4 Hydrolysis of nylon 6,6 and nylon 4,6

The depolymerization of nylon 6,6 and nylon 4,6 involves hydrolysis of the amide linkages which are vulnerable to both acid- and base-catalyzed hydrolysis. Polk et al., 1999 reported the depolymerization of nylon 6,6 and nylon 4,6 in aqueous sodium hydroxide solutions containing a phase transfer catalyst. Benzyltrimethylammonium bromide was discovered to be an effective phase-transfer catalyst in 50% sodium hydroxide solution for the conversion of nylon 4,6 to oligomers. The depolymerization efficiency (% weight loss) and the molecular weight of the reclaimed oligomers were dependent on the amount and concentration of the aqueous sodium hydroxide and the reaction time. Nylon 4,6 fibers (M_v = 41,400 g/mole) did not undergo depolymerization on exposure to 100 mL of 25 wt% sodium hydroxide solution at 165^0C. Out of 6.0 g of nylon fibers fed for depolymerization, 5.95 g were unaffected. When the concentration of sodium hydroxide was increased to 50 wt%, the depolymerization process resulted in the formation of low molecular weight oligomers. Hence, even in the presence of a phase transfer agent, a critical sodium hydroxide concentration exists between 25 and 50 wt% which is required to initiate depolymerization under the conditions used. Soluble amine salts, were also obtained.

In order to establish the feasibility of alkaline hydrolysis in respect to recycling of nylon 4,6, it was necessary to determine whether the recovered oligomers could be repolymerized to form nylon 4,6. For this purpose, solid state polymerization was performed on nylon 4,6 oligomers formed via alkaline hydrolysis with 50 wt% NaOH at 165^0C for 24 hours. Solid state polymerization of the nylon 4,6 oligomers resulted in an increase in intrinsic viscosity from 0.141 to 0.740 dl/g. That corresponds to an increase in viscosity average molecular weight from 1846 g/mole to 16,343 g/mole.

The product of the depolymerization of nylon 6,6 with 50% aqueous sodium hydroxide solution was relatively low molecular weight oligomers. A series of experiments were run in order to examine the applicability and efficiency of benzyltrimethylammonium bromide

[BTEMB] as a phase transfer catalyst in the depolymerization of nylon 6,6. The product of the run with no phase transfer agent showed a 15.9% increase in weight compared to the weight of the original nylon 6,6. The calculated percent increase in weight for a 19-fold decrease in molecular weight (due to the addition of water) would be ca. 1%. Therefore, a large part of the increase must be due to leaching of silicates of the glass container (resin reaction kettle) by the strong alkali (50 wt%) at the temperature of the reaction (130⁰C) over 24 hours. The oligomer obtained had a viscosity average molecular weight of 1644 g/mole (the original nylon 6,6 had a molecular weight of 30,944 g/mole). The runs with phase transfer agent produced oligomers with decreases in weight of 40-50%. Although the occurrence of leaching of silicates from the glass container made quantitative assessment difficult, these results suggested that in the absence of phase transfer agent only oligomers are formed; however, soluble low molecular weight products are formed in the presence of phase transfer agent. The oligomers obtained were repolymerized in the solid state by heating at 200⁰C in a vacuum. The viscosity-average molecular weight of the solid state polymerized nylon 6,6 obtained was ca. 23,000 g/mole (the molecular weight of the oligomeric mixture was 1434 g/mole).

In order to isolate adipic acid, nylon 6,6 fibers were depolymerized under reflux with a 50% NaOH solution in the presence of catalytic amounts of benzyltrimethylammonium bromide. The oligomers formed in successive steps were depolymerized under similar conditions. However, hexamethylene diamine was not isolated. The overall yield of adipic acid was 59.6%.

8.4.1 Ammonolysis of nylon 6,6

Ammonolysis currently is the preferred route currently in use at the DuPont Company for the depolymerization of nylon 6,6 carpet waste [Kassera, 1998]. McKinney, 1994, has described the reaction of nylon 6,6 and nylon 6,6/nylon 6 mixtures with ammonia at temperatures between 300 and 350⁰C and a pressure of about 68 atmospheres in the presence of an ammonium phosphate catalyst to yield a mixture of the following monomeric products: HMDA, adiponitrile, and 5-cyanovaleramide from nylon 6,6 and ε-caprolactam, 6-aminocapronitrile, and 6-aminocaproamide from nylon 6. The equilibrium is shifted toward products by continuous removal of water formed. Most of the monomers may be transformed into HMDA by hydrogenation. Kalfas, 1998 has developed a mechanism for the depolymerization of nylon-6,6 and nylon-6 mixtures by the ammonolysis process. The mechanism includes the amide bond breakage and amide end dehydration (nitrilation) reactions, plus the ring addition and ring opening reactions for cyclic lactams present in nylon 6. On the basis of the proposed mechanism, a kinetic model was developed for the ammonolysis of nylon mixtures.

Bordrero, *et al., 1999* utilized a two step ami/ammonolysis process to depolymerize nylon 6,6. The first step is based on an amminolysis treatment of nylon 6.6 by n-butylamine at a temperature of 300°C and a pressure of 45 atm. Free HMDA and NN'-dibutyladipamide are generated. The second step is ammonolysis of NN'-dibutyladipamide at a temperature of 285°C and a pressure of 50 atm. The end product is adiponitrile (ADN). It is estimated that the yields could be about 48% for ADN and about 100% for HMDA at optimized reaction conditions.

8.4.2 Recovery of nylon 6,6 monomers

Adipic acid and hexamethylene diamine (HMDA) are obtained from nylon 6,6 by the hydrolysis of the polymer in concentrated sulfuric acid (Figure 18). The adipic acid is purified by recrystallization and the HMDA is recovered by distillation after neutralizing the acid. This process is inefficient for treating large amounts of waste because of the required recrystallization of adipic acid after repeated batch hydrolyses of nylon 6,6 waste. In a continuous process, nylon 6,6 waste is hydrolyzed with an aqueous mineral acid of 30-70% concentration and the resulting hydrolysate is fed to a crystallization zone. The adipic acid crystallizes and the crystals are continuously removed from the hydrolysate. Calcium hydroxide is added to neutralize the mother liquor and liberate the HMDA for subsequent distillation.
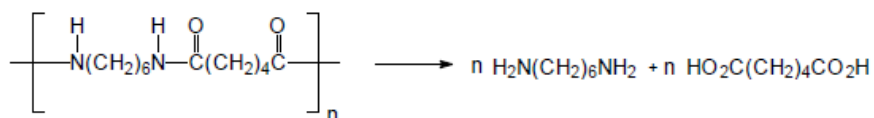
Fig. 18. Depolymerization of nylon 6,6 by hydrolysis.

Continuous recovery requires adipic acid crystals having an average diameter of ca. 40-50 nm. Such crystals are obtained by continuously introducing the hot hydrolysate containing 10-20% adipic acid into an agitated crystallization vessel while maintaining an average temperature of 20-30^{0}C. The slurry obtained from the crystallization vessel is filtered to collect the adipic acid crystals and the filtrate which contains the HMDA acid salt is continuously neutralized with calcium hydroxide. The calcium salt formed is removed by filtration and the HMDA in the filtrate is isolated by distillation.

In the case of nylon 6,6 waste recycled by ammonolysis, nylon is treated with ammonia in the presence of a phosphate catalyst. Reaction occurs at 330^{0}C and 7 MPa. Distillation of the reaction mixture produces ammonia which is recycled and three fractions containing (a) caprolactam, (b) HMDA and aminocapronitrile and (c) adiponitrile. Aminocapronitrile and adiponitrile are hydrogenated to yield pure HMDA and the caprolactam is either converted to aminocapronitrile by further ammonolysis or distilled to produce pure caprolactam. The HMDA produced by this process is extremely pure (>99.8). The main impurities are aminomethylcyclopentylamine and tetrahydroazepine which are expected to be removed more effectively in the larger distillation columns employed in larger plants.

9. Chemical recycling of poly(methyl methacrylate)

Poly(methyl methacrylate) (PMMA) is a major type of thermoplastics used throughout the world in such applications as transparent all-weather sheets, electrical insulation, bathroom units, automotive parts, surface coating and ion exchange resins, etc. The plastics made from PMMA are widely used under the commercial trade names PLEXIGLAS or PERSPEX. In

Western Europe alone approximately 327 000 tones of PMMA are consumed each year with an increasing percentage of approximately 4% per year. In contrast with condensation polymers (e.g. PET), addition polymers, like PMMA, cannot be easily recycled to monomer by simple chemical methods. Instead, thermo-chemical recycling techniques like pyrolysis are usually applied. Thus, various processes for the depolymerization of PMMA have been described in literature. Among them the most prominent ones are the molten metal bath process and the fluidized bed pyrolysis [Kaminsky et al., 2004; Smolders and Baeyens, 2004; Sasse and Emig, 1998]. The first one although widely used in several countries exhibits several serious disadvantages including that the raw condensate MMA may be contaminated by the metal used (usually lead) or other by-products [Sasse and Emig, 1998]. The effect of temperature, addition of filler and amount of feed on the amount and distribution of pyrolytic products was investigated by Kaminsky and co-workers in a fluidized bed reactor [Kaminsky et al., 1991; 2001; 2004, Grause et al., 2006]. Furthermore, PMMA thermal pyrolysis results in a close to 97% recovery of the monomer methyl methacrylate (MMA) at relatively low temperatures (400–500 °C) [Smolders and Baeyens, 2004]. It has been reported that the liquid pyrolysis product was so pure that it could be polymerized again without any further treatment [Kaminsky et al., 1991].

Achilias, 2006 and 2007 investigated the chemical recycling of PMMA using pyrolysis, aiming at the recovery of pure monomer able to be re-polymerized back to polymer. Conventional (thermal) pyrolysis was carried out using either model polymer or a commercial product as feedstock. The experiments were carried out in a laboratory fixed bed reactor at 450 °C, which was found in literature to be the optimum temperature for the maximization of MMA monomer amount [Kaminsky et al., 2001]. The liquid product obtained from both the model and the commercial samples was very high, 99% and 98%, respectively. The monomer recovery was higher by feeding pure PMMA (98.3 wt.%) compared to the commercial sample (94.9 wt.%). In both experiments the gas fraction was very small. Only 0.6 or 1.5 wt.% of gases were produced. Also the residue obtained was very low 0.1 and 0.4 wt.%. Furthermore, the gas composition of both samples was approximately the same with large amounts of CO_2 followed by CO and methane. The former are degradation products of PMMA and MMA due to the existence of oxygen in the macromolecular chain. The liquid fraction mostly consists of the monomer MMA in a large amount (99 and 97 wt.% for the model polymer and the commercial product, respectively) with a small percentage of some other organic compounds mainly esters.

The potential use of the liquid pyrolysis fraction as a raw material for the reproduction of PMMA by polymerization was also investigated (Achilias, 2007).

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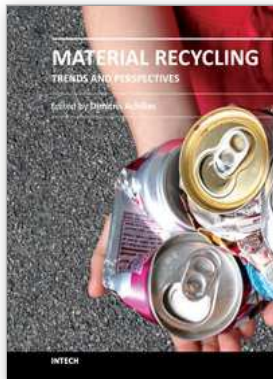
Material Recycling - Trends and Perspectives

Edited by Dr. Dimitris Achilias

The presently common practice of wastes' land-filling is undesirable due to legislation pressures, rising costs and the poor biodegradability of commonly used materials. Therefore, recycling seems to be the best solution. The purpose of this book is to present the state-of-the-art for the recycling methods of several materials, as well as to propose potential uses of the recycled products. It targets professionals, recycling companies, researchers, academics and graduate students in the fields of waste management and polymer recycling in addition to chemical engineering, mechanical engineering, chemistry and physics. This book comprises 16 chapters covering areas such as, polymer recycling using chemical, thermo-chemical (pyrolysis) or mechanical methods, recycling of waste tires, pharmaceutical packaging and hardwood kraft pulp and potential uses of recycled wastes.

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