Postprint of: Datta J., Kopczyńska P., From polymer waste to potential main industrial products: Actual state of recycling and recovering, Critical Reviews in Environmental Science and Technology, Vol. 46, Iss. 10, (2016), pp. 905-946, DOI: 10.1080/10643389.2016.1180227

FROM POLYMER WASTE TO POTENTIAL MAIN INDUSTRIAL PRODUCTS: ACTUAL STATE OF RECYCLING AND RECOVERING ROUTES

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ABSTRACT

Plastics have become widely used materials in everyday life due to their special properties such as durability, easy processing, light-weight and low-cost of production. However, because of their stable and non-biodegradable nature, postconsumer plastics become an issue to the environment. The growing amounts of waste are generated, as plastic products are commonly used only once before disposal. The alternatives of practical techniques for solid waste management are: redesign, reprocessing and recycling. Even thus recycling is not the most profitable technique for the treatment of plastic waste it should be constantly developed. The recycling of plastic waste helps to conserve natural resources due to polymeric materials are made from oil and gas. There are four main recycling methods: reuse, mechanical recycling, chemical recycling and energy recovery. Mechanical recycling turns polymeric waste into new polymer products when energy recovery process releases the energy contained within plastics through combustion and chemical recycling converts waste polymers into feedstock for chemicals/monomers/fuels production. Nowadays chemical recycling of plastic waste is the most noteworthy of polymer recovery technique. This manuscript presents a literature review on chemical recycling methods of various polymers, such as polyethylene (LDPE or HDPE), polypropylene or mixture of this polymer waste, poly(ethylene terephthalate), polycarbonate, polyurethane etc. We described the effect of the

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reaction parameters on obtained products, used catalysts and agents and used equipment for specific methods of chemical recycling. In this way, the state of the art of the chemical recycling methods of several polymers is presented.

KEYWORDS: chemical recycling; feedstock recycling; plastic waste; depolymerisation; decomposition

1. INTRODUCTION

Plastics are materials which are used in almost every branch of industry. They often replace traditional resources like wood, metal, glass and in many applications they do not have natural equivalent. In last decades a growing trend in plastics production was observed, yearly on the level of 9.9% and therefore it can be stated that polymers are very useful materials. The first polymers were discovered and developed at the turn of the 19th and 20th century, with the discovery of polystyrene (PS) and poly(vinyl chloride) (PVC) (1839 and 1872) and the development of Bakelite in 1907. In the following years, commercial production of PVC and PS began further discovering of new polymers (polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP)). Together with polymers growing production, the pollution of seas and environment was increasing and in 80s and 90s and the restrictions and legislations were introduced (Thompson et al. 2009). First plastic waste recycling mill in the world was created in 1972 (Conshohocken, Pennsylvania), after that the government programs and eco-friendly communities were formed to popularise this attitude.

In Europe, the largest application sector constitutes packaging with almost 40%, the second sector is building and construction with 20% of the demand, the third sector shares automotive with 8.5% of the total demand. In last half century productions of polymer materials increased from 1.3 million tons to over 290 million tons. With continuous growth the global plastics production in 2013 risen to 299 million tons – a 3.9% increase in comparison to 2012, so waste management become a large problem (PlasticsEurope 2015).

A very common practice of handling polymer waste is landfilling. It is first option of waste handling in many EU countries. 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; Achilias et al. 2012).

The costs of plastics disposing are high and the impact on the environment has taken many forms of damage: toxic gases as the result of incineration and permanent landfill accumulation. However, in 2012 in Europe, 63% from over 25 million tons of plastic waste were recovered through recycling (26%) and energy recovery processes (36%), 38% were landfilled. Table 1 presents distribution of post-consumer plastic waste from 2005 to 2012. EU aims to zero plastics to landfill by 2020. Some EU countries, namely Sweden, Germany and Luxemburg recover more than 90% of their polymers waste (PlasticsEurope 2015). According to European Directive 2008/98/EC (European Parliament and Council of the European Union 2008) the waste management should be applied in following hierarchy:

1) Prevention (measures taken before a substance, material has become waste to reduce the quantity of waste, the adverse impact on environment and human health and the content of harmful substances)
2) Preparing for re-use (any operations by which products or materials are used again for the same purpose which they were produced)
3) Recycling (any recovery operation by which products or materials are reprocessed into new products, materials or substances)
4) Other recovery (i.e. energy recovery)
5) Disposal (any operations which is not recovery)

Table 1. Handling of post-consumer plastic waste over past few years.

Year	Post-consumer plastic waste [Mt]	Disposal		Recycling		Energy recovery		References
		[Mt]	[%]	[Mt]	[%]	[Mt]	[%]	
2005	22	11.6	53	4.0	18	6.4	29	(PlasticsEurope 2007)
2006	23	11.5	50	4.5	19.7	7.0	30.3	(PlasticsEurope 2008a)
2007	24.6	12.4	50	5.0	20.4	7.2	29.2	(PlasticsEurope 2008b)
2008	24.9	12.1	48.7	5.3	21.3	7.5	30	(Plastics Europe 2009)
2009	24.3	11.2	46	5.5	22.5	7.6	31.5	(PlasticsEurope 2010)
2010	24.7	10.4	42.1	6.0	24.1	8.3	33.8	(PlasticsEurope 2011)
2011	25.1	10.2	40.9	6.3	25.1	8.6	34	(PlasticsEurope 2012)
2012	25.2	9.6	38.1	6.6	26.3	8.9	35.6	(PlasticsEurope 2013)

Less and less worn out plastic is going to landfill each year. Improved waste management is also crucial to reduce the risk of littering. When it comes to marine litter in particular, plastic manufacturers give priority to actions that prevent plastics from ending up as litter in the oceans. The amount of plastics that can be sustainably recycled has increased in the last decades due to improved identification and sorting technology. However incineration is still often used technique to manage plastic waste.

The options for plastic waste reduction are:

a) to gain monomers from plastics and recreate virgin polymers suitable for further production
b) to develop cost-effective recycling processes that will justify reuse of plastic
c) to develop biodegradable, naturally sourced polymers to replace synthetic polymers
d) to introduce biochemical processes which will degrade synthetic polymers down to environmentally degradable short polymer chains.

WRAP (Waste & Resources Action Programme) published a report about environmental benefits of recycling. In that report the cases of life cycle assessment (LCA) of plastics and biopolymers were described and compared. The results showed that recycling (mechanical recycling) is the best alternative taking into account the climate change potential, reduction of natural resources and energy demand. The analysis emphasised that the environmental benefits are mainly brought by the avoided material production, which means to maximise benefits by recovering good quality material with high purity (to limit the rejected fraction) that once recycled can replace virgin plastics on a high ratio. Energy recovery is a good option of plastic waste treatment in terms of reducing waste volume, but it is also associated with greenhouse gases emission (GHG). Nerveless, the worst option with the greater environmental burden is landfill. On the contrary, the use of biopolymer waste as a in the feedstock recycling does not bring substantial benefits, but composting presents better results that incineration with energy recovery regarding GHG emissions, under the condition of a low degradation rate (<50%). However, anaerobic digestion accomplishes better than composting regarding climate change and energy demand, because it allows the recovery of the biogas produced (Michaud et al. 2010).

Therefore, recycling seems to be the best solution. The recycling of waste polymers can be carried out in many ways. Recycling of polymer materials consists of few activity phases: collection, separation, processing/manufacturing and marketing. Effective separation of mixed plastic waste is necessary because only clean, homogeneous polymer can produce the highest quality recycled plastic products (Hodzic 2004).

Recovery of waste containing polymers is carried out in three basic areas: mechanical recycling, chemical recycling and energy recovery. Each of these fields include a number of specific technological solutions, suitable for the size of streams and the quality of the processed polymer waste (Błędzki 1997; Wasielewski and Piechaczek 2009). Different recycling or waste disposal methods are shown in Figure 1.

Figure 1. Types of recycling (Maier and Calafut 1998).

In mechanical recycling plastic solid waste is separated, melted, extruded and regranulated to use in new products. In feedstock recycling, polymers are turned down into their monomers or converted to oil or gases for uses in other processes. Energy recovery uses plastic waste to produce heat or energy. The rest material waste, which is neither recycled or already after many recycling processes is landfilled (Maier and Calafut 1998).

There are several options of plastic recycling: reuse, primary recycling, mechanical recycling, chemical or feedstock recycling and energy recovery.

Reuse is the most common method of waste management for glass containers or drinks bottles, they are cleaned and used again (Hamad et al. 2013). Reuse of plastic material can be considered as a “zero order” recycling technique (Nikles and Farahat 2005). Reusing plastics is desirable because it uses less energy and fewer resources. However reuse is not very common method in relation to plastics product. It is common practise for PET-bottles to be refilled and reused. Nevertheless it should be done very carefully because plastic bottles are likely to absorb contaminants which could be released into food when bottle is refilled. Refilling of a PET-bottle with high-alcoholic degree liquids can lead to degradation of the macromolecular chains. Some detergent manufactures market refill sachets for bottled washing liquids and fabric softeners (Achilias et al. 2012; Hamad et al. 2013). In general, plastics reuse has a lot of advantages such as conservation of fossil fuels, reduction of energy and municipal solid waste, reduction of carbon-dioxide, nitrogen-oxides and sulphur dioxide emissions (Al-Salem et al. 2009).

Primary recycling (also known as re-extrusion) refers to the “in-plant” recycling of the scrap material of controlled history. Industrial scraps or single-polymer plastics are reintroduced to the extrusion cycle in order to produce products of the similar material (Lettieri and Al-Salem 2011). This process is commonly used because it ensures simplicity and low-cost, but yet this method is only appropriate for recycling of clean and uncontaminated single type waste (Al-Salem et al. 2009; Achilias et al. 2012). For example a plastic yoghurt pot is recycled into an identical plastic yoghurt pot (Williams et al. 2010).

Mechanical recycling is also called physical recycling or secondary recycling. Generally, it is process of recovering plastic for the reuse in manufacturing plastic products by mechanical means. The plastic solid waste is ground down, reprocessed and compounded to produce a new product (Cui and Forssberg 2003). Mechanical recycling of plastic waste can be performed on single-polymer plastic such as PP, PS, PE. For more complex and contaminated plastics, the adaptation of mechanical recycling is more difficult. Mechanical recycling involves a number of treatments and preparation steps, including size reduction of the plastic to more suitable form (flakes pellet, powder). This can achieved by milling, grinding or shredding. Aznar et al. (Aznar et al. 2006) described general scheme of mechanical recycling, which is shown in the Figure 2.

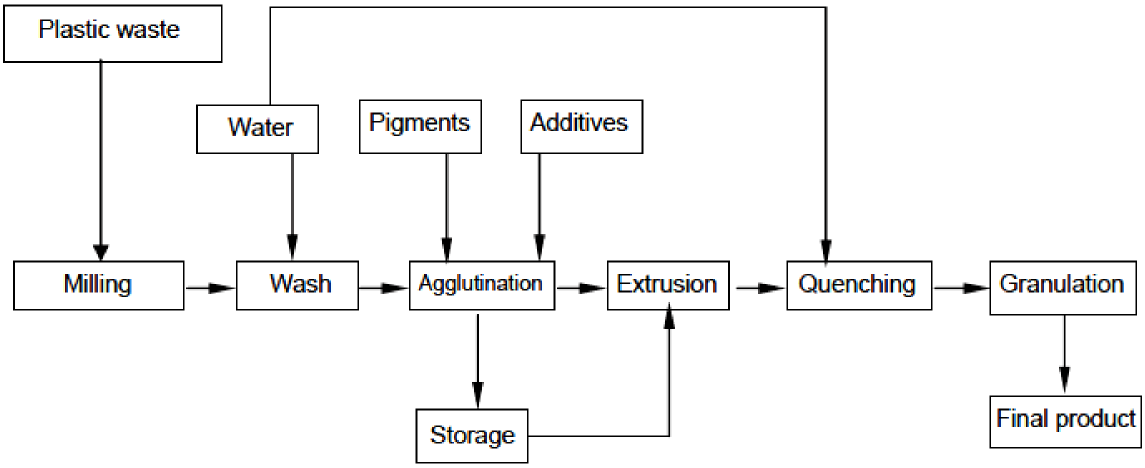

Figure 2. Stages of mechanical recycling (Aznar et al. 2006).

General steps of mechanical recycling include as follows: shredding, separation, washing, extrusion and regranulation (Aznar et al. 2006; Al-Salem et al. 2010). These all steps are necessary to produce clear, high quality and homogenous products (Al-Salem et al. 2009). The disadvantage of this process is the decrease of product properties with every cycle. This occurs because the molecular weight of the recycled resin is reduced due to chain scission reactions caused by the presence of water and trace acidic impurities (Antonakou and Achilias 2013).

Chemical or Feedstock recycling (tertiary recycling) has been defined as the process leading in total depolymerisation to the monomers in case of polyesters and polyamides and into oil/hydrocarbon component in the case of polyolefin's or partial degradation to oligomers and other secondary valuable materials. The monomers could be repolymerised to regenerate the original polymer (Achilias et al. 2007; Achilias et al. 2012; Hamad et al. 2013). Regenerated monomer polymer or both may be blended with virgin materials. The regeneration process may involve a variety of monomer/polymer purification steps in addition to different purification processes such as distillation, crystallization and additional chemical reaction (Nikles and Farahat 2005).

The name chemical is used, because an alteration is bound to occur to the chemical structure of the polymer. Under the category of chemical recycling process appear pyrolysis, gasification, liquid-gas hydrogenation, viscosity breaking, steam or catalytic cracking. The depolymerisation of plastics up to monomers is obtained through hydrolysis, alcoholysis, glycolysis, ammonolysis, valid for some polymer as PET, nylon, polyurethanes (PU) and using decomposition agent like water, methanol, glycol, amine etc.(Aznar et al. 2006; Al-Salem et al. 2009).

Energy recovery (quaternary recycling) implies waste heating to produce energy in the form of heat, steam and electricity (European Parliament and Council of the European Union 2008). This is the most effective way to reduce the volume of organic materials, but it is only considered, when material recovery process fail due to economical constrains. Plastic materials possess a very high calorific value, in particular when they are derived from crude oil. Table 2 shows the calorific value of polymer to oil and plastics solid waste (Al-Salem et al. 2009; Achilias et al. 2012).

Table 2. Calorific value of some major plastics compared with common fuels (Williams and Williams 1997).

Item	**Calorific value (MJ kg^{-1})**
PE	43.30-46.50
PP	46.50
PS	41.90
Kerosene	46.50
Gas oil	45.20

Heavy oil	42.50
Petroleum	42.3
Households PSW mixture	31.8

Plastics have high heating values and the formation of water and carbon dioxide upon combustion makes them similar to other petroleum based fuels. These properties make plastics a good energy source (Al-Salem et al. 2009). Although that method has been charged as ecologically unacceptable owing to the health risk from air born toxic substances e.g. dioxins, nitrogen oxides, sulphur oxides (Achilias et al. 2012).

Chemical recycling of plastics is based on the polymer decomposition by means of heat, chemical or catalytic agent, to yield products ranging from the chemical monomers to the mixtures of compounds, which can be a source of chemicals or fuels. Feedstock recycling processes can be classified into three main areas: recycling to fuels (gasoline, liquefied petroleum gas (LPG) and diesel oils), recycling to monomers and recycling to industrial chemicals (Ylä-mella 2005).

This review describes the main methods of recycling plastic waste and focuses on the tertiary recycling. This topic has not been previously described in such broad approach of various process of chemical recycling. The article is divided into two parts. The first part shows ways of polymers handling such as polyethylene, polystyrene and the second part is about different methods of solvolysis, which means treating polymers such as polyethylene terephthalate and polycarbonate, with solvent agent to obtain monomer. The aim of this article is to provide review of the methods applied and proposed in the literature, on the chemical recycling of plastic waste.

2. THERMO-CHEMICAL PROCESSING

An overview of thermo-chemical processes for recovery of chemicals. fuels from different polymer waste is described below.

2.1.PYROLYSIS

Pyrolysis is also known as thermal cracking, involves the degradation of the plastics by heating in the absence of oxygen (very often in nitrogen atmosphere) to extract valuable products e.g. monomers or fuel-type oils. This process is capable of recycling of many different polymers, when they are converted to produce clean fuel gas with high calorific value. Pyrolysis is carried out in different temperatures, depending on polymer type (i.e. pyrolysis of PE or PP is carried out in temperatures >700 ^{o}C) (Achilias et al. 2009; Al-Salem et al. 2010). A monomer can be produced with high efficiency (i.e. in pyrolysis of poly(methyl methacrylate) (PMMA) or a fuel type liquid fraction can be produced from polyolefins (PE, PP). Pyrolysis, besides high calorific value products, provides other advantages like reduction of toxic gases and it is alternative solution to landfilling (Al-Salem et al. 2009; Butler et al. 2011). Thermal cracking in inert atmosphere of PP and PE produces due to a thermal degradation and formation of a lot of products from C_1 to C_{50}. Pyrolysis produces different phases: a solid phase (char), a liquid phase (tars) and a gas phase. Products in the range of C_{20} to C_{50} are cracked in gas phase to obtain hydrocarbons such as ethane or propene, which are unstable at high temperatures and react to form aromatic compounds (i.e. benzene) (Aznar et al. 2006). If pyrolysis time is long, coke, methane and hydrogen are formed (Westerhout et al. 1998). The pyrolysis of polyolefins leads to monomers such as ethane and propane, but also wax, aliphatic oil, aromatic oil and gas can be found in the product. At about 450 ^{o}C pyrolysis leads to waxes. Higher temperatures provide higher cracking strength and in result the production of aliphatic oils and gases. In temperatures of more than 600 ^{o}C aromatics from gaseous olefins by Diels-Alder reactions are obtained (Grause et al. 2011). Recovery of few polymers by pyrolysis gives monomer predominantly, e.g. poly(methyl methacrylate), PET and PS. Polystyrene can be converted into styrene at rate of 76.8 wt.% at 520 ^{o}C (Kaminsky et al. 2004).

There are various types of reactors used for the pyrolysis of plastic waste. The most common solutions are a fluidised bed reactor and rotary kilns. Batch or continuous stirred tank reactors are characterised by insufficient heat transfer, which results in the formation of char. In the dehydrochlorination of PVC, degradative extrusion (Buekens and Schoeters 1998) is used.

The fluidised bed is suitable for pyrolysis, because it provides good heat and material transfer rates. In the Figure 3 the diagram of the pilot plant for pyrolysis in an indirectly heated fluidised bed is shown. A polymer is added by a screw (or lock) into fluidised bed of quartz sand at temperature in range of 600-900 ^{o}C. The process heat is introduced into the bed through radiant-heat tubes. The pyrolysis gas leaves the reactor and is cleaned of dust and soot in a cyclone and cooled in a quencher with a cycle of product oil. The gas is condensed into oils when passes through two quenching columns, which are filled with glass bodies. The oils are distilled and further products are high-boiling tar and fraction rich in toluene and benzene. The gas is purified in an electrostatic precipitator, pressurised by parallel diaphragm compressors and stored in gasometers. Some of the gas is combusted, some preheated to serve to fluidise the bed, the excess gas is flared (Kaminsky et al. 2004).

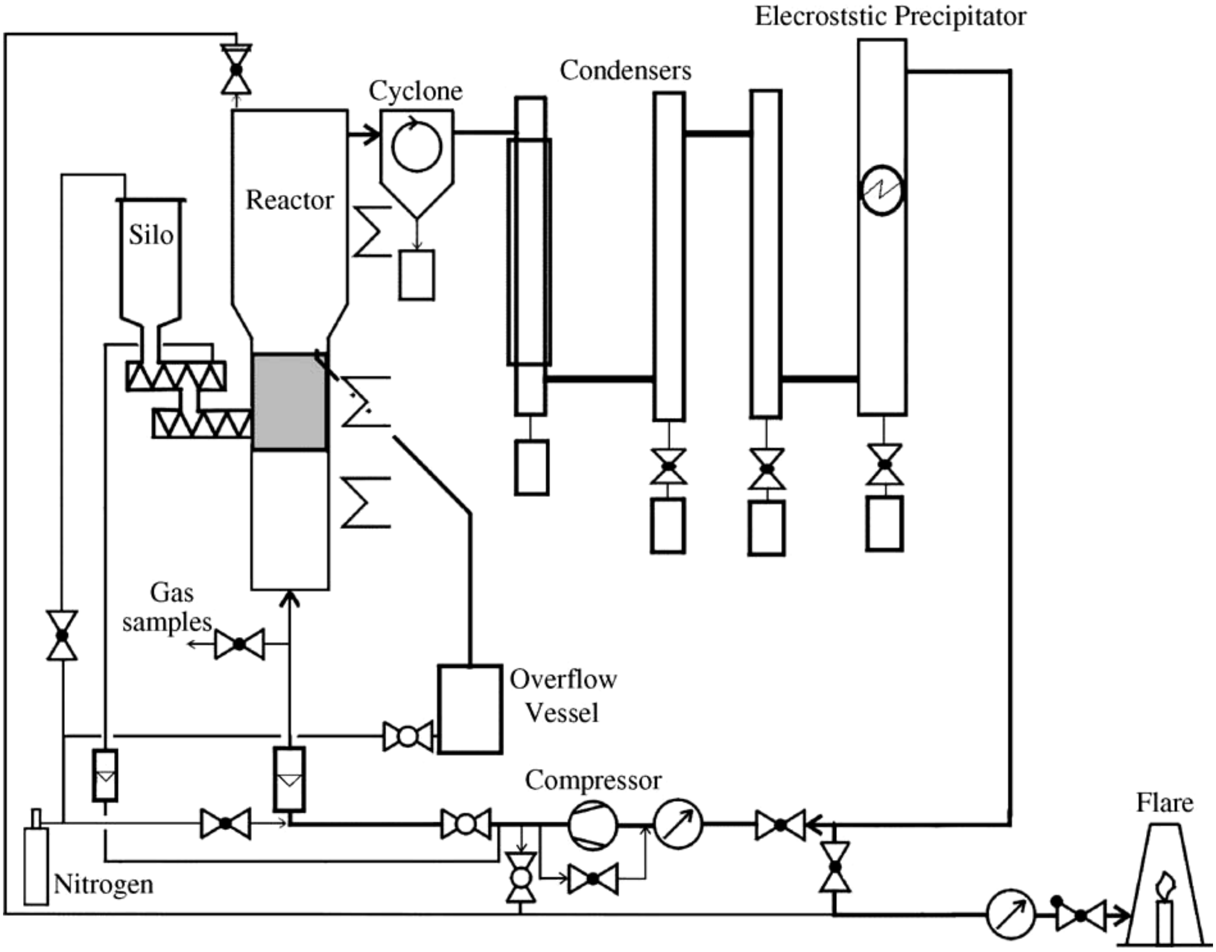

Figure 3. Flow scheme of the fluidised bed pyrolysis plant (Kaminsky et al. 2004).

Hájeková and Bajus (2005) investigated the thermal decomposition of polyalkenes (LDPE and PP). LDPE and PP were thermally decomposed separately in stainless steel batch reactor at 450 ^oC under nitrogen atmosphere. They fed the reactor with 12 g of LDPE or PP and heated polymers with programmed heating rate. The temperature of 450 ^oC was reached with PE after 55 min, with PP after 40 min. This temperature was maintained for further 10 min to obtain the maximum amount of decomposing products from reactor. The result was homogeneous solution of oil/wax which was further dissolved in heavy naphtha in boiling flask under a reflux condenser. The solution was yellow-coloured and clear. After several analyses of gases from LDPE thermal decomposition provided the following product: propane, butane, 1-butane, propene, ethane and 1-pentene. In the gases from thermal decomposition of PP the following products were obtained in decreasing order: propene, pentane, ethane and methylpropene.

Westerhout et al. (1998) investigated the influence of temperature, residence time, concentration level of reactants and products, polymer type and the composition of polymer mixture on the product obtained from pyrolysis of polyethylene and polypropylene. Pyrolysis was performed in a tubular reactor. Temperature was varied between 650 and 850 ^{o}C, whereas residence times between 0.1 and 1 s were used. More ethane is formed at higher temperatures during pyrolysis, but at low temperatures the main products of thermal decomposition of PP are propene and butane, but at higher temperatures these products are converted into other products. The effect of residence time on the product spectrum for pyrolysis of PE is very small for residence times below 1 s. The main gas-phase products of PE pyrolysis at 750 ^{o}C and 1 s residence timer are ethane, propene and butene. Similar effect was observed for product of PP pyrolysis. The yields of propene and butene decrease with increasing temperature, when the quantity of ethene and methane increase. The polymer type (LLDPE, LDPE or HDPE) or mixing of LDPE wit PP has no influence on the product spectrum.

Achilias (2007) studied pyrolysis of poly(methyl methacrylate). The reaction was carried out in a bed reactor using mode polymer and commercial product based on PMMA as feedstock. The polymer was pyrolysed at temperature of 450 ^{o}C. for 17 min. Liquid products were collected in a bath. The gaseous products were collected and measured by water displacement and the amount of solid residue was measured by weighting. The liquid product obtained from model and commercial PMMA is very high: 99% and 98%, respectively. The monomer recovery is higher by model PMMA (98.3 wt.%) in comparison to commercial sample (94.9 wt.%). Gas fraction was very small. 0.6 and 1.5 wt.% respectively for model and commercial PMMA. The amount of residue was very low 0.1 and 0.4 wt.%. Temperature 450 ^{o}C was chosen because above this temperature the amount of gas produced is increased and it was found decreasing of methyl methacrylate (MMA) fraction. Achilias (2007) used liquid fraction of pyrolysed PMMA to produce new PMMA compared to corresponding data from neat MMA monomer. The produced polymer was very similar to that obtained from polymerisation of neat MMA.

Meissner et al. (2004) examined the results of the pyrolysis of waste polytetrafluoroethylene (PTFE) to useful compounds. They compared waste gaskets and chip of PTFE with homopolymer PTFE. The polytetrafluoroethylene depolymerisation was carried out in two-stage nickel reactor. It consisted of basic part, which was vertical reactor and two-section horizontal reactor. Decomposition was started at a temperature below 400 ^{o}C (first stage of reactor). Vapours from the primary decomposition were heated to the temperature 600-800 ^{o}C in order to produce perfluorocarbon compounds. The pyrolysis of PTFE waste results in the formation of light ends light saturated fluorocarbons (mainly CF_4 or C_2F_6), tetrafluoroethylene (TFE), hexafluoropropylene (HFP), octafluorocyclobutane (OFCB) and heavy ends (mainly 1- and 2-octafluorobutylene 1-and 2-OFB). TFE was collected from the first section of horizontal reactor and the best parameters to obtain TFE were 600 ^{o}C and pressure 100 mmHg, HFP were obtained at 750 ^{o}C and pressure 420 mmHg and collected from the second section of horizontal reactor. OFCB was produced under following parameters: temperature of second section 600 ^{o}C, pressure 100 mmHg and the product was collected from the second section of the horizontal reactor, the most advantageous parameters were: temperature in the first section 800 ^{o}C, pressure 760 mmHg. The products were collected from the first section of horizontal reactor and under such conditions were achieved: TFE 95, HFP 83, OFCB 55, 1 and 2-OFB 45 wt.%.

Jung et al. (2013) studied pyrolysis of high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS) and the influence of temperature, feed rate and kind of fluidising medium on resulting products The pyrolysis was carried out in a fluidised bed reactor. The maximum oil yields were 87.3 wt.% at 474 °C for HIPS and 84.2 wt.% at 525 °C for ABS. For HIPS and ABS, the oil yield tended to increase with increasing temperature and then decrease. It implied the optimum reaction temperature for oil yield. Main oil compounds obtained from the pyrolysis of HIPS were toluene, ethylbenzene, styrene, α-methylstyrene and styrene oligomers. However the highest styrene content (59.1 wt.%) from decomposed HIPS oil was obtained at 515 °C. The oil from ABS was similar, but it also contained nitrogenated compounds like aliphatic or aromatic nitriles. The main compounds of gaseous products from HIPS and ABS were methane, ethane, ethene, propene, butene and butadiene. The amount of gas was negligible compared to other products. A higher feed rate and the use of product gas as the fluidising medium increased the oil yield, but decreased the char yield. The pyrolysis products obtained from HIPS seems to be useable as a fuel or chemical source, but those from ABS require further treatment due to high nitrogen content.

2.2.CATALYTIC CRACKING

Catalytic cracking is one of the methods of producing various fuel fractions from plastic waste. Catalytic cracking facilitates the selective degradation of waste plastics. This method of decomposition is limited to pure polymers (predominantly using polyolefins and PS) and is resulted to gas, liquid and waxy products using fresh acid catalysts such as (i.e. zeolites), silica-alumina, aluminas, aluminium pillared clays, hybrid zeolitic-mesoporous materials and sulphated zirconia. These materials effectively convert polymers into liquid fuels giving lighter fractions in comparison with pyrolysis. The addition of catalyst is expected to reduce decomposition temperature, promote degradation speed and modify the resulting products (De La Puente et al. 2002; Garforth et al. 2004; Gobin and Manos 2004; Lin and Yang 2005; Aguado et al. 2009).

De La Puente et al. (2002) investigated the chemical recycling of low density polyethylene using fluid catalytic cracking (FCC) method at 500 °C in the presence of commercial catalysts. LDPE was dissolved in toluene. Results were qualitatively similar in all catalysts. The product contains mainly hydrocarbons in the range of gasoline fraction, with high aromatic content and highly olefinic C_3-C_4 gases, saturated C_4-C_5 were isoparafins.

Pyrolysis over catalysts of post-consumer plastics mixture (PP/PE/PS/PVC) was studied by Lin and Yang (2005). The catalytic degradation performed in a fluidised-bed reactor operating isothermally at ambient pressure and carried out using various catalyst such as: H-ultrastabilised Y(HUSY), zeolite HZSM-5 (HZSM-5), zeolite H-mordenite (HMOR), Synclyst 25 (silica–alumina) (SAHA) and MCM-41. Generally catalytic pyrolysis products are grouped as hydrocarbon gases ($<C_5$), gasoline up to C_9, liquids, HCl and residues (Table 3).

Table 3. Plastics mixture degradation products depending on catalysts type (Parameters of reaction: temperature-=360 °C, fluidising N_2, plastics to catalyst ratio=40% (wt./wt.), total time of collection=30 min) (Lin and Yang 2005).

Degradation results	**Catalyst type**				
	HZSM-5	**HUSY**	**HMOR**	**SAHA**	**MCM-41**
Yield (wt.% feed)					
Gaseous	90.65	87.51	86.63	83.56	84.15
Liquid	3.71	4.03	4.55	6.43	5.11
Residue	5.12	7.92	8.33	9.56	10.23
Involatile residue	3.43	4.27	5.22	7.93	7.31
Coke	1.96	3.75	3.11	2.63	2.92
HCl	0.52	0.54	0.49	0.45	0.51
Mass balance (%)	93.15	90.56	93.68	88.68	89.41
Distribution of gaseous products (wt.% feed)					
Hydrocarbon gases (ΣC_1-C_4)	56.37	31.64	51.58	25.34	27.31
Gasoline (ΣC_5-C_9)	34.28	50.84	35.95	53.71	56.84
Styrene	4.15	4.21	3.87	5.23	5.11
BTX (benzene, toluene, xylene)	1.66	0.82	1.96	0.26	0.14

The highest yield (almost 90%) of volatile was obtained for HZSM-5 and the highest level of unconverted plastics was observed with non-zeolitic catalysts (SAHA and MCM-41). The zeolite catalysts (HZSM-5, HMOR and HUSY), catalysed pyrolysis showed in much more amounts of volatile hydrocarbons compared to non-zeolitic catalysts. Product of catalytic degradation using HZMS-5 contained more olefinic materials with 60 wt.% in the range of C_3-C_5. HMOR and HUSY gave more paraffinic streams with large amounts of butane. MCM-41 and SAHA produced an olefin-rich product in the range of C_3-C_7. The differences in product yields and product distribution can be attributed to the microstructure of catalysts.

Thermal-catalytic degradation kinetics of PP over BEA, ZSM-5 and MOR zeolites was investigated by Durmuş et al. (2005). Degradation rate was studied by thermogravimetric analysis (TGA). The catalytic activity of zeolites decreased as BEA>ZSM- 5>MOR depending on pore size and acidity of the catalysts. Initial degradation is going faster using MOR and BEA catalysts than ZSM-5. The acidity of the catalyst is the most important parameter in determining the polymer degradation and structural parameters as pore structure and pore size.

The catalytic degradation of linear LDPE over two commercial catalysts. containing 20% and 40% ultra-stable Y (US-Y) zeolite was investigated by Akpanudoh et al. (2005). The process was performed in a semi-batch reactor. The first catalyst contained 20% US-Y, second 40%. The conversion was almost 100% and yield of liquid product was in the range of 66-89% and 41-78% for 20% US-Y and 40% US-Y, respectively.

Panda and Singh (2011) studied thermal and catalytic cracking of polypropylene in order to obtain suitable liquid fuels. Degradation was carried out in a semi-batch reactor in the temperature range from 400 to 550 ^{o}C. PP was catalytically cracked in the presence of kaolin and silica alumina. The major product of thermal degradation up to 450 ^{o}C was liquid oil, in the range of 475-550 ^{o}C was viscous liquid or wax. The highest yield of pyrolysis is 82.85 wt.% at 500 ^{o}C, use of catalysts decreased the reaction time and increased the yield of liquid fraction. The major catalytic cracking product at all temperatures was low viscous liquid oil. The use of silica alumina was better than kaolin in liquid yield and in reducing the reaction temperature. The maximum oil yield was 91% and 89.5% using silica alumina and kaolin respectively.

Aguado et al. (2009) investigated catalytic cracking of low density polyethylene using different mordenite zeolite as catalyst. They have prepared new mordenite samples with different textural properties. Synthesis method of these new materials based on the functionalisation of the zeolite seed with an organosilane. Catalytic degradation of LDPE were performed at 420 ^{o}C for 2 h in a batch reactor. Thermally decomposition of LDPE leads to polymer conversion lower than 30%, while using traditional mordenite 40%. When mordenite samples with enhanced textural properties were used, a plastic conversion of 60% is reached. Gas (C_1-C_5) and gasoline (C_6-C_{12}) fractions are obtained as main products. Heavier hydrocarbon fractions in the rage C_{13}-C_{15} are detected in product of thermal cracking and catalytic cracking over traditional mordenite. The formation of hydrocarbon fraction in the range C_6-C_{12} over mordenite samples with enhanced textural properties is related to the higher activity and accessibility of their acid sites which promotes end-chain and random scission cracking reaction of the polymer molecules.

2.3.HYDROGENATION

Hydrogenation (hydrocracking) means the addition of hydrogen (H_2) by chemical reaction through unit operation. Many technologies of plastic waste hydrocracking have failed in pilot stages. Veba process is now generally used in hydrogenation of waste. The process bases on the coal liquefaction technology. Using this process Veba Oel AG converted coal by this process into naphtha and gas oil. Technology of plastic waste treatment includes a depolymerisation section where plastics are kept in temperature between 350 and 400 ^{o}C (Al-Salem et al. 2009). Hydrocracking of plastic waste involves reaction with hydrogen over a catalyst (in a stirred batch autoclave).

Vasile et al. (2007) studied thermal and catalytic hydrogenation of waste electric and electronic equipment (WEEE such as casings, keyboards, printed circuits board (PCB)). Reaction was carried out in a batch autoclave. Hydrogenation was made at 350 ^{o}C with reaction time of 120 min. The effect of thermal hydrogenation was improved by using catalyst such as DHC-8 and metal loaded activated carbon (M-Ac). The obtained products were separated into three fractions: residue, liquids and gases. To characterise products, authors used following methods: gas chromatograph, infrared and ^{1}H-NMR spectroscopy, elemental analysis. In the Table 4 results of product distribution are presented.

Table 4. Product distribution of hydrogenation processes of pyrolysis oils from different computer scraps (Vasile et al. 2007).

Sample	**Hydrogenation method**	**Liquid (wt.%)**	**Solid (wt.%)**	**Gas (wt.%)**
Casings	Thermal	64.8	3.9	31.3
	DHC-8	60.7	2.1	37.3
	M-Ac	11.4	10.0	78.6
Keyboard	Thermal	62.5	0.3	37.2
	DHC-8	70.5	2.0	27.5
	M-Ac	23.2	6.7	70.1
PCB	Thermal	56.5	5.9	37.5
	DHC-8	50.9	11.0	38.1
	M-Ac	33.2	7.7	59.1
Mixture	Thermal	72.4	0.1	27.5
	DHC-8	65.7	0.1	34.3
	M-Ac	49.1	3.3	47.6

The obtained oils consisted of mainly aromatic hydrocarbons and contained halogen-compounds coming from the flame retardants. Liquids having high amount of aromatics were obtained by using catalyst caused upgrading. The metal loaded activated carbon (M-Ac) catalyst was more effective than conventional acidic catalyst (DHC-8) in removal of hazardous compounds from oils. Toxic compounds in liquid e.g. halogens were removed by converting them into gaseous hydrogen chloride and bromide.

Zhou et al. (2014) established that chemical recycling of plastic waste from the landfill can be applied after pre-treatment, such as cleaning, drying, cutting and sorting. Methods of chemical recycling were gasification, pyrolysis and hydrogenation.

2.4.GASIFICATION

The main aim of gasification is to produce fuels or combustible gases from plastic waste. This process is performed by the partial oxidation of organic feedstock and coal by steam, oxygen or carbon dioxide. Air is used as a gasification agent and the main advantage, of using air instead of oxygen, is reducing the cost and simplify process. The disadvantage of gasification is the presence of nitrogen (inert) in air, which causes reduction in the calorific value of obtained product due to the dilution effect on fuel gases. During gasification process a significant amount of a char is produced, which needs to be burnt The gaseous product contains of hydrogen and carbon monoxide. An ideal gasification of plastic waste should produce a high calorific gas, completely combusted char (Al-Salem et al. 2009; Al-Salem et al. 2010; Grause et al. 2011; Achilias et al. 2012; Arena and Di Gregorio 2014).

Wilk and Hofbauer (2013) studied steam gasification of plastic waste in a dual fluidised bed (DFB). They investigated different types of plastics as: PE, PE, mixtures of PE+PS, PE+PET and PE+PP. The gas product from PE was rich in CH_4 and C_2H_4 and had a lower calorific value (LCV) of 24 MJ/m^3. 22% of polyethylene was converted to the ethylene. Mixtures of PE with other polymers showed, that the concentration of methane and ethylene increased with an increasing proportion of PE. Gas product of gasification of PP contained more CH_4 and less C_2H_4 compared to the product gas from PE. More H_2 and CO were produced from PE+PP and PE+PS compared to pure polymers. The gasification product of the mixture of PE+PET resulted in 28% of CO_2, because of high oxygen content of PET. Gasification of polymers resulted in high tar loads in the products in the range of 100 g/Nm^3 or 13 g/kWh fuel.

Gasification of plastic waste by steam reforming was investigated by Tsuji and Hatayama (2009). The process was carried out in a fluidised bed to derive oil from polyethylene and polystyrene. They examined gasification in terms of carbon conversion, gas yield and gas composition. Oil derived from waste contained mainly heavy carbons and aromatics at gasification temperature above 750 ^{o}C. The hydrogen contents of the gas product from PE derived oil and PS derived oil were 72 vol.% and 68 vol.%, respectively.

Air gasification of mixed plastic waste was examined in a newly two-stage gasifier by Kim et al. (2011). The fraction consisted of PE, PP, PS, PVC, PMMA and PET. They studied influence of the reaction parameters, such as equivalence ration (ER, air to fuel weight ratio used in the gasification divided by the air to fuel weight ratio for stoichiometric combustion), upper reactor temperature, feed size and the effect of activated carbon and dolomite on the producer gas and tar removal. A very clean gas was obtained, at an equivalence ratio of 0.21. with a LHV of 13.44 MJ/Nm^3. At higher ERs, an increase of CO_2 and decrease of H_2, CO, CH_4 and hydrocarbons were observed. The concentration of H_2 and CO increased with higher upper reactor temperature. The amount of additive was also an important factor for efficient tar removal. When activated carbon was used, the production of tar was significantly decreased and caused a high production of H_2. Authors suggest that the producer gas formed during gasification of mixed wastes can be a strong candidate as a fuel gas for internal combustion engines.

Kamo et al. (2011) investigated steam gasification in the presence of carbonate compounds (various mixtures of lithium, sodium and potassium carbonate) as an effective method to recover useful gaseous products that can be used for energy production. In the absence of carbonates, small amounts of product gases were obtained. Hydrogen and carbon dioxide were obtained from conversion of activated carbon in the presence of these mixtures, at 700 ^{o}C under 0.1 MPa pressure. The presence of lithium carbonates accelerated steam gasification. The results suggest that steam gasification with mixed carbonates can be effective way in converting plastics from electronic waste in gaseous product.

2.5.SUMMARY OF THERMO-CHEMICAL PROCESSES

In Table 5, the comparison of thermo-chemical processes is shown.

Table 5. Summary of thermo-chemical processes, their operating conditions and products.

Process	Conditions	Plastic waste	Obtained products	Yield	Notes [adv. (+); disadv. (-)]	References
Pyrolysis	T.: 400-1000 °C Inert atmosphere	Polyolefins, PS, PMMA, PTFE,	Monomers, clean fuel, oils, gas, waxes; hydrocarbons: C_1-C_{50}	High yield in monomers (99% recovery of MMA)	High calorific value products (+); Reduction of toxic gases (+); Higher fraction needs to be cracked to form ethane, propene (-); Higher temperatures result in lighter fractions of aliphatic oils and gases;	(Butler et al. 2011)
Catalytic cracking	T.: 300-500 °C Over catalyst (zeolites, silica, aluminas)	PE, PP, PS	Gas, liquid fuel, wax, C_3-C_4: highly olefins, C_4-C_5: isoparafins	High (90% of gaseous products)	Obtained lighter fraction than in pyrolysis (+); Only for pure polymers (even PVC is problematic) (-); Expensive catalysts (-);	(Wong et al. 2015)
Hydrogenation	T.: 350-400 °C p.: 3-10 MPa Addition H_2 to reaction over catalyst	Polyolefins, PET, PS, PVC, mixed plastic	Oils: aromatic, hydrocarbons		Veba process;	(Al-Salem et al. 2009)
Gasification	T. :400- 800 °C p.: 3 -7 MPa Partial oxidation Atmosphere: steam, oxygen, CO_2, air	Neat polymers: PP, PE, PS, ABS, PMMA, PET, PVC, mixed plastics	ethylene, methylene, heavy hydrocarbons and aromatics	Up to 90%	A lot of char is formed, needs to be reduced (-);	(Wilk and Hofbauer 2013b)

The very efficient way of neat polymers recycling in order to obtain valuable products is catalytic cracking, however the process is not appropriate for mixed plastics waste. Pyrolysis seems to be the best way to recover high yield of monomer in a case of PMMA, PTFE or PS, but gasification is efficient for both, pure or mixed plastics waste.

3. CHEMICAL PROCESSING (decomposition with decomposing agent-solvolysis)

For polymers such as PU, PET and PC have been developed processes which are designed to reproduce the original monomers or starting substances from plastics. For such processes the terms depolymerisation and decomposition are used. Polyamides, polyesters, nylons can be depolymerised by reversible synthesis reactions to obtain diacids, diols and diamines. Recycling of plastic waste via chemical routes can be divided into: hydrolysis, glycolysis, aminolysis, methanolysis etc. and yield high conversion to their monomers (Sasse and Emig 1998; Garforth et al. 2004).

3.1.HYDROLYSIS

Hydrolysis is a method of plastic waste recycling by the reaction of polymer with water leading to total depolymerisation to monomers. The main drawback of this method is the use of high temperatures (above 200 ^{o}C), high pressure (i.e. for hydrolysis of PET 1.4-2 MPa) and long-time needed for complete depolymerisation (Karayannidis and Achilias 2007; Sinha et al. 2010). The hydrolysis of a polymer matrix occurs through two processes: water diffusion into polymer and hydrolysis reaction (Piemonte et al. 2013). Using this recycling method polyols and amine intermediates can be produced form polyurethanes. Hydrolysis is common for polymers such as PET, PU and polyamide 6 (PA6). The obtained products from hydrolysis are intermediates and polyols which can be used as fuels and to produce virgin polymer, respectively (Al-Salem et al. 2009). In general, aliphatic polyesters and phenol resin can be hydrolysed (Goto 2009). It has been reported that hydrolysis of phenolic resin in dilute sodium hydroxide yields novolac resins with 70-80% recovery. Recovered novolacs have composition products similar to conventional novolacs (Goto and Santorelli 2010). Hydrolysis of PET can be carried out in three different environments: acid, alkaline and neutral hydrolysis (Achilias and Karayannidis 2004).

Alkaline hydrolysis of PET is carried out using alkaline solution of NaOH or KOH (concentration 4-20%). The main reaction products are ethylene glycol (EG), disodium or dipotassium terephthalate salt, according to the chemical reaction shown in Figure 4. The process runs for 3-5 h at temperatures in the range of 210-250 ^{o}C, under pressure 1.4-2 MPa (Paszun and Spychaj, 1997). The mixture before process can be heated up to 340 ^{o}C to evaporate ethylene glycol. Pure product of hydrolysis can be obtained by neutralisation with a strong acid (i.e. H_2SO_4) (Karayannidis and Achilias 2007).

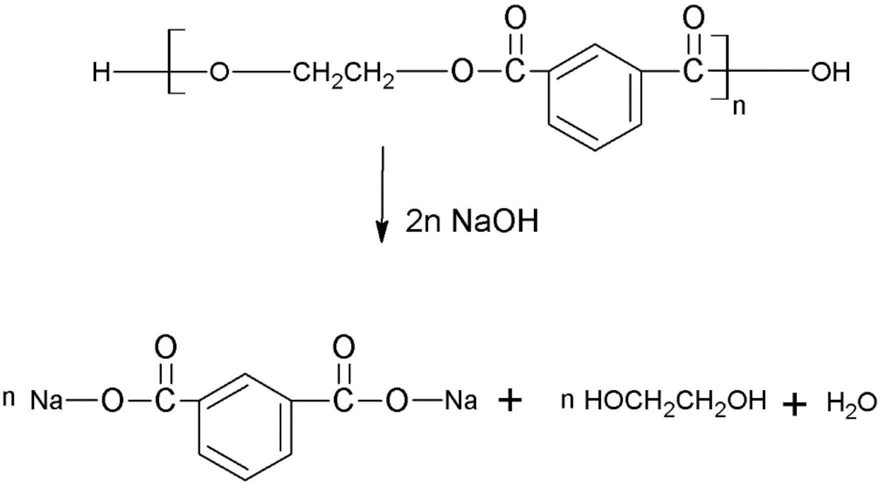

Figure 4. Alkaline hydrolysis of PET. The reaction products are EG and the disodium terephthalate salt, TPA-Na_2.

Chemical depolymerisation of PET waste to obtain TPA (terephthalic acid) was studied by Aguado et al. (2014). Authors examined influence of a particle size, NaOH /PET molar ratio and temperature on TPA yield. Hydrolysis was carried out in batch stainless steel reactor with temperature 100, 150 or 200 ^{o}C. The molar ratios of NaOH/PET were 1.2., 2.0 or 2.4. After depolymerisation, the product was filtered to remove non-reacted and degraded

PET. The optimum results were recorded for hydrolysis in condition such as, temperature 150 °C, NaOH/PET ratio 2.4/1, size particle of PET in the range of 0.2-0.5 mm. The obtained yields of TPA were up to 90%.

Achilias and Karayannidis (2004) investigated alkaine hydrolysis of PET. They carried out depolymerysation without and with catalyst (trioctyl metyl ammonium bromide). Figure 5 shows effect of temperarture on the amount of monomer obtained from PET hydrolysis with and without catalyst. Reaction was conducted in sodium hydroxide solution (5-15%).

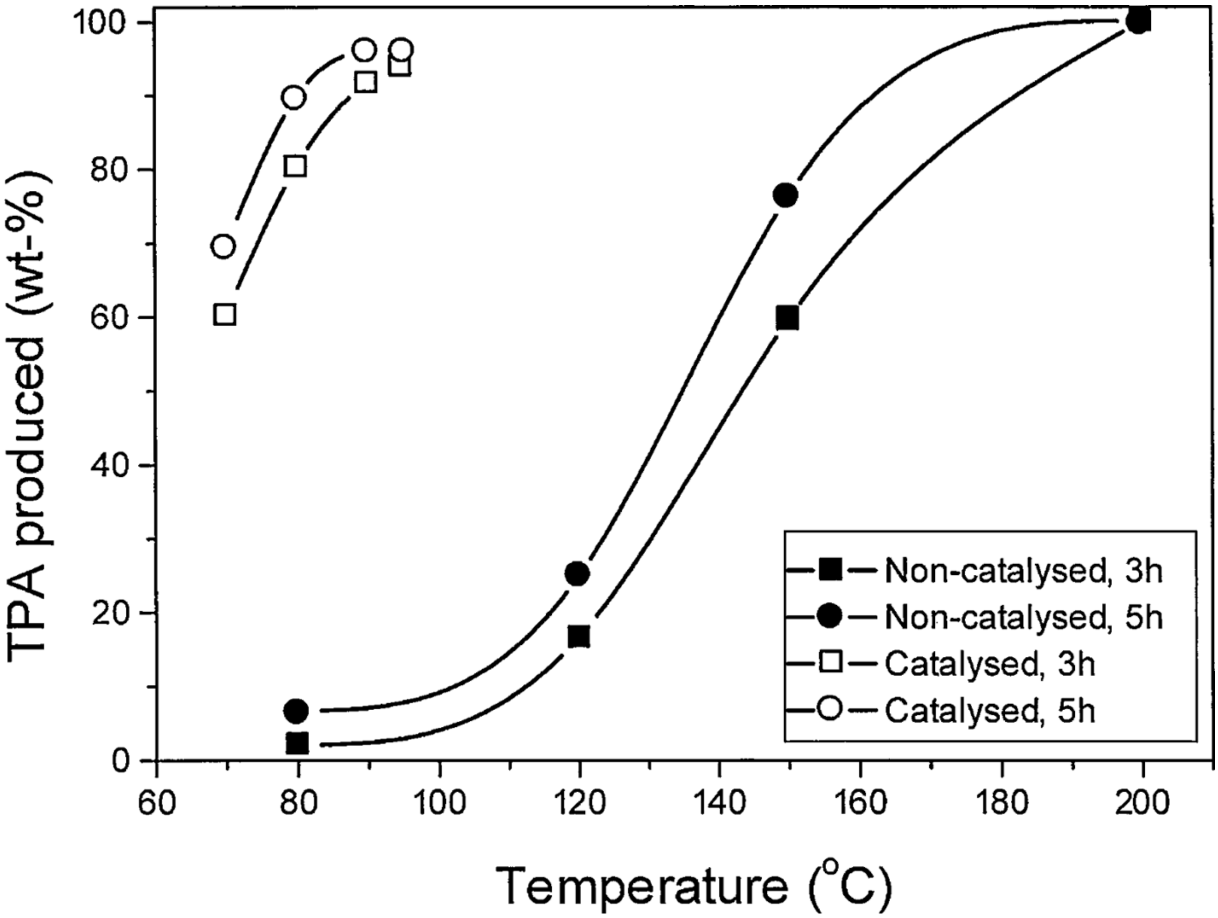

Figure 5. Effect of temperature on the amount of TPA produced during the alkaline hydrolysis PET with and without the use of catalyst at time periods 3 h and 5 h (Achilias and Karayannidis 2004).

Higher reaction temperature leads to increased decomposition of PET. Using catalyst allowed to use lower temperatures in the procces (70-95 °C instead of 200 °C). After process, the sample was neutralised with H_2SO_4 to receive pH 7. Obtained terephtalic acid (monomer) was pure, 99.6%. In the case of using catalyst, a high purity monomer was produced and the secondary materials were H_2SO_4 and NaOH.

Acid hydrolysis can be performed using concentrated mineral acid as a solvent. Mostly used is concentrated sulphuric acid, however phosphoric or nitric acid are also used (Paszun and Spychaj 1997). In US 4355175 patent using a concentrated sulphuric acid (>14.5 M) was proposed to avoid high temperatures and pressures in PET hydrolysis (Pusztaszeri 1982). Yet, in this process costs are relatively high due to the need to recycle the large amounts of concentrated H_2SO_4 and the purification of ethylene glycol from acid. Yoshioka et al. (1994) proposed acid hydrolysis of PET in relatively dilute sulphuric acid (<10 M), the acid can be reused by recovery methods such as dialysis. They studied influence of H_2SO_4 concentration, reaction time on the obtained products. The reaction was carried out at 150 °C. The degradation of PET was increased with higher concentration of sulphuric acid, precisely 48.7 wt.% at 6 M. 95.5 wt.% at 7 M and 100 wt.% at 10 M. The yield of TPA reached to 100 unit % at 10 M. The degradation increased with increasing time. Achilias and Karayannidis (2004) also investigated acid hydrolysis of PET. The sulphuric acid solution (70-83 wt.%) with PET were added to the reactor and heated to 30-90 °C. After the depolymerisation the product was filtered. At 90 °C complete decomposition was achieved with very concentrated acid solution (80 wt.%). The reaction is very slow if the concentration is less than 76 wt.%. The hydrolysis of PET in an acid environment proceeds according to the reaction in Figure 6.

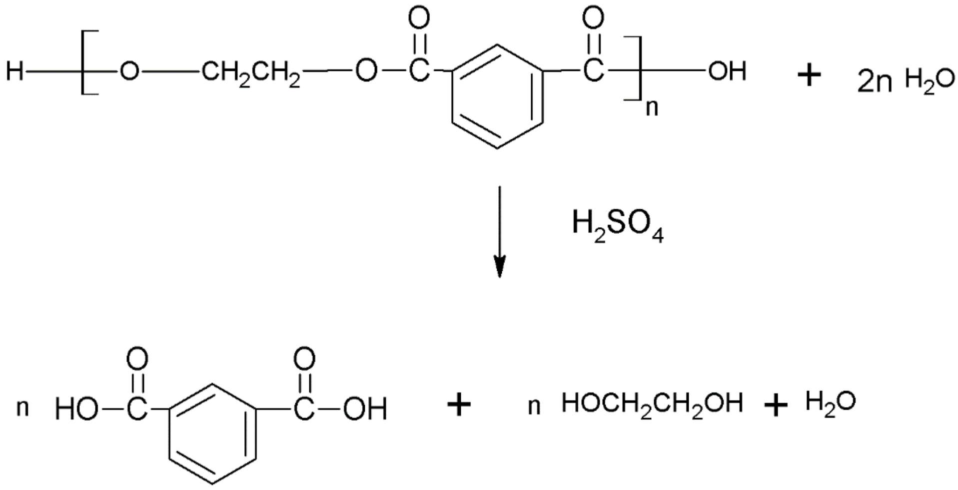

Figure 6. The depolymerisation reaction of PET with water in an acid environment.

Neutral hydrolysis is carried out with the use of hot water or steam. The process is conducted at a pressure 1-4 MPa and temperatures in the range of 200-300 °C. The pH of depolymerisation products is 3.5-4.0, which is caused by the formation of TPA monoglycol ester during the reaction (Paszun and Spychaj 1997). Neutral hydrolysis was carried out by Güçlü et al. (2003) with different amounts of water and different catalysts, in the presence of xylene to provide greater degrees of depolymerisation at lower temperatures and pressures and it provided concentrated EG solutions yielding intermediates suitable for PET preparation. It was indicated that at 140 °C no hydrolysis took place, but at 190 °C hydrolysis was almost complete.

Hydrolysis of aliphatic polyesters was carried out by Partini and Pantani (2007). The polymers were poly(ethylene dodecanedioate) and poly(tetramethylene dodecanedioate). The hydrolytic degradation was performed in sodium hydroxide aqueous solution at pH=12.7 and at T=50 °C. They found that the hydrolysis of ester bond proceeds linearly with time. The results suggest that the controlling mechanism, e.g. the slowest one, is the chemical reaction rather than diffusion.

Hydrolysis of polyurethane can produce polyols and amine intermediates. When the aim is to recovery the polyol, the reaction temperature should be around 288 °C. Too high temperature results in decreasing useful polyol recover (Zia et al. 2007). In US 4,025,559 is reported method for continuous hydrolysis of polyurethane foam (Johnson 1977). The hydrolysis method of polyurethane foam is described in US 4,196,148 (Mahoney 1980). The patent claims also method of recovery of diamines and polyethers (or polyesters). Hydrolysis is carried out in near atmospheric pressure and temperatures about 185 ^{o}C. Volatilised diamines separated from polyurethanes are removed from the reaction zone (i.e. in overhead stream), while polyols separated from the foam are recovered as liquid bottoms from the reaction zone.

Mahoney et al. (1974) performed the reaction of PU foam with superheated water. The hydrolysis was carried out for 15 min with superheated water at 200 ^{o}C. The low-density foam was converted to a liquid more dense than water. From the liquid were isolated 68% and 90%, theoretical yield of toluene diamines and yield of liquid polypropylene oxide, respectively.

Supercritical and subcritical fluids as water or alcohol are solvents with unique features due to their properties are intermediate between liquid and gas. These fluids are very often a solvent reaction medium and a reactant (Antonakou and Achilias 2013). Using sub- and supercritical fluids depolymerisation of polymers proceeds rapidly and selectively. Plastics obtained by condensation polymerisation are easily decomposed into their monomers in water which acts as reagent. Also this decomposition method can be applied to addition polymerisation plastics (Goto 2009). Nylon 6 was depolymerised by hydrolysis in sub- and supercritical water and obtained products were ε-caprolactam and ε-aminocaproic acid. The yields of these product were approx. 100% for reaction at 300 ^{o}C in 60 min and 330 ^{o}C in 30 min. When reaction time increased, the yield of ε-caprolactam and ε-aminocaproic acid decreased. Addition polymerisation plastic such as prepolymers phenol resin were decomposed into monomers at 250-450 ^{o}C in sub- and supercritical water. The maximum yield of monomers reached 78% in the reaction at 450 ^{o}C for 30 min. When decomposition was accelerated by the addition of Na_2CO_3, the yields of monomers reached more than 90%. Phenol resin was depolymerised mainly into phenol and cresols in supercritical water (Goto et al. 2006).

Tsintzou and Achilias (2013) investigated depolymerisation of polycarbonate with water under microwave irradiation. The reaction was done in an alkaline aqueous NaOH solution and using a phase transfer catalyst (1-hexadecyl trimethyl ammonium bromide). When reaction time was 40 min and temperature 160 ^{o}C, the conversion of PC was almost 100% in a 5% NaOH solution. If the concentration of NaOH solution is 10%, it reduces the required reaction time to 10 min. The obtained monomer, bisphenol-A (BPA), was very pure and it could be reused for the reproduction of the polymer.

Hydrolysis degradation of polycarbonate was studied by Deirram and Rahmat (2012). Hydrolysis was performed under microwave irradiation, using various concentration of NaOH as catalyst, different amount of water as main solvent and co-solvent was tetrahydrofuran (THF) and 1,4-dioxane. The highest yield of bisphenol A (94%) was obtained during 12.5 min at 110 ^{o}C using 20 g THF, 3.5 g H_2O as a main solvent and 0.5 g NaOH as catalyst. Other co-solvent, 1,4-dioxane gave 85% yield of BPA.

Tsuji et al. (2003) examined hydrolysis in the melt in high-temperature and high-pressure water of poly(L-lactic acid) (PLLA). The depolymerisation was carried out in the temperature range of 180-350 ^{o}C for a period of 30 min. The highest yield of L-lactic acid (90%) was achieved at 250 ^{o}C after 10-20 min, but the lowest yield of monomer (ca. 30%) was obtained at high temperatures such as 350 ^{o}C due to decomposition of lactic acid. In the temperature range of 250-350 ^{o}C more than 90% of PLLA was hydrolysed to water-soluble oligomers and monomers. Authors believe that hydrolysis of PLLA in the melt is an effective method to obtain L-lactic acid.

3.2.GLYCOLYSIS

Glycolysis is typical depolymerisation reaction for condensation polymers such as polyamides (nylons), polyesters, polyethylene terephthalate or addition polymers like polyurethanes. The conversion of waste to raw monomers is relatively high (Garforth et al. 2004; Grause et al. 2011). This kind of depolymerisation of plastic waste leads to obtaining products such as diols, diamines, diacids or oligomerols. Compounds acting as glycolysis agents can be aliphatic compounds or oligomerols contained at least two hydroxyl groups. The compounds can contain in their chains oxygen or nitrogen. The most widely used are glycols like: ethylene glycol (EG), propylene glycol (PG), butylene glycol, diethylene glycol (DEG), dipropylene glycol (DPG). The kind of used glycol for glycolysis has influence on time and temperature reaction (Datta and Rohn 2007b; Abdelaal et al. 2011). In the literature, glycolysis of PET and PU waste, is very well described. Very often the product from glycolysis is used to produce original polymer or new material.

Glycolysis of PET is a transesterification between PET ester groups and a diol (mostly ethylene glycol) to obtain monomer, BHET (bis(hydroxyethyl) terephthalate) (Aguado et al. 2014). Glycolysis of PET is conducted in the range of temperatures from 180 to 240 ^{o}C. Metal compounds such as zinc, copper, lead, cobalt acetate are used as catalyst of glycolysis reaction (Karayannidis and Achilias 2007). Sodium carbonate, sodium bicarbonate, sodium sulphate, potassium sulpahte and ionic liqiuds like 1-butyl-3-methylimidazolium acetate were used in expertimental works as catalysts (López-Fonseca et al. 2010; López-Fonseca et al. 2011; Al-Sabagh et al. 2014). Pardal and Tersac (2006) studied the kinetics of poly(ethylene terephthalate) glycolysis by diethylene glycol, dipropylene glycol and glycerol. In the mixture of dipropylene glycol and glycerol, PET was decomposed more quickly than in pure dipropylene glycol or glycerol.

Glycolysis process of polyester is described in US 6,410,607 (Ekart et al. 2002). The process should be carried out in an agitated reactor vessel. The depolymerisation of polyester requires to provide glycol in a molar ratio 1 to 5 total glycol units to total dicarboxylic acid units at temperature between 150 to 300 ^{o}C and pressure 0.5 to 3 bar.

As a decomposing agents for glycolysis can be used 1,4-butanediol (BDO) and triethylene glycol (TEG) (Mansour and Ikladious 2002). PET was depolymerised in the presence of zinc acetate as catalyst. The glycolysed products consisted mostly of monomer and dimer by using 1,4-butanediol, while using triethylene glycol resulted in products TEG-terephthalic acid-TEG.

Xi et al. (2005) investigated depolymerisation of PET waste to obtain monomer bis(2-hydroxyethyl terephthalate). The reaction was executed at 196 ^{o}C with ethylene glycol (EG) to PET weight ratios from 0.5 to 6 and time between 1-5 h in the presence of zinc acetate as catalyst. The highest yield of BHET (85.6%) was obtained when reaction time was 3 h, weight ratio (EG to PET) was 5 h.

The high yields of monomer BHET (more than 90%) were obtained in sub- and supercritical glycolysis of PET with ethylene glycol, which was studied by Imran et al. (2010). They examined three variants of glycolysis reaction. Supercritical glycolysis was carried out at 450 ^{o}C and 15.3 MPa. Subcritical process was performed in two different conditions, at 350 ^{o}C and 2.49 MPa or at 300 ^{o}C and 1.1 MPa. Complete PET depolymerisation was observed after 30 min for supercritical glycolysis, after 75 min and 120 min in cases of subcritical glycolysis.

Glycolysis of PET using oligoesters as a new type of glycolysis agent was proposed by Colomines et al. (2005). The oligoesters were synthesised via the transesterification of dimethyl isophthalate with neopentyl glycol or teraethylene glycol and the esterification of adipic acid with neopentyl glycol or theraethylene glycol. The depolymerisation was carried out in the presence of zinc acetate. The products of glycolysis were statistical copolymers made of oligoseter units and esters of terephthalic acid with free diol segments.

Abdelaal et al. (2011) proposed to produce unsaturated polyester resin using recycled PET. They carried out glycolysis of PET with different glycols (propylene glycol, diethylene glycol, triethylene glycol and their mixture). The glycolysis products were converted into unsaturated polyester after reaction with maleic anhydride, styrene was used as a cross linker. They found that the yield of glycolysis depends on the type of glycol used. The similar idea was described by Karayannidis et al. (2005). They investigated the production of i.e. alkyd resins derived from the glycolysis of PET waste using diethylene glycol as glycolysis agent. The obtained oligomers were synthesised with maleic anhydride, phthalic anhydride and propylene glycol to form unsaturated polyester resins. These products were mixed with styrene and cured using benzoyl peroxide/amine initiator. The obtained products were compared corresponding to a typical alkyd resin recipe. The elongation at the break point of the resin was higher and the tensile strength lower.

Glycolysis of polyurethane is the degradation of material, which causes disintegration of urethane and urea gropus, occuring under influence of glycols or amines mixture (Datta 2012b). The product of polyurethane waste glycolysis (glycolysate) can be homogenous mixture or it can be divided into two or three separated phases. Upper phase consists mainly of polyols, which are similar to virgin polyols and bottom phase consists of aromatic carbamates, ureas, unreacted glycol and amines. The products of polyurethane waste glygolysis should be purified. The common methods of purfication are extraction, distillation and removal of amine groups using i.e. alkylene oxides (Datta and Rohn 2007c). Glycolysates are non-Newtonian fluids and optiumum glycolysates processing temperature is 75 ^{o}C (Głowińska and Włoch 2014). Datta (2012a) investigated influence of glycols on chemical structure and thermal stability of glycolysates obtained from polyurethane depolymerisation.

The reaction was performed using different glycolys, from ethylene glycol to hexane-1,6-diol. It was found that kind of glycol had insignificant infulence on chemical composition of glycolysates. Glycerine and pentaerythriol were proposed as an efficient glycolysis agents (Nikje et al. 2007; Nikje and Nikrah 2007; Nikje and Garmarudi 2010). The glycolysis reaction can be carried in the presence or absence of catalyst. Although, if catalyst is not added to reaction zone, the time of glycolysis is longer. Generally, glycolysis catalysts can be divided into three main groups, viz. metal salts and metal hydroxides (i.e. potassium acetate, zinc stearate, stannous octaoate, NaOH, KOH), organometallic compounds (dibutyltin dilaurate, titanium(IV) butoxide, titanium(IV) 2-ethylhexyloxide) and amines (triethylenediamine, 1,4-dimethylpiperazine, dimethylaniline) (Datta and Rohn 2007b). Molero et al. (2009) found that lithium and stannous octoate show high catalytic activity. The depolymerisation rate and the purity of polyol obtained from glycolysis of polyurethane in the presence of stannous octoate were greater than those in the presence of conventional catalysts (Molero et al. 2009b; Simón et al. 2013).

"Split-phase" glycolysis was investigated by Molero et al. (2008). The glycolysis was carried out in a jacketed flask with refluxing condenser under nitrogen atmosphere to avoid oxidation in the range of temperature 175-195 °C and with different catalyst concentrations 0.0-7.8%. The glycolysis agent was diethylene glycol. Table 6 reports the properties of recovered polyol. A carboxylate catalyst improves degradation rate, but in order to obtain high quality recovered polyol, amount of catalyst should be reduced. The use of 2.2% of catalyst appears as a good choice.

Table 6. Properties of recovered polyols (upper phase) obtained with different catalyst concentration in the glycolysis agent (DEG) (Molero et al. 2008).

Catalyst concentration (wt.)	0.0%	1.1%	2.2%	3.3%	5.6%	7.8%
Viscosity 25 °C (cP)	838	-	591	600	551	539

Water (%)	-	0.12	0.21	0.60	1.03	1.17
Acidity (mg KOH/g)	<0.05	<0.05	<0.05	<0.01	<0.01	<0.05
OH number (mg KOH/g)	-	161	171	186	195	206
Total amine (mg KOH/g)	-	-	9.59	11.19	14.41	13.93
Primary amine (mg KOH/g)	-	-	8.86	10.55	13.41	13.17
K content (ppm)	-	3	11	21	44	52

T_R=190°C, W_{DEG}/W_{PU}=1.5. Raw polyol properties: viscosity 560-630 cP, acidity < 0.1 mg KOH/g, water content <0.1%, OH number 48 mg KOH/g, alkaline < 5ppm.

In Table 7 properties of polyols obtained at different reaction temperatures are shown. Amine value and hydroxyl number increase with temperature up to 190 °C as the result of secondary reactions and the breakdown of transesterification carbamates.

Table 7. Properties of recovered polyols obtained at different reaction temperatures (Molero et al. 2008).

Reaction temperature, °C	175	184	190	195
Viscosity 25 °C (cP)	-	-	591	694
Acidity (mg KOH/g)	0.012	0.039	0.018	0.015
OH number (mg KOH/g)	158	166	171	172
Total amine (mg KOH/g)	378	4.52	9.59	9.80
K content (ppm)	7	-	11	4

Catalyst concentration in the glycolysis agent= 2.2%; W_{DEG}/W_{PU}=1.5.

Increasing reaction temperature and catalyst (potassium octoate) concentration enhances the degradation rate, but also promotes secondary reaction and contaminates polyol phase. When the reaction conditions are extreme, the carbamate is not formed, yielding an aromatic structure and glycol. This predictions were confirmed using IR spectra.

Simón et al. (2014) investigated glycolysis of flexible foams containing polymeric polyol. They showed that it is possible to carry out glycolysis of these foams using similar reaction conditions as the glycolysis of conventional foams synthesised with flexible polyether polyol. The upper phase (liquid) was obtained as a result of glycolysis and further was purified by extraction so it could be used in further foam synthesis. The recovered polyol had hydroxyl number approx. 60 mg KOH/g. They concluded that polyurethane waste coming from conventional foams can be treated with foams containing polymeric polyol due to obtain similar final product.

Borda et al. (2000) examined glycolysis of flexible polyurethane foams and elastomers based on polyether polyol using aliphatic glycols, diethanolamine or ethylene glycol and diethanolamine mixture. The authors observed that glycolysis runs the fastest when degradation agent is diethanolamine, however the obtained product had a high viscosity. To solve this problem, they used ethylene glycol and diethanolamine mixture in ratio from 1:1 to 1:9. It was found that the reaction time decreased with increasing quantity of diethanolamine. They proposed the mechanism of polyurethane depolymerisation (Figure 7). Glycol probably takes part in an esterification reaction and polyol is recovered.

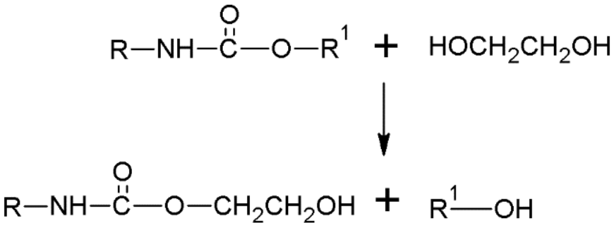

Figure 7. The reaction of polyurethane transesterification with ethylene glycol.

Wu et al. (2003) investigated glycolysis of flexible polyurethane from car waste. The reaction was performed under atmospheric pressure and isothermal condition (220 ^{o}C). As a glycolysis agent was used diethylene glycol (DEG) and potassium acetate (KAc) as a catalyst. They determined that the adequate reaction time was 90 min and the optimum concentration of DEG and KAc was 150 and 1% of the mass of the polyurethane. Further, the polyol was recovered by distillation.

The products of polyurethane glycolysis (glycolysates) were applied to form new polyurethane materials (Datta and Pasternak 2005; Datta and Kacprzyk 2008; Datta and Pniewska 2008; Datta and Rohn 2008). Datta and Rohn (2007a) carried out glycolysis of polyurethane foams using 1,6-hexanediol as a glycolysis agent. The glycolysates with molecular weight 670 and 600 g mol^{-1} were selected to polyurethane synthesis. Polyurethane elastomers were formed by prepolymer method using methylene diphenyl diisocyanate (MDI) and various chain extenders: buthanediol (BDO), ethylene glycol (EG), hexanediol (HDO). Obtained polyurethane elastomers had tensile strength in range 13.4-15.6 MPa, hardness in range 85-84 ^{o}Sh A and density 1.016-1.053 g/cm^3 (according to used chain extender). Elastomers had glass transition temperatures at 0.5 and 0.8 ^{o}C.

Nikje and Mohammadi (2009) proposed polyurethane glycolysis using sorbitol/glycerine/water mixture as a destroying agent and sodium hydroxide as a catalyst. Rigid polyurethane foams were obtained from virgin and recovered polyol to compare mechanical properties. Increasing content of recovered polyol in foam caused decrease in elongation at break and increase in storage modulus of PU foam.

Czupryński et al. (2010) studied glycolysis of rigid polyurethane-polyisocyanurate (PUR-PIR) foams and formation of new PU-PIR foams. Glycolysis was executed using the mixture of ethylene glycol, diethylene glycol and ethanolamine as a glycolysis agent. They used obtained product to form new foams with glycolysate content in the range of 0 to 15 wt.%. With increasing content of glycolysates in foams density increased from 36.9 kg/m^3 (0 wt.%) to 57.8 kg/m^3 (15 wt.%) and decreased flammability of foams. With higher content of glycolysates in foam formulation, compressive strength increased.

Mechanism of glycolysis of nylon 6.6 and hexamethylenebis(hexamide) (HMHA) was proposed by Kim et al. (2006). Both compounds were decomposed by ethylene glycol in an autoclave reactor. Glycolysis of HMHA with EG (1:5 mole ratio) and glycolysis of nylon 6.6 with EG (1:2 mole ration) were carried out at temperature 250 and 275 °C, respectively. The authors expected that glycolysis reaction of nylon 6,6 is similar to its model compound (HMHA). The main glycolysis products of nylon 6,6 were compounds having β-hydroxyethylester end group, bis(β-hydroxyethyl)hexanoate and δ-valerolactone. Proposed glycolysis reaction is shown in Figure 8.

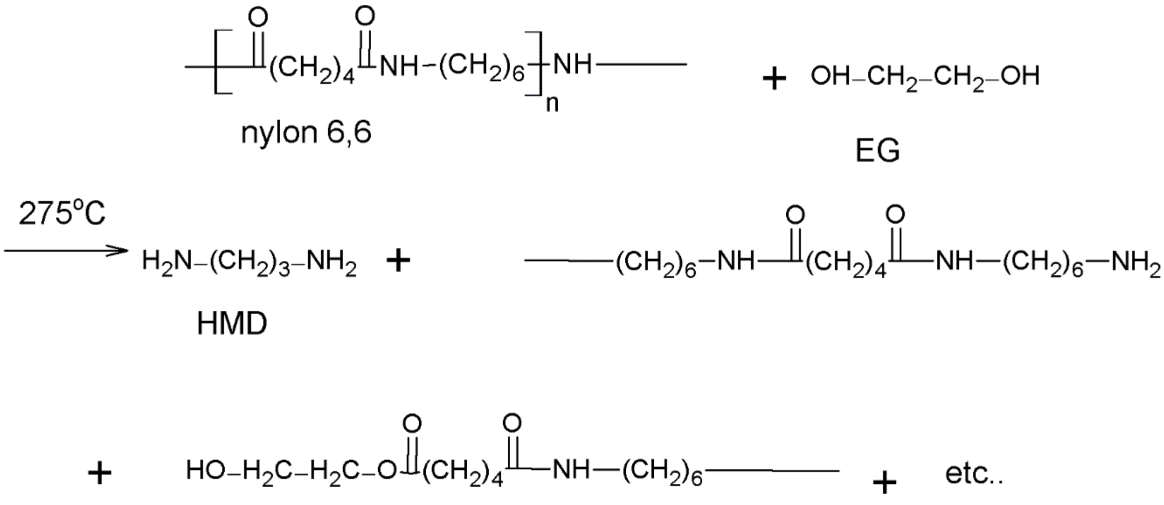

Figure 8. Overall glycolysis reaction of nylon 6,6 predicted from the basis of the glycolysis reaction of HMHA.

3.3.ALCOHOLYSIS

Alcoholysis leads to depolymerisation of polymers using alcohol (i.e. ethanol, butanol) and for example pentaerythrytol (PENTE) can be used in PET alcoholysis (Mendes et al. 2011). Chemical recycling of PET was carried out in a mixer Haake Rheomix, at 250 °C, 60 rpm for 10 min, in the presence of zinc acetate as a catalyst. The alcoholysis brought about PET oligomerisation and oligoester bis(tri-hydroxylneopentyl) terephthalate was obtained. Few researchers investigated alcoholysis using isooctyl alcohol in sub- and supercritical conditions (Liu et al. 2013a; Ding et al. 2014). Liu et al. (2013a) performed alcoholysis of PET to produce dioctyl terephthalate (DOTP) using sub- and super-critical isooctyl alcohol

(2-EH). The optimal alcoholysis conditions to obtain DOTP were as follows: reaction temperature 300 °C, weight ratio of 2-EH/PET 4/1 and reaction time 3 h. The degradation rate of poly(ethylene terephthalate) was 100% and the yield of DOTP was 97%.

The isooctanol alcoholysis of PET waste to produce dioctyl terephthalate and ethylene glycol was conducted by Liu et al. (2013b). The degradation was performed in the presence of Broensted-Lewis acidic ionic liquid (IL). It was found that (3–sulfonic acid) propyltriethylammonium chloroironinate was an efficient catalyst. The conversion of PET was 100% and the yields of DOTP and EG were 97.6% and 96.6%, respectively. Ionic liquid can be easily separate from the product and reuse even seven times. Ionic liquid was used also in butanol alcoholysis of PET (Liu et al. 2013c). N-butanol was used to produce dibutyl terephthalate (DBTP) and ethylene glycol in the presence of a Broensted-Lewis acidic ionic liquid. The conversion of PET was 100% and the yields of DBTP and EG were 95.3% and 95.7%, respectively, when reaction conditions were as follows: reaction temperature 205 °C for 8 h.

Hirao et al. (2010) investigated alcoholysis of poly(L-lactic acid) under microwave irradiation. Alcoholysis rates in ethanol (140-180 °C) and butanol (130-210 °C) were greater under microwave irradiation than under conventional heating.

3.4.METHANOLYSIS

In methanolysis, methanol is a decomposing agent for polymeric materials. Very often methanolysis of polycarbonates is performed in sub- and supercritical conditions or in the presence of large quantities of concentrated acids or bases as catalysts. This reaction leads to obtain monomer, namely bisphenol A (BPA) (Antonakou and Achilias 2013). Reaction formula is as follows in Figure 9.

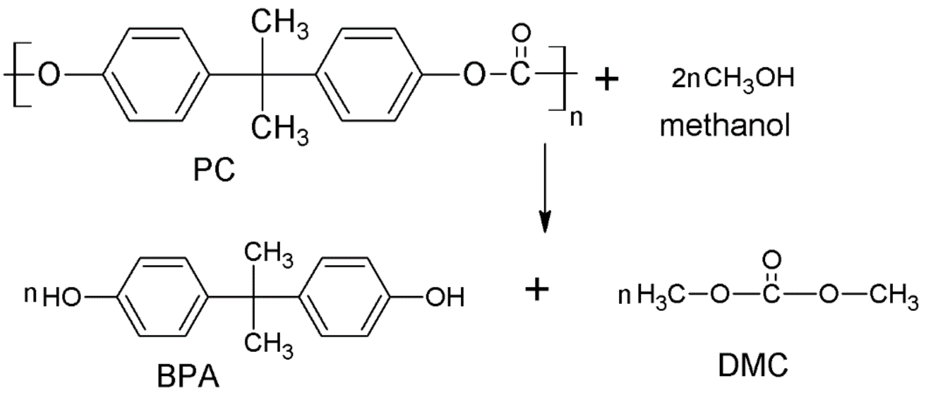

Figure 9. Methanolysis reaction of polycarbonate.

Monomer recovery from polycarbonate by methanolysis was investigated by Chiu et al. (2008). Depolymerisation with molar ratio of methanol and PC ranging from 12.5 to 50 was carried out from 170 to 300 °C for up to 30 min. The obtained products were two monomers, bisphenol A and dimethyl carbonate (DMC) and two by-products, phenol and 4-tertbutylphenol. The complete depolymerisation was achieved when the reaction temperature was higher than 260 °C. The researchers found that the most important factors that influence on polycarbonate methanolysis are reaction time and molar ratio of MeOH/PC. The optimal decomposition conditions of PC were as follow molar ratio of MeOH/PC equal to 37.5, reaction time 5 min at 240 °C. Under such conditions, recovery of BPA and DMC were 90.7% and 95.2%, respectively.

Alkali-catalysed methanolysis of PC in a mixed solvent of methanol and toluene or dioxane was examined by Hu et al. (1998). In a mixed solvent of methanol and toluene, PC was completely depolymerised. Another research group (Liu et al. 2009) studied alkali-catalysed methanolysis of polycarbonate in a solvent such as N-methyl-2-pyrrolidone, 1,4-dioxane and tetrahydrofuran, NaOH was catalyst. The aim of this study was to obtain bisphenol A and carbon carbonate. Table 8 shows yields of methanolysis in various solvents.

Table 8. Effect of solvent on the result of methanolysis (Liu et al. 2009).

Solvents	**Solvent dosage (g)**	**Yield od BPA (%)**	**Yield of DMC (%)**
Methanol	8	-	-
Tetrahydrofuran	8	78	81
1,2-dichloroethane	8	75	78
Toluene	8	28	30
1,4-dioxane	8	79	77
N-methyl-2-pyrrolidone	8	74	77

Reaction time 10 min, reaction temperature 40 °C, PC 5 g, NaOH 0.15 g, CH_3OH 5 g.

No BPA and DMC were found when methanolysis was carried out under given conditions in methanol without co-solvent. When co-solvents were used the yield of BPA and DMC was accelerated. The conversion of PC was almost 100% and the yield of BPA over 95%, when reaction conditions were as follow: reaction temperature 40 °C, mole ratio m(PC):m(MeOH)=1:1, reaction time 35 min and tetrahydrofuran was used as solvent.

Methanolysis of PC in an ionic liquid without catalyst was investigated by Liu et al. (2010). The chosen iconic liquid was 1-n-butyl-3-methylimidazolium chloride ([Bmim][Cl]). Under moderate condition, viz. mole ratio of m(PC):m(CH3OH):([Bmim][Cl])-2:3:4, reaction temperature 105 °C and time 2.5 h, the decomposition conversion of PC was almost 100% and the yields of BPA and DMC (dimethyl carbonate) were more than 95%. The ionic liquid can be reused 8 times.

Methanolysis is well known method of recycling PET waste (Paszun and Spychaj 1997). Methanolysis converts PET waste into dimethyl terephthalate (DMT) and ethylene glycol (EG). This reaction can be carried out in various temperatures depending on reaction environment and sometimes under high pressure to avoid evaporation of methanol (Lorenzetti et al., 2006). Kishimoto et al. (1999) performed methanolysis of poly(ethylene terephthalate) and poly(ethylene 2.6-naphthalenedcarboxylate) (PEN). Methanolysis of PET in the presence of catalytic CH_3ONa was complete. PEN was depolymerised in methanol to dimethyl 2,6-naphthalenedicarboxylate and ethylene glycol up to 290 ^{o}C without any catalyst or by heating up to 210 ^{o}C in the presence of CH_3ONa. Other researchers, Kurokawa et al. (2003) used aluminium tiisoropoxide (AIP) as a catalyst of methanolysis. The depolymerisation at 200 ^{o}C in methanol with an AIP catalyst provided to obtain dimethyl terephthalate (DMT) and ethylene glycol in 64% and 63% yields, respectively. The yields were increased, using a toluene/methanol solvent, to 88% for DMT and 87% for EG. Decomposition of PET powder by methanolysis was investigated by Mishra and Goje (2003). They carried out methanolysis using zinc acetate in the presence of lead acetate as a catalyst at 120-140 ^{o}C in a batch reactor. The experiments were conducted from 60 to 150 min. The results showed that optimal reaction time was 120 min and at 120 ^{o}C and the conversion of PET into DMT and EG was 97.8%, while using higher temperatures, 130 and 140 ^{o}C, the conversion was 100%. The authors used temperatures below 150 ^{o}C to avoid oxidation or carbonisation.

Polyurethanes methanolysis was investigated by Asahi et al. (2004). Examined materials were model polyurethane, poly[ethylene=methylene bis(4-phenylcarbamate) and commercial PUR foam. The decomposition was carried out under sub- and supercritical conditions, at the temperature range from 160 to 300 ^{o}C at pressures up to 15 MPa in methanol. The decomposition percentages were over 90% at temperatures above 200 ^{o}C. The products of methanolysis were methyl carbamate, which can be pyrolysed into methanol and MDI. Liu et al. (2013b) studied decomposition of thermoplastic polyurethane elastomer (TPU) in sub- and supercritical methanol. TPU was based on MDI, poly(1,4-butylene adipate) and 1,4-butanediol. Methanolysis was carried out with the mass ratio TPU:MeOH equal to 1:10 at temperatures in the range of 200-290 ^{o}C and pressures 3-13 MPa, respectively. The aim product was 4,4'-methylene diphenyl carbamate (MDC), which can be important material in synthesis of MDI. Subcritical conditions were more appropriate to obtain MDC, than supercritical. The maximum yield of MDC was 98.2%. The authors claim that during methanolysis the chains of TPU were separated into soft and hard segment, then the ester exchange reacted between methanol and the urethane group of the hard segment and further the ester group of the soft segment. The main products of methanolysis in subcritical conditions were BDO, dimethyl adipate (DMA) and MDC, while in supercritical conditions were obtained BDO, DMA, amines and tetrahydrofuran.

Decomposition of poly(lactic acid) by methanolysis in the presence of ionic liquid as a catalyst was examined by Song et al. (2013). Methyl lactate was obtained after distilling methanolysis product. Optimum conditions of reaction were as follow: mole ratio n(CH_3OH):n(PLA) - 5:1, temperature 115 ^oC and reaction time 3 h. The best catalyst appeared 1-butyl-3-methylimidazolium acetate ([Bmim][Ac]) and the conversion of PLA was 97.2% and yield of methyl lactate was 92.5%. In another work, acidic functionalised ionic liquids (IL) were used as catalysts of PLA methanolysis (Song et al. 2014). It was found that functionalised HSO_3^- exhibited higher catalytic activity than non-functionalised and traditional acid catalyst. In this reaction as catalyst was used 1-methyl-3-(3-sulfopropyl)-immidazolium hydrogen sulphate ([HSO_3-pmim][HSO_4]). The conversion yields of PLA and methyl lactate were over 97% and 88.7% respectively were obtained under optimal conditions: reaction temperature 115 ^oC, reaction time 3.5 h, weight ratio of PLA:IL was 1:0.02 and molar ratio of PLA:CH_3OH was 1:5.

3.5.AMINOLYSIS

Aminolysis is an efficient method of polymer waste chemical recycling, in particular it is very common method for PET decomposition. Commonly used solvent in aminolysis is ethanolamine and the product of this method depolymerisation is bis(2-hydroxyethylene) terephthalamide (BHETA) (Elsaeed and Farag 2009; Pingale and Shukla 2009; Shamsi et al. 2009; Tawfik and Eskander 2010; Achilias et al. 2011; Hoang and Dang 2013). There are other solvents used in aminolytic degradation: hydrazine monohydrate (Parab et al. 2012), 2-amino-2-methyl-1-propanol, 1-amino-2-propanol (Shah and Shukla 2012) or 3-amino-1-propanol (Shah et al. 2013). Hoang and Dang (2013) studied aminolysis of PET with ethylenediamine (EDA). As the products of aminolytic depolymerisation were obtained bis(2-aminoethyl) terephthalamide (BAET, trimer) and α.ω-aminoligo(ethylene terephthalamide) (AOET, oligomers). The yield of trimer BEAT was 75% while molar ratio of EDA:PET was more than 14:1. The process of aminolysis of PET was described by El-hameed (2011). He used monoethanole amine (MEA) as an aminolysis agent. The reaction was carried out at weight ratio of PET:MEA equal to 1:1 using 1% of sodium acetate as a catalyst in nitrogen atmosphere at temperature about 170-190 ^{o}C for 4 h and at 200 ^{o}C for 3 h. The temperature was lowered to 100 ^{o}C for 1 h. At the end of reaction, distilled water was added to precipitate out of the product, poly(bis(2-hydroxy ethylene)terephthal)amide (PHETA). Crystalline powder of BHETA was obtained by recrystallisation in distilled water. Heidari and Tahvildari (2013) studied depolymerisation of PET using different aminolysis agents: monoethanoloamine (MEA, diethanoloamine (DEA) and triethanoloamine (TEA). In decomposed products of PET with MEA and DEA two hydroxyl groups, with TEA four hydroxyl groups were observed at the end of polymer chains. The recovered polyol compound can be alternative of polyols used in common synthesis. Recycling of poly(ethylene terephthalate) using 3-amino-1-propanol by conventional or microwave irradiation was proposed by Shah et al. (2013). Heating under microwave reduced of aminolysis time from 5 h to 7 min. The obtained product was found to be bis(3-hydroxy propyl)terephthalamide and was subjected to cyclisation reaction using thionyl chloride to obtain bis-oxazin. Bis-oxazin can be used as chain extender or a cross linking agent in polymer synthesis.

The products of aminolysis can be applied to form new materials. Elsaeed and Farag (2009) synthesised unsaturated polyester through reaction of bis(2-hydroxyethylene) terephthalamide with different long-chain dibasic acids such as decanedioic acid, tetradecanoic acid octadecanoic acid with maleic anhydride. Polyurethane based on aminolysis of PET were investigated by Shamsi et al. (2009). Polyurethanes were prepared based on BHETA, 1,4-butanediol, ether polyol and hexamethylene diisocyanate. Similar research were performed also by Sadegehi et al. (2011).

Hata et al. (2002) studied aminolysis of poly(carbonate) to 1,3-dimethyl-2-imidazolidinone (DMI) and bisphenol A (BPA). The aminolysis was performed using N.N'-dimethyl-1,2-diaminoethane (DMDEA) in dioxane with/without a catalyst (i.e. Na_2CO_3) at 100 ^oC. As the products of aminolysis were obtained BPA (87%), DMI (82%) and small amount of bis(carbamate) (2-5%).

Rigid polyurethane foam was decomposed by aminolysis method (Chuayjuljit et al. 2002). The reaction was carried out at 180 ^oC for 70 min using diethylenetriamine (DETA) as a degrading agent and NaOH as a catalyst. The products of decomposition was 4,4'-methylenedaniline (MDA) and low molecular weight urethane oligomers.

3.6.OTHER SOLVOLYSIS

There are other methods of chemical recycling which are not so widely described in the literature. One of these methods is ammonolysis. This method was used by Jain and Soni (2007) in chemical recycling of PET. The research was performed in the absence and in the present of catalyst. The use of catalyst (zinc acetate) reduces the needed time of degradation from 45 to 15 days. The end product of ammonolysis was 1,4-benzene dicarboxamide. Ammonolysis can be applied for nylon (Duch and Allgeier 2007). High temperature ammonolysis leads to reversion of the nylon-6 and nylon-6,6 to monomers and dehydration of amide monomers to nitrile molecules. The obtained product is the mixture of 6-aminocapronitrile, caprolactam, adpiponitrile, hexamethylenediamine and others. Recycling of thermoset polymer was investigated by (Mormann and Frank 2006). The final products of cyanurate polymers and polymaleimides ammonolysis are melamine and bisphenol, amines and linear polymer containing imide and diamide units, respectively.

Troev et al. (2000) proposed depolymerisation of polyurethane foams by triethyl phosphate. The degradation was carried out at 190 ^{o}C for 1-4 h. In all cases, degree of degradation was 100%. The decomposition of PU by triethyl phosphate includes two reactions: an exchange reaction with the participation of the urethane group and the ethoxy group of phosphoric acid- breakdown of polymer chains and the alkylation of urethane group by triethyl phosphate. The obtained products were phosphorous containing oligourethanes.

Beneš et al. (2012) decomposed polyurethane using castor oil and fish oil. Depolymerisations were carried out at 250 ^{o}C and 200 ^{o}C for castor oil and fish oil respectively. Chopped PU, decomposing agent and optionally catalyst (NaOH or diethanoloamine) were added to the flask fitted with a stirrer, reflux condenser and nitrogen inlet. After 2 hours of depolymerisation, the produced liquid product was filtered. Aliphatic polyol was obtained in the range 9-49% according to molar ratio PU to reagent and reaction temperature. The obtained products had hydroxyl number in the range of 96-168 mg KOH/g.

3.7.SUMMARY OF SOLVOLYSIS

In Table 9 the specific characterisations of main solvolysis processes for PET, PU, PC are shown. The processes are described by conditions, obtained products and yield.

Table 9. Summary of solvolysis process for specific polymers, namely PET, PU, PC, PA and PLA/PLLA.

Polymer waste	**Characteristic**	**Hydrolysis**	**Glycolysis**	**Alcoholysis**	**Methanolysis**	**Aminolysis**	**References**
	Agent:	Water, steam	Glycols: BDO, EG, DEG, PG, DPG, TED	Alcohols: ethanol, butanol, pentaerythrol, isooctyl alcohol	Methanol	Amines: methylamine, ethanolamine, MEA, DEA, TEA, hydrazine monohydrate	
PET	*Conditions:*	T: <200-250 °C in acid environment T: 70-100 °C in alkaline environment T: 200-300 °C in neutral environment p: 1- 4 MPa	T: 180-240 °C p:0.1-0.6 MPa t: 0.5-8 h	T: 300 °C Sub- and supercritical conditions	T: 180-280 °C p: 2-4 MPa	T: 170-220 °C P: 2 MPa	(Sinha et al. 2010; Al-Sabagh et al. 2015)
	Products:	TPA, sodium or potassium terephthalate, EG	BHET, DMT, EG	DOTP,EG	DMT, EG	BHETA, N, N'-bisallyl terephthalamide,	
	Yield:	70-100%	85-99%	95-100%	65-90%	75%	
	Notes:	Long time High pressure	In supercritical conditions high yield	Long time	In supercritical conditions high efficiency	microwave reduced of aminolysis time	
PU	*Conditions:*	T: 200 - 340 °C p: high	T: 180-220 °C	T: 170 °C	T: 160-300 °C p: 15 MPa Sub- and	T:180 °C	(Zia et al. 2007; Datta and Rohn 2007b)

					supercritical conditions		
	Products:	Polyols, amine intermediates, toluene diamines	Polyols, aromatic carbamates, ureas, amines	Polyol, amine	4,4’-methylene diphenyl carbamate, DMA, MDC, BDO, amines, THF	Polyol, aromatic amines, DETA, MDA	
	Yield:	70-90%	80-95%		App. 95%		
	Notes:	Too high temperature gives a decrease in useful polyol recovery					
PC	*Conditions:*	T: 200-250 ºC Microwave irradiation; Sub- and supercritical conditions	T: 160-200 ºC Microwave irradiation	T: 200 ºC	T: 170-300 ºC Sub- and supercritical conditions In ionic liquids	T: 100 ºC	(Nikje 2011; Antonakou and Achilias 2013)
	Products:	BPA, phenol	monohydroxyethyl ether, bishydroxyethyl ether, ethylene carbonate	BPA, DEC	BPA, DMC, phenol, 4-tertbutylphenol	BPA, DMDEA	
	Yield:	80-100%	50-80%	90%	90-95%	Over 80%	

	Notes:	Catalyst decrease reaction temperature	Recovery yields increased with increasing reaction times and catalyst concentration		In ionic liquids lower reaction temperature	
PA	*Conditions:*	T: >300 ^{o}C Sub- and supercritical conditions	T: 250-275^{o}C			(Kim et al. 2006; Goto 2009)
	Products:	ε –caprolactam, ε-aminocaproic acid	β-hydroxyethylester,bis(β-ydroxyethyl) hexanoate, δ-valerolactone			
	Yield:	Over 78-90%				
	Notes:	Accelerate with catalyst				
PLA/ PLLA	*Conditions:*	T: 180-350 ^{o}C Sub- and supercritical conditions		T: 130-210 ^{o}C Microwave irradiation	T: 115 ^{o}C In ionic liquids	(Hirao et al. 2010; Song et al. 2013)
	Products:	L-lactic acid			Methyl lactate	
	Yield:	Depend on			88-89%	

	temperature
Notes:	

The most appropriate decomposition process for PU and PET is glycolysis, because the reaction gives high yields and does not require very special conditions (high pressure is not required) like in hydrolysis. The depolymerisation agents are glycols. For polycarbonate mostly the sub- and supercritical conditions are required. Very efficient way to PC decompose is methanolysis in such conditions. Very quick depolymerisation occurs due to using ionic liquids, which can shorten the required time of process.

4. CONCLUSIONS

Chemical recycling can be classified into recycling to fuels, monomers or industrial chemicals. During these processes, polymeric waste can be converted into valuable resources, such as useful chemical substances or compounds, by thermal or catalytic processes. Methods for feedstock recycling of plastic waste can be summed up into the following categories: thermo-chemical and chemical processes. To thermo-chemical methods are included: pyrolysis (plastic waste are decomposed by the effect of heat in an inert atmosphere), catalytic cracking (the polymer chains are broken down by the effect of catalyst, which promotes cleavage reactions), gasification (plastic waste reacts with oxygen and/or steam to produce synthesis gas (CO and H_2), hydrogenation (the polymers are degraded by the combined action of heat, hydrogen and in many cases catalysts). Chemical processes include chemical depolymerisations, such as glycolysis, hydrolysis, aminolysis, where plastic waste reacts with certain agents to yield monomers. Products from tertiary recycling may be used in the production of new polymers, refined chemicals or fuels.

According to researchers works, it is known, that through chemical recycling of polymer materials, the useful substances, such as gasoline, chemicals or monomers can be obtained. Feedstock recycling should be further developed and improved in order to reduce the amounts of waste in landfills and to save the natural resources. H&S Anlagentechnik

(Sulingen, Germany) made steps in this direction, which developed equipment and processing technologies for the chemical recycling of polyurethane and PET waste. This can cause to popularise feedstock recycling instead of using landfills or waste incineration.

The next steps of chemical recycling will be searching new ways or new decomposing agents like proposed in the work of Beneš et al. (2012b). They used castor oil and fish oil for polyurethane decomposition. Probably researchers will focus on natural or renewable resources as decomposing agents. Also the efficiency of the processes will be developed to obtain high yield of valuable products (monomers, fuels) in lighter conditions (lower temperature and pressure), to save energy. For this application, the ionic liquids seem to be good solution. Ionic liquids can be used in the process several times (even up to 8), these shorten needed reaction time and gave high yield products (Liu et al. 2013c).

References

Abdelaal MY, Sobahi TR, Makki MSI (2011) Chemical transformation of pet waste through glycolysis. Constr Build Mater 25:3267–3271. doi: 10.1016/j.conbuildmat.2011.03.013

Achilias D, Karayannidis G (2004) The chemical recycling of PET in the framework of sustainable development. Water, Air, Soil Pollut Focus 4:385–396. doi: 10.1023/B:WAFO.0000044812.47185.0f

Achilias DS (2007) Chemical recycling of poly(methyl methacrylate) by pyrolysis. Potential use of the liquid fraction as a raw material for the reproduction of the polymer. Eur Polym J 43:2564–2575. doi: 10.1016/j.eurpolymj.2007.02.044

Achilias DS, Andriotis L, Koutsidis IA, et al (2012) Recent Advances in the Chemical Recycling of Polymers (PP, PS, LDPE, HDPE, PVC, PC, Nylon, PMMA). In: Achilias DS (ed) Material Recycling - Trends and Perspectives. InTech, pp 1–63

Achilias DS, Antonakou EV, Koutsokosta E, Lappas AA (2009) Chemical Recycling of Polymers from Waste Electric and Electronic Equipment. J Appl Polym Sci 114:212–221. doi: 10.1002/app.30533

Achilias DS, Roupakias C, Megalokonomos P, et al (2007) Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP). J Hazard Mater 149:536–542. doi: 10.1016/j.jhazmat.2007.06.076

Achilias DS, Tsintzou GP, Nikolaidis AK, et al (2011) Aminolytic depolymerization of poly(ethylene terephthalate) waste in a microwave reactor. Polym Int 60:500–506. doi: 10.1002/pi.2976

Aguado A, Martínez L, Becerra L, et al (2014) Chemical depolymerisation of PET complex waste: hydrolysis vs. glycolysis. J Mater Cycles Waste Manag 16:201–210. doi: 10.1007/s10163-013-0177-y

Aguado J, Serrano DP, Escola JM, Peral a. (2009) Catalytic cracking of polyethylene over zeolite mordenite with enhanced textural properties. J Anal Appl Pyrolysis 85:352–358. doi: 10.1016/j.jaap.2008.10.009

Akpanudoh NS, Gobin K, Manos G (2005) Catalytic degradation of plastic waste to liquid fuel over commercial cracking catalysts: Effect of polymer to catalyst ratio/acidity content. J Mol Catal A Chem 235:67–73. doi: 10.1016/j.molcata.2005.03.009

Al-Sabagh AM, Yehia FZ, Eissa AMF, et al (2014) Cu- and Zn-acetate-containing ionic liquids as catalysts for the glycolysis of poly(ethylene terephthalate). Polym Degrad Stab 110:364–377. doi: http://dx.doi.org/10.1016/j.polymdegradstab.2014.10.005

Al-Sabagh AM, Yehia FZ, Eshaq G, et al (2015) Greener routes for recycling of polyethylene terephthalate. Egypt J Pet. doi: 10.1016/j.ejpe.2015.03.001

Al-Salem SM, Lettieri P, Baeyens J (2009) Recycling and recovery routes of plastic solid waste (PSW): A review. Waste Manag 29:2625–2643. doi: 10.1016/j.wasman.2009.06.004

Al-Salem SM, Lettieri P, Baeyens J (2010) The valorization of plastic solid waste (PSW) by primary to quaternary routes: From re-use to energy and chemicals. Prog Energy Combust Sci 36:103–129. doi: 10.1016/j.pecs.2009.09.001

Antonakou E V., Achilias DS (2013) Recent advances in polycarbonate recycling: A review of degradation methods and their mechanisms. Waste and Biomass Valorization 4:9–21. doi: 10.1007/s12649-012-9159-x

Arena U, Di Gregorio F (2014) Energy generation by air gasification of two industrial plastic wastes in a pilot scale fluidized bed reactor. Energy 68:735–743. doi: 10.1016/j.energy.2014.01.084

Asahi N, Sakai K, Kumagai N, et al (2004) Methanolysis investigation of commercially available polyurethane foam. Polym Degrad Stab 86:147–151. doi: 10.1016/j.polymdegradstab.2004.04.002

Aznar MP, Caballero M a., Sancho J a., Francés E (2006) Plastic waste elimination by co-gasification with coal and biomass in fluidized bed with air in pilot plant. Fuel Process Technol 87:409–420. doi: 10.1016/j.fuproc.2005.09.006

Beneš H, Černá R, Ďuračková A, Látalová P (2012a) Utilization of Natural Oils for Decomposition of Polyurethanes. J Polym Environ 20:175–185. doi: 10.1007/s10924-011-0339-8

Beneš H, Vlček T, Černá R, et al (2012b) Polyurethanes with bio-based and recycled components. Eur J Lipid Sci Technol 114:71–83. doi: 10.1002/ejlt.201000123

Błędzki AK (1997) Recycling of polymeric materials. WNT, Warszawa

Borda J, Pásztor G, Zsuga M (2000) Glycolysis of polyurethane foams and elastomers. Polym Degrad Stab 68:419–422. doi: 10.1016/S0141-3910(00)00030-6

Buekens AG, Schoeters JG (1998) Technical Methods in Plastics Pyrolysis. Macromol Symp 135:63–81. doi: 10.1002/masy.19981350110

Butler E, Devlin G, McDonnell K (2011) Waste polyolefins to liquid fuels via pyrolysis: Review of commercial state-of-the-art and recent laboratory research. Waste and Biomass Valorization 2:227–255. doi: 10.1007/s12649-011-9067-5

Chiu S, Tsai C, Chang Y (2008) Monomer recovery from polycarbonate by methanolysis. e-Polymers 1–13.

Chuayjuljit S, Norakankorn C, Pimpan V (2002) Chemical Recycling of Rigid Polyurethane Foam Scrap via Base Catalyzed Aminolysis. J Met Mater Miner 12:19–22.

Colomines G, Robin JJ, Tersac G (2005) Study of the glycolysis of PET by oligoesters. Polymer (Guildf) 46:3230–3247. doi: 10.1016/j.polymer.2005.02.047

Cui J, Forssberg E (2003) Mechanical recycling of waste electric and electronic equipment: A review. J Hazard Mater 99:243–263. doi: 10.1016/S0304-3894(03)00061-X

Czupryński B, Liszkowska J, Paciorek-Sadowska J, et al (2010) Recykling surowcowy sztywnych pianek poliuretanowo-poliizocyjanurowych. Inżynieria i Apar Chem 49:33–34.

Datta J (2012a) Effect of glycols used as glycolysis agents on chemical structure and thermal stability of the produced glycolysates. J Therm Anal Calorim 109:517–520. doi: 10.1007/s10973-012-2530-0

Datta J (2012b) Glikoliza poliuretanów. Wydawnictwo Politechniki Gdańskiej, Gdańsk

Datta J, Kacprzyk M (2008) Thermal analysis and static strength of polyurethanes obtained from glycolysates. J Therm Anal Calorim 93:753–757. doi: 10.1007/s10973-008-9140-x

Datta J, Pasternak S (2005) Oligourethane glycols obtained in glycolysis of polyurethane foam as semi-finiszed products for cast urethane elastomers preparation. Polimery 50:352–357.

Datta J, Pniewska K (2008) Syntheses and properties of polyurethanes got from glycolysis products obtained from wadte polyurethane foams. Polimery 53:27–32.

Datta J, Rohn M (2007a) Thermal properties of polyurethanes synthesized using waste polyurethane foam glycolysates. J Therm Anal Calorim 88:437–440. doi: 10.1007/s10973-006-8041-0

Datta J, Rohn M (2007b) Glycolysis of polyurethane wastes. Part I. Glycolysis agents and catalysts. Polimery 52:579–582.

Datta J, Rohn M (2007c) Glycolysis of polyurethane wastes. Part II. Purification and use of glycolysis products. Polimery 52:625–710.

Datta J, Rohn M (2008) Structure, thermal stability and mechanical properties of polyurethanes based on glycolysate from polyurethane foam waste, prepared with use of 1,6-hexanediol as a glycol. Polimery 53:871–875.

De La Puente G, Klocker C, Sedran U (2002) Conversion of waste plastics into fuels recycling polyethylene in FCC. Appl Catal B Environ 36:279–285. doi: 10.1016/S0926-3373(01)00287-9

Deirram N, Rahmat AR (2012) Hydrolysis Degradation of Polycarbonate Using Different

Co–solvent Under Microwave Irradiation. APCBEE Procedia 3:172–176. doi: 10.1016/j.apcbee.2012.06.065

Ding J, Chen J, Ji Y, et al (2014) Kinetics of alcoholysis of poly(ethylene terephthalate) in sub- and super-critical isooctyl alcohol to produce dioctyl terephthalate. J Anal Appl Pyrolysis 106:99–103. doi: 10.1016/j.jaap.2014.01.005

Duch MW, Allgeier AM (2007) Deactivation of nitrile hydrogenation catalysts: New mechanistic insight from a nylon recycle process. Appl Catal A Gen 318:190–198. doi: 10.1016/j.apcata.2006.11.003

Durmuş A, Naci Koç S, Selda Pozan G, Kaşgöz A (2005) Thermal-catalytic degradation kinetics of polypropylene over BEA, ZSM-5 and MOR zeolites. Appl Catal B Environ 61:316–322. doi: 10.1016/j.apcatb.2005.06.009

Ekart MP, Murdoch WS, Pell TM (2002) United States Patent. 1–5.

El-hameed RSA (2011) Aminolysis of polyethylene terephthalate waste as corrosion inhibitor for carbon steel in HCl corrosive medium. Adv Appl Sci Res 2:483–499.

Elsaeed SM, Farag RK (2009) Synthesis, Characterization, and Chemical Degradation of Segmented Polyurethanes with Butylamine for Chemical Recycling. J Appl Polym Sci 112:3327–3336. doi: 10.1002/app.29527

European Parliament and Council of the European Union (2008) Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives. Off J Eur Union L 312:1–30. doi: 2008/98/EC.; 32008L0098

Garforth A a., Ali S, Hernández-Martínez J, Akah A (2004) Feedstock recycling of polymer wastes. Curr Opin Solid State Mater Sci 8:419–425. doi: 10.1016/j.cossms.2005.04.003

Głowińska E, Włoch M (2014) Rheology of glycolyzates produced by conversion of polyetherurethane wastes. Przem Chem 93:1308–1310. doi: dx.medra.org/10.12916/przemchem.2014.1308

Gobin K, Manos G (2004) Polymer degradation to fuels over microporous catalysts as a novel tertiary plastic recycling method. Polym Degrad Stab 83:267–279. doi: 10.1016/S0141-3910(03)00272-6

Goto J, Santorelli M (2010) Recycling. In: Pilato L (ed) Phenolic Resins: A Century of Progress. Springer Berlin Heidelberg, pp 517–524

Goto M (2009) Chemical recycling of plastics using sub- and supercritical fluids. J Supercrit Fluids 47:500–507. doi: 10.1016/j.supflu.2008.10.011

Goto M, Sasaki M, Hirose T (2006) Reactions of polymers in supercritical fluids for chemical recycling of waste plastics. J Mater Sci 41:1509–1515. doi: 10.1007/s10853-006-4615-2

Grause G, Buekens A, Sakata Y, et al (2011) Feedstock recycling of waste polymeric material. J Mater Cycles Waste Manag 13:265–282. doi: 10.1007/s10163-011-0031-z

Güçlü G, Yalçınyuva T, Özgümüş S, Orbay M (2003) Simultaneous glycolysis and hydrolysis of polyethylene terephthalate and characterization of products by differential scanning calorimetry. Polymer (Guildf) 44:7609–7616. doi: 10.1016/j.polymer.2003.09.062

Hájeková E, Bajus M (2005) Recycling of low-density polyethylene and polypropylene via copyrolysis of polyalkene oil/waxes with naphtha: product distribution and coke formation. J Anal Appl Pyrolysis 74:270–281. doi: http://dx.doi.org/10.1016/j.jaap.2004.11.016

Hamad K, Kaseem M, Deri F (2013) Recycling of waste from polymer materials: An overview of the recent works. Polym Degrad Stab 98:2801–2812. doi: 10.1016/j.polymdegradstab.2013.09.025

Hata S, Goto H, Yamada E, Oku A (2002) Chemical conversion of poly(carbonate) to 1,3-dimethyl-2-imidazolidinone (DMI) and bisphenol A: a practical approach to the chemical recycling of plastic wastes. Polymer (Guildf) 43:2109–2116. doi: 10.1016/S0032-3861(01)00800-X

Heidari S, Tahvildari K (2013) Preparation and Characterization of Diols and Polyols Based on Aminolysis of Poly (ethylene terephthalate) Wastes with Alkanolamines. J Appl Chem Res 7:33–42.

Hirao K, Nakatsuchi Y, Ohara H (2010) Alcoholysis of Poly(l-lactic acid) under microwave irradiation. Polym Degrad Stab 95:925–928. doi: 10.1016/j.polymdegradstab.2010.03.027

Hoang CN, Dang YH (2013) Aminolysis of poly(ethylene terephthalate) waste with ethylenediamine and characterization of a,u-diamine products. Polym Degrad Stab 98:697–708. doi: 10.1016/j.polymdegradstab.2012.12.026

Hodzic A (2004) Re-use, recycling and degradation of composites. In: Baillie C (ed) Green Composites: Polymer Composites and the Environment. Woodhead Publishing, pp 252–271

Hu L, Oku A, Yamada E (1998) Alkali-catalyzed methanolysis of polycarbonate. A study on recycling of bisphenol A and dimethyl carbonate. Polymer (Guildf) 39:3841–3845. doi: 10.1016/S0032-3861(97)10298-1

Imran M, Kim BK, Han M, et al (2010) Sub-and supercritical glycolysis of polyethylene terephthalate (PET) into the monomer bis(2-hydroxyethyl) terephthalate (BHET). Polym

Degrad Stab 95:1685–1693. doi: 10.1016/j.polymdegradstab.2010.05.026

Jain A, Soni RK (2007) Spectroscopic investigation of end products obtained by ammonolysis of poly (ethylene terephthalate) waste in the presence of zinc acetate as a catalyst. J Polym Res 14:475–481. doi: 10.1007/s10965-007-9131-9

Johnson OB (1977) Method for continuous hydrolysis of polyurethane foam in restricted tubular reaction zone and recovery.

Jung SH, Kim SJ, Kim JS (2013) The influence of reaction parameters on characteristics of pyrolysis oils from waste high impact polystyrene and acrylonitrile-butadiene-styrene using a fluidized bed reactor. Fuel Process Technol 116:123–129. doi: 10.1016/j.fuproc.2013.05.004

Kaminsky W, Predel M, Sadiki A (2004) Feedstock recycling of polymers by pyrolysis in a fluidised bed. Polym Degrad Stab 85:1045–1050. doi: 10.1016/j.polymdegradstab.2003.05.002

Kamo T, Wu B, Egami Y, et al (2011) Influence of mixed molten carbonate composition on hydrogen formation by steam gasification. J Mater Cycles Waste Manag 13:50–55. doi: 10.1007/s10163-010-0307-8

Karayannidis GP, Achilias DS (2007) Chemical Recycling of Poly(ethylene terephthalate). Macromol Mater Eng 292:128–146. doi: 10.1002/mame.200600341

Karayannidis GP, Achilias DS, Sideridou ID, Bikiaris DN (2005) Alkyd resins derived from glycolized waste poly(ethylene terephthalate). Eur Polym J 41:201–210. doi: 10.1016/j.eurpolymj.2004.10.001

Kim J-W, Mun T-Y, Kim J-O, Kim J-S (2011) Air gasification of mixed plastic wastes using a two-stage gasifier for the production of producer gas with low tar and a high caloric value. Fuel 90:2266–2272. doi: 10.1016/j.fuel.2011.02.021

Kim KJ, Dhevi DM, Lee JS, et al (2006) Mechanism of glycolysis of nylon 6,6 and its model compound by ethylene glycol. Polym Degrad Stab 91:1545–1555. doi: 10.1016/j.polymdegradstab.2005.09.019

Kishimoto Y, Kajihara T, Kato S (1999) Study on the alcoholysis of aromatic polyesters and related esters using a high-pressure calorimeter. Polym Bull 300:295–300. doi: 10.1007/s002890050466

Kurokawa H, Ohshima M, Sugiyama K, Miura H (2003) Methanolysis of polyethylene terephthalate (PET) in the presence of aluminium tiisopropoxide catalyst to form dimethyl terephthalate and ethylene glycol. Polym Degrad Stab 79:529–533. doi: http://dx.doi.org/10.1016/S0141-3910(02)00370-1

Lettieri P, Al-Salem SM (2011) Thermomechanical treatment of plastic solid waste. In: Letcher TM, Vallero DA (eds) Waste: A Handbook for Management. Academic Press, pp 234–242

Lin YH, Yang MH (2005) Catalytic reactions of post-consumer polymer waste over fluidised cracking catalysts for producing hydrocarbons. J Mol Catal A Chem 231:113–122. doi: 10.1016/j.molcata.2005.01.003

Liu F, Chen J, Li Z, et al (2013a) Alcoholysis of poly(ethylene terephthalate) to produce dioctyl terephthalate with sub- and super-critical isooctyl alcohol. J Anal Appl Pyrolysis 99:16–22. doi: doi:10.1016/j.jaap.2012.11.008

Liu F, Li Z, Yu S, et al (2010) Environmentally benign methanolysis of polycarbonate to recover bisphenol A and dimethyl carbonate in ionic liquids. J Hazard Mater 174:872–

875. doi: 10.1016/j.jhazmat.2009.09.007

Liu F-S, Li Z, Yu S-T, et al (2009) Methanolysis and Hydrolysis of Polycarbonate Under Moderate Conditions. J Polym Environ 17:208–211. doi: 10.1007/s10924-009-0140-0

Liu L, Tang L, Wu Y, et al (2013b) Degradation process investigation of thermoplastic polyurethane elastomer in supercritical methanol. Polym Degrad Stab 98:2520–2528. doi: 10.1016/j.polymdegradstab.2013.09.010

Liu S, Wang Z, Li L, et al (2013c) Butanol alcoholysis reaction of polyethylene terephthalate using acidic ionic liquid as catalyst. J Appl Polym Sci 130:1840–1844. doi: 10.1002/app.39246

Liu S, Zhou L, Li L, et al (2013d) Isooctanol alcoholysis of waste polyethylene terephthalate in acidic ionic liquid. J Polym Res 20:310. doi: 10.1007/s10965-013-0310-6

López-Fonseca R, Duque-Ingunza I, de Rivas B, et al (2010) Chemical recycling of post-consumer PET wastes by glycolysis in the presence of metal salts. Polym Degrad Stab 95:1022–1028. doi: 10.1016/j.polymdegradstab.2010.03.007

López-Fonseca R, Duque-Ingunza I, de Rivas B, et al (2011) Kinetics of catalytic glycolysis of PET wastes with sodium carbonate. Chem Eng J 168:312–320. doi: 10.1016/j.cej.2011.01.031

Mahoney LR (1980) Ammonia, diamine and polymer recovery.

Mahoney LR, Weiner SA, Ferris FC (1974) Hydrolysis of Polyurethane Foam Waste. Environ Sci Technol 8:135–139. doi: 10.1021/es60087a010

Maier C, Calafut T (1998) Recycling. In: Polypropylene:The Definitive User’s Guide and Databook. Elsevier, Norwich, pp 75–78

Mansour S., Ikladious N. (2002) Depolymerization of poly(ethylene terephthalate) wastes using 1,4-butanediol and triethylene glycol. Polym Test 21:497–505. doi: 10.1016/S0142-9418(01)00115-5

Meissner E, Wróblewska A, Milchert E (2004) Technological parameters of pyrolysis of waste polytetrafluoroethylene. Polym Degrad Stab 83:163–172. doi: 10.1016/S0141-3910(03)00259-3

Mendes LC, Dias ML, Rodrigues TC (2011) Chemical Recycling of PET Waste with Multifunctional Pentaerythrytol in the Melt State. J Polym Environ 19:254–262. doi: 10.1007/s10924-010-0276-y

Michaud J-C, Farrant L, Jan O, et al (2010) Environmental benefits of recycling - 2010 update.

Mishra S, Goje a?S (2003) Kinetic and thermodynamic study of methanolysis of poly(ethylene terephthalate) waste powder. Polym Int 52:337–342. doi: 10.1002/pi.1147

Molero C, de Lucas A, Rodríguez JF (2009a) Activities of octoate salts as novel catalysts for the transesterification of flexible polyurethane foams with diethylene glycol. Polym Degrad Stab 94:533–539. doi: 10.1016/j.polymdegradstab.2009.01.021

Molero C, de Lucas A, Rodríguez JF (2008) Recovery of polyols from flexible polyurethane foam by “split-phase” glycolysis: Study on the influence of reaction parameters. Polym Degrad Stab 93:353–361. doi: 10.1016/j.polymdegradstab.2007.11.026

Molero C, de Lucas A, Rodríguez JF (2009b) Glycolysis of flexible polyurethane wastes using stannous octoate as the catalyst. J Mater Cycles Waste Manag 11:130–132. doi: 10.1007/s10163-008-0224-2

Mormann W, Frank P (2006) (Supercritical) Ammonia for Recycling of Thermoset Polymers. Macromol Symp 242:165–173. doi: 10.1002/masy.200651024

Nikje MMA (2011) Glycolysis of polycarbonate wastes with microwave irradiation. Polimery/Polymers 56:381–384.

Nikje MMA, Garmarudi AB (2010) Ive. Iran Polym J 19:287–295.

Nikje MMA, Mohammadi FHA (2009) Sorbitol/glycerin/water ternary system as a novel glycolysis agent for flexible polyurethane foam in the chemical recycling using microvawe radiation. Polimery 54:541–545.

Nikje MMA, Nikrah M (2007) Glycerin as a new glycolysing agent for chemical recycling of cold cure polyurethane foam wastes in “split-phase” condition. Polym Bull 58:411–423. doi: 10.1007/s00289-006-0683-3

Nikje MMA, Nikrah M, Haghshenas M (2007) Microwave Assisted “Split-phase” Glycolysis of Polyurethane Flexible Foam Wastes. Polym Bull 59:91–104. doi: 10.1007/s00289-007-0753-1

Nikles DE, Farahat MS (2005) New motivation for the depolymerization products derived from poly(ethylene terephthalate) (PET) waste: A review. Macromol Mater Eng 290:13–30. doi: 10.1002/mame.200400186

Panda AK, Singh R (2011) Catalytic performances of kaoline and silica alumina in the thermal degradation of polypropylene. J Fuel Chem Technol 39:198–202. doi: 10.1016/S1872-5813(11)60017-0

Parab YS, Pingale ND, Shukla SR (2012) Aminolytic depolymerization of poly (ethylene terephthalate) bottle waste by conventional and microwave irradiation heating. J Appl

Polym Sci 125:1103–1107. doi: 10.1002/app.34855

Pardal F, Tersac G (2006) Comparative reactivity of glycols in PET glycolysis. Polym Degrad Stab 91:2567–2578. doi: 10.1016/j.polymdegradstab.2006.05.016

Partini M, Pantani R (2007) FTIR analysis of hydrolysis in aliphatic polyesters. Polym Degrad Stab 92:1491–1497. doi: 10.1016/j.polymdegradstab.2007.05.009

Paszun D, Spychaj T (1997) Chemical Recycling of Poly(ethylene terephthalate). Ind Eng Chem Res 36:1373–1383. doi: 10.1021/ie960563c

Piemonte V, Sabatini S, Gironi F (2013) Chemical Recycling of PLA: A Great Opportunity Towards the Sustainable Development? J Polym Environ 21:640–647. doi: 10.1007/s10924-013-0608-9

Pingale ND, Shukla SR (2009) Microwave-assisted aminolytic depolymerization of PET waste. Eur Polym J 45:2695–2700. doi: 10.1016/j.eurpolymj.2009.05.028

Plastics Europe (2009) The Compelling Facts About Plastics 2009: An analysis of European plastics production, demand and recovery for 2008.

PlasticsEurope (2015) Plastics - the facts 2014/2015: An analysis of European plastics production, demand and waste data.

PlasticsEurope (2007) The Compelling Facts About Plastics:An analysis of plastics production, demand and recovery for 2005 in Europe.

PlasticsEurope (2008a) The Compelling Facts About Plastics: An analysis of plastics productions, demand and recovery for 2006 in Europe.

PlasticsEurope (2008b) The Compelling Facts About Plastics 2007: An analysis of plastics production, demand and recovery for 2007 in Europe.

PlasticsEurope (2010) Plastics - the facts 2010: An analysis of European plastics production, demand and recovery for 2009.

PlasticsEurope (2011) Plastics - the Facts 2011: An analysis of European plastics production , demand and recovery for 2010.

PlasticsEurope (2012) Plastics-the Facts 2012: An analysis of European plastics production , demand and waste data for 2011.

PlasticsEurope (2013) Plastics-The Facts 2013: An analysis of European latest plastics production, demand and waste data.

Pusztaszeri SF (1982) Method for recovery of therephtalic acid from polyester scrap. 1–5.

Sadegehi GMM, Shamsi R, Sayaf M (2011) From Aminolysis Product of PET Waste to Novel Biodegradable Polyurethanes. J Polym Environ 19:522–534. doi: 10.1007/s10924-011-0283-7

Sasse F, Emig G (1998) Chemical recycling of polymer materials. Chem Eng Technol 21:777–789. doi: 10.1002/(SICI)1521-4125(199810)21:10<777::AID-CEAT777>3.0.CO;2-L

Shah R V., Borude VS, Shukla SR (2013) Recycling of PET waste using 3-amino-1-propanol by conventional or microwave irradiation and synthesis of bis-oxazin there from. J Appl Polym Sci 127:323–328. doi: 10.1002/app.37900

Shah R V., Shukla SR (2012) Effective Aminolytic Depolymerization of Poly(ethylene terephthalate) Waste and Synthesis of Bisoxazoline Therefrom. J Appl Polym Sci 125:3666–3675. doi: 10.1002/app.36649

Shamsi R, Abdouss M, Sadeghi GMM, Taromi FA (2009) Synthesis and characterization of novel polyurethanes based on aminolysis of poly(ethylene terephthalate) wastes, and evaluation of their thermal and mechanical properties. Polym Int 58:22–30. doi: 10.1002/pi.2488

Simón D, Borreguero AM, de Lucas A, Rodríguez JF (2014) Glycolysis of flexible polyurethane wastes containing polymeric polyols. Polym Degrad Stab 109:115–121. doi: 10.1016/j.polymdegradstab.2014.07.009

Simón D, García MT, De Lucas A, et al (2013) Glycolysis of flexible polyurethane wastes using stannous octoate as the catalyst: Study on the influence of reaction parameters. Polym Degrad Stab 98:144–149. doi: 10.1016/j.polymdegradstab.2012.10.017

Sinha V, Patel MR, Patel J V. (2010) Pet Waste Management by Chemical Recycling: A Review. J Polym Environ 18:8–25. doi: 10.1007/s10924-008-0106-7

Song X, Wang H, Zheng X, et al (2014) Methanolysis of poly(lactic acid) using acidic functionalized ionic liquids as catalysts. J Appl Polym Sci 131:40817/1–40817/6. doi: 10.1002/app.40817

Song X, Zhang X, Wang H, et al (2013) Methanolysis of poly(lactic acid) (PLA) catalyzed by ionic liquids. Polym Degrad Stab 98:2760–2764. doi: 10.1016/j.polymdegradstab.2013.10.012

Tawfik ME, Eskander SB (2010) Chemical recycling of poly(ethylene terephthalate) waste using ethanolamine. Sorting of the end products. Polym Degrad Stab 95:187–194. doi: 10.1016/j.polymdegradstab.2009.11.026

Thompson RC, Swan SH, Moore CJ, vom Saal FS (2009) Our plastic age. Philos Trans R Soc Lond B Biol Sci 364:1973–1976. doi: 10.1098/rstb.2009.0054

Troev K, Grancharov G, Tsevi R, Tsekova A (2000) A novel approach to recycling of polyurethanes: chemical degradation of flexible polyurethane foams by triethyl phosphate. Polymer (Guildf) 41:7017–7022. doi: 10.1016/S0032-3861(00)00054-9

Tsintzou GP, Achilias DS (2013) Chemical recycling of polycarbonate based wastes using alkaline hydrolysis under microwave irradiation. Waste and Biomass Valorization 4:3–7. doi: 10.1007/s12649-012-9125-7

Tsuji H, Daimon H, Fujie K (2003) A new strategy for recycling and preparation of poly(L-lactic acid): hydrolysis in the melt. Biomacromolecules 4:835–40. doi: 10.1021/bm034060j

Tsuji T, Hatayama A (2009) Gasification of waste plastics by steam reforming in a fluidized bed. J Mater Cycles Waste Manag 11:144–147. doi: 10.1007/s10163-008-0227-z

Vasile C, Brebu MA, Karayildirim T, et al (2007) Feedstock recycling from plastics and thermosets fractions of used computers. II. Pyrolysis oil upgrading. Fuel 86:477–485. doi: 10.1016/j.fuel.2006.08.010

Wasielewski R, Piechaczek M (2009) Directions of waste plastics recovery in countries of European Union The. Arch Gospod Odpad i Ochr Środowiska 11:1–12.

Westerhout RWJ, Kuipers JAM, Swaaij WPM Van (1998) Experimental Determination of the Yield of Pyrolysis Products of Polyethene and Polypropene. Influence of Reaction Conditions. Ind Eng Chem Res 37:841–847. doi: 10.1021/ie970384a

Wilk V, Hofbauer H (2013a) Conversion of mixed plastic wastes in a dual fluidized bed steam gasifier. Fuel 107:787–799. doi: 10.1016/j.fuel.2013.01.068

Wilk V, Hofbauer H (2013b) Conversion of mixed plastic wastes in a dual fluidized bed steam gasifier. Fuel 107:787–799. doi: 10.1016/j.fuel.2013.01.068

Williams EA, Williams PT (1997) The pyrolysis of individual plastics and a plastic mixture in a fixed bed reactor. J Chem Technol Biotechnol 70:9–20. doi: 10.1002/(SICI)1097-4660(199709)70:1<9::AID-JCTB700>3.0.CO;2-E

Williams TGJL, Heidrich O, Sallis PJ (2010) A case study of the open-loop recycling of mixed plastic waste for use in a sports-field drainage system. Resour Conserv Recycl 55:118–128. doi: 10.1016/j.resconrec.2010.08.002

Wong SL, Ngadi N, Abdullah TAT, Inuwa IM (2015) Current state and future prospects of plastic waste as source of fuel: A review. Renew Sustain Energy Rev 50:1167–1180. doi: 10.1016/j.rser.2015.04.063

Wu C-H, Chang C-Y, Cheng C-M, Huang H-C (2003) Glycolysis of waste flexible polyurethane foam. Polym Degrad Stab 80:103–111. doi: 10.1016/S0141-3910(02)00390-7

Xi G, Lu M, Sun C (2005) Study on depolymerization of waste polyethylene terephthalate into monomer of bis(2-hydroxyethyl terephthalate). Polym Degrad Stab 87:117–120. doi: 10.1016/j.polymdegradstab.2004.07.017

Ylä-mella J (2005) Recycling of Polymers. Oulu

Yoshioka T, Sato T, Okuwaki A (1994) Hydrolysis of waste PET by sulfuric acid at 150°C for a chemical recycling. J Appl Polym Sci 52:1353–1355. doi: 10.1002/app.1994.070520919

Zhou C, Fang W, Xu W, et al (2014) Characteristics and the recovery potential of plastic wastes obtained from landfill mining. J Clean Prod 80:80–86. doi:

10.1016/j.jclepro.2014.05.083

Zia KM, Bhatti HN, Ahmad Bhatti I (2007) Methods for polyurethane and polyurethane composites, recycling and recovery: A review. React Funct Polym 67:675–692. doi: 10.1016/j.reactfunctpolym.2007.05.004