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Poly(bisphenol A carbonate) Recycling: High Pressure Hydrolysis Can Be a Convenient Way

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1. Introduction

Polycarbonates are polymers characterized by a carbonate group. Their molecular structure can be of various kinds depending on the unit (G) that is connected with the carbonate. Table 1 reports some of the most used polycarbonates.
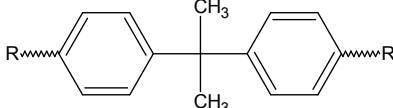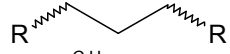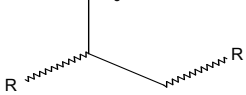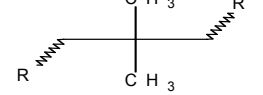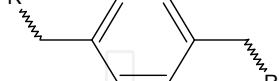
group G	Polymer name	
	Poly(bisphenol A)carbonate	BAPC
	Polytrimethylencarbonate	PTMC
	Polypropylencarbonate	PPC
	Polyneopentylencarbonate	PNPC
	Poly(p-xylilene)carbonate	PPXC

Table 1. most diffused polycarbonates.

Among them, the poly(bisphenol A) carbonate (PC in the following) is the most diffused. It is commonly referred as polycarbonate because of its vast number of industrial applications. It is a lightweight, high-quality plastic. It is well known and appreciated for its transparency, its excellent resistance to impact and its ability to withstand high temperature during the lifespan of the final article. Generally speaking, materials based on polycarbonates are resistant, rigid till 140°C and not fragile under –20°C. They are amorphous and have excellent mechanical properties and dimensional stability. Some restrictions in their use consist in a limited resistance to chemicals and to scrapes, and to color changes after exposition to UV ray. These problems can be solved by means of the proper additives or making use of mechanical mixing with other polymers. The main physical properties are resumed in table 2.

Physical properties		
Traction resistance	70-80	N/mm²
Impact resistance	60-80	kJ/m²
Maximum temperature	125	°C
Density	1.2	g/cm³

Table 2. PC physical properties.

PC also shows a high limiting oxygen index (LOI=27), and can produce a large amount of char on combustion conditions. PC is widely used in mixture with other polymers with the aim of enhancing resistance to external factors. Typical mixtures include PC with poly(butylene-terephthalate) or with ABS. These latter exhibit effective flame retardant properties upon the addition of conventional halogen and/or non halogen flame retardant agents, and this supports their large use in electrical appliances. Its properties make it appropriate for durable goods applications. PC is used in the construction of many everyday products, including CDs and DVDs, dinnerware, computer casings, medical equipments, bicycle helmets, automotive parts, packaging, sports and optical materials. Other applications are for paintings and covertures of buildings.

Two industrially significant syntheses for PC are mainly adopted. They were developed in 1960s . The first one was developed by Bayer in 1962 and consists in a two phase reaction (Schnell et al., 1962). In this process bisphenol A (BPA) is added first to the reactor in methylene chloride (with a monohydroxylic phenol to control molecular weight). Subsequently, phosgene is added to the reactor, along with aqueous sodium hydroxide (HCl scavenger), to produce a biphasic liquid-liquid system. This process allows obtaining high molecular weight polymer with excellent optical clarity and color. Major disadvantage is the use of phosgene and the generation of a large amount of wastewater and methylene chloride to be treated or disposed. The second process, developed by GE in 1964, is a melt transesterification between diphenil carbonate and BPA (Fox, 1964a, Fox 1964b). This results in intermediate molecular weight product with phenol as a condensation byproduct. This route is solvent free and avoids the direct use of phosgene. The high viscosity of the melt limits however the final molecular weight of the polymer.

According to the research "Polycarbonate: 2009 World Market Outlook and Forecast" (http://www.reportlinker.com) the PC market has been shown in not favourable perspectives in recent times. In facts the application of PC in optical media segment shrank as a result of lower demand for CDs and DVDs. Moreover a health concern raised over Bisphenol A (BPA) has negatively influenced the demand as well. PC could disappear from the food and beverage container market in the future. Notwithstanding, the global demand is expected to grow of 6-7% annually, driven by Asia and China in particular (2.4 Mt were produced in 2004). Demand would catch up with production capacity and the market would strengthen. This fact suggests that PC recycling will cover in the future more and more importance. It is therefore necessary to optimize and develop processes for PC wastes treatment. Because it is not a suitable alternative for waste treatment to landfill or incinerate wasted PC products, it is important to find resourceful recycling processes both for environmental protection and for economical benefits purposes. PC recycling can be performed in three main different ways: direct recycle (mechanical recycling or blending with other materials), pyrolysis and chemical treatment.

Mechanically recycled PC is less resilient, because it has decreased impact resistance when compared with newly manufactured polycarbonate. The addition of fillers and pigments can also decrease the plastic's resilience. This problem can be addressed by blending with other materials to modify impact resistance in recycled polycarbonate (Elmaghor et al., 2004).

Thermal degradation or pyrolysis is intrinsically characterized by a low selectivity. This is due to the prevailing radical mechanism of the thermal decomposition that is substantially acting randomly over the backbone of the polymer macromolecules and over the obtained monomer, then producing their further degradation. It is well known that in this kind of radical reactions, all the H active positions can be attacked by metathetical transfer reaction of H and then giving place to different products. Moreover additive reactions can occur on aromatic rings, producing more and more condensed molecules, which are char precursors. Of course, the most active H positions are those of the two methyl groups. It is worthwhile to mention that these kind of attacks are active also on the formed BPA. Moreover the simultaneous crosslinking elementary process, and polycondensation reactions on aromatic rings, give place to the formation of char precursors. These aspects make the simple thermal degradation a not particularly suitable process because of the low selectivity in restoring monomer and the large amount of byproducts.

Several studies of possible depolymerization processes, based on the use of chemicals, have been reported in the literature for decomposing PC to its original monomer, BPA. They are based, for instance, on the use of solvent systems (Pan et al., 2006; Piñero et al., 2005) such as methylene chloride with ammonia, phenol in combination with an alkali catalyst, or via trans-esterification (alcoholysis) in super- or sub- critical conditions. These processes can require a complicate product separation in addition with environmental safety problems related to the use of more or less toxic organic solvents. Also decomposition of PC in sub- and super- critical water has been taken into account by Tagaya et al. (1999).

The chapter firstly resumes and shortly analyzes most of the proposed processes. Then, the results obtained by adopting a PC recycling process based on hydrolysis using subcritical liquid water are reported (Bozzano et al., 2010). In this study both pure PC and CDs wastes are used. The driving concept came from an analogy with the fats hydrolysis producing fatty acids and glycerol in the soap production field or with the hydrolysis of oils (see for instance Khuwijitjaru et al., 2004 and Pinto & Lanças, 2006;). A concerted path de-polymerization mechanism is proposed. A characterization of the process kinetics is presented and compared with lab-scale experimental data. The results show that this process can be a valuable alternative for BPA recovery mainly for its simplicity and absence of toxic agents or non-desired byproducts. It is of interest to mention that similar hydrolysis mechanisms can take place in other fields, like for instance the production of bio-oils from biomasses.

2. Pyrolysis of poly(bisphenol A carbonate)

Pyrolysis is a thermal process taking place typically in the temperature range of 300-1000°C in absence of oxygen. It decomposes organic molecules in gaseous and carbonaceous products. After cooling, the vapors give place to condensed mixtures (the so called tars). Uncondensed products are typically CO, H_2, CH_4 and other hydrocarbons with low

molecular weight. The ratio among solid, liquid and gaseous products depends on the pyrolysis conditions in terms of temperatures and residence times. As mentioned before, pyrolysis is one of possible routes for PC recycling (Jang & Wilkie, 2004). The idea is to transform plastic wastes to fuels or valuable products. Several papers related to the study of PC degradation are reported into the literature (Day et al., 1999; McNeil & Rinchon, 1991; McNeil & Basan, 1993; Montaudo & Puglisi, 1992; Montaudo et al., 2002; Oba et al., 2000; Puglisi et al., 1999). Also the pyrolysis in presence of active catalysts has been studied (Ali et al., 2002; Chiu et al., 2006). Figure 1 shows some thermogravimetries of PC from three different research groups. Decomposition occurs in the temperature range of about 300-500°C. The remaining residue is in the range of 20-30 wt%.
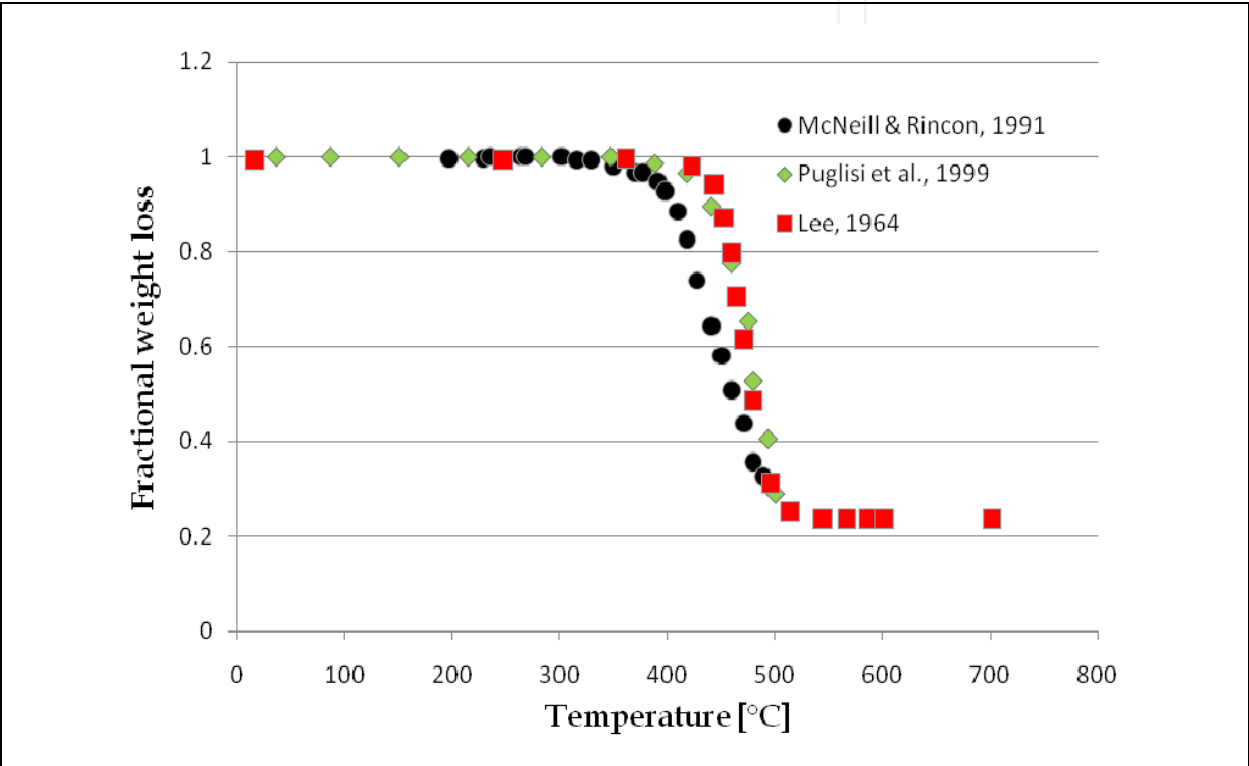

Fig. 1. fractional weight loss during thermal degradation of PC.

At 360°C, gas fraction is composed (wt%) by: 95% CO_2, 3% CO and 2% CH_4. At higher temperature CO and CH_4 increase their amount (Davis & Golden, 1968).

The condensed pyrolysis product has been found to be constituted by resins and a crystalline part. The latter contains BPA which amount depends on the operating conditions (time and temperature). In table 3 phenolic products obtained by different researchers are reported. Non phenolic products are present in minor amounts.

Authors report also the presence of xanthone units, which examples of structures are reported in figure 2. Dibenzofurane and fluorenone are also present in the residue, together with ethers and products coming from crosslinking, substitutive addition and branching reactions. This brief information regarding products obtained from pyrolysis of PC shows that thermal decomposition is not offering a good solution for PC recycling because of the difficulty of separation and low selectivity.
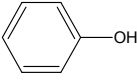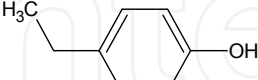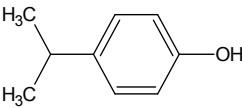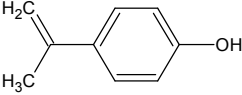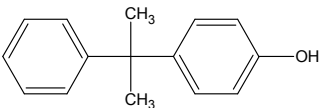
Phenolic products	*Lee(475°C)*	*Davis-Golden (360°C)*
![phenol structure with OH]	Large amounts	Significative amounts
![H3C structure with OH]	Large amounts	Present
![H3C CH2 structure with OH]	Large amounts	Present
![H3C isopropyl structure with OH]	Large amounts	Present
![H2C isopropenyl structure with OH]	Small amounts	
![bisphenol structure with CH3 and OH]		Significative amounts

Table 3. main phenolic products obtained from pyrolysis.

Some researchers (Chiu et al., 2006) have also studied thermal degradation in presence of an active catalyst. The expected advantage is to lower the required temperature, to shorten the degradation time, to increase the extent of the degradation, reduce the portion of solid residue and to narrow the product distribution (Ali et al., 2002). In their paper, Chiu et al. report experiments related to the use of ten different metal chlorides. They found $SnCl_2$ and $ZnCl_3$ to be catalytically active for degradation. They can efficiently perform the expected improvements in thermal treatment of PC and, therefore, some benefits can be obtained. In particular by using these catalysts, liquid degradation products are reduced from 20 to respectively 10 and 8.
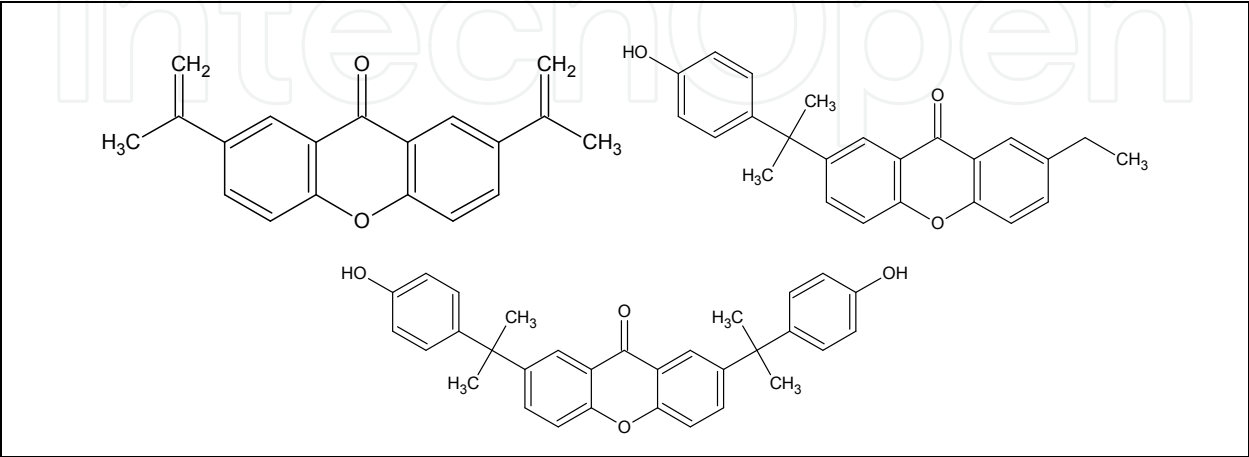

Fig. 2. Examples of xanthone structures.

No chlorinated products were formed. Main obtained liquid products are phenol, p-iso-propylphenol, diphenil carbonate and BPA.

Other researchers (Mitan et al., 2007) proposed to co-pyrolyse at 450°C PC wastes (as for instance DVDs and CDs) with vegetable cooking oil (VCO). They found an increased yield in liquid fraction, at the expense of solid residue, not coming just from the sum of the liquid and solid yields of individual components. This fact was also confirmed by the analysis of degradation rates that results increased by the addition of VCO. Metal contained into DVDs and CDs became 2.5 more concentrated into the solid residue compared to that deriving from thermal treatment of individual reagents.

Grause et al. (2009) studied the pyrolysys of PC with steam in the presence of earth –alkali oxides and hydroxides at temperature between 300°C and 500°C. The experiments were carried out in a semibatch reactor, in steam atmosphere, in the presence of MgO, CaO, Mg(OH)$_2$, Ca(OH)$_2$. All these catalysts accelerated the decomposition, in comparison with the hydrolysis of PC alone, MgO and Mg(OH)$_2$ resulting more effective that CaO and Ca(OH)$_2$. BPA were obtained as the main product at 300°C with a yield of 78% with MgO. Grause et al. (2009) suggested then to further increase the temperature at 500°C in order obtain high yields of phenol and isopropenylphenol and a drastic reduction of the residue.

3. Ester exchange reaction and hydrolysis of poly(bisphenol A carbonate)

Obviously pyrolysis presents some disadvantages such as non-uniform heat flux distribution, low yield of the preferred products and excessive char and gas formation, even if some mitigations towards these aspects have been shown to be possible by using catalysts or by co-pyrolysis. Degradation in liquid solution has been proposed to overcome some of these problems. In this method, the polymer is dissolved in a solvent and degraded thermally in a single phase. Yoshiki et al. (2005) obtained high yields of oil but low selectivity of BPA using tetralin, decalin and ciclohexanol as solvent. Also methylene chloride with ammonia or phenol in combination with an alkali catalyst were applied successfully for PC decomposition (Fox & Peters, 1989; Shafer, 1994). In these cases, however, a complicated product separation is required in addition to environmental problems related to the toxicity of the solvents. Supercritical and subcritical fluids are attractive solvents. They have unique properties, many of their physical and transport properties are intermediate between liquid and gas. The diffusion limited reactions are enhanced because of the increased solubilities and diffusivities. Polymers can therefore be degraded to low molecular weight products by thermolysis in supercritical fluids with high degradation rates. Water and alcohols were mainly used as sub- and supercritical fluids in depolymerization processes of plastics (Goto, 2009). In most of the case the role of the sub- or supercritical fluids is to act both as a solvent reaction medium and as a reactant. In table 4 are reported the critical parameters of water and some simple oxygenated compounds. The critical temperature of methanol is lower than that of water. Properties of water, such as dielectric constant and ion product, change drastically around the critical point (Kruse & Dinjius, 2007). Thus, special effect of water can be expected. When the de-polymerized products are not sufficiently stable, and solvent and supercritical condition are required, alcohols may be better solvents than water, because of their lower critical temperature. During the de-polymerization process, plastic phase is often solid or melt status. In that case, dissolution of solvent into solid or melt phase is essential to enhance the reaction rate,

especially at the beginning of de-polymerization. The selection of the appropriate solvent will depend on the evaluation of the efficiency of reaction, separation and purification process.

	Critical temperature [°C]	Critical pressure [MPa]
Water	373.94	22.064
Methanol	239.48	8.097
Ethanol	240.76	6.148
1-propanol	263.62	5.175
Acetone	234.94	4.700
Benzyl alcohol	441.84	4.300

Table 4. critical parameters of water and alcohols.

Pyrolysis of PC in subcritical and supercritical water was studied by Tagaya et al. (1999). Water has the advantage to be in-expensive and non-toxic. In these conditions the decomposition reaction is more selective and the products are reduced to phenol, bisphenol A, p-isopropenylphenol and p-isopropylphenol.

Tagaya et al. (1999) decomposed PC in the temperature range from 230°C to 430°C. No decomposition occurred below 230°C even for a reaction time of 24 h. Production of phenol, BPA, p-isopropenylphenol and p-isopropylphenol begin starting from 240°C. At 250°C a significant decomposition starts after 2 h, while at 300°C, after 2h, 38.1% of the former products were obtained. However estension of reaction time resulted ineffective for increasing the yield. NaCl and CH_3COOH addition was no effective for decomposition reaction. The latter results to be accelerated by the addition of Na_2CO_3. At 300°C no BPA was detected in the product because of its transformation into phenol catalysed by Na_2CO_3. Phenol reached in these conditions, after 10 h, a yield of more than 30% indicating that subcritical water is also an advantageous medium for decomposing polymeric compounds. On the contrary supercritical water, in decomposing polymeric materials, has the disadvantage to cause rapid corrosion of equipments at very severe operating conditions. Chen et al. (2004) observed that high yields of BPA and dimethylcarbonate (DMC) were obtained using methanol. DMC is a valuable byproduct, a nontoxic and environmentally benign carbonylating and methylating agent that can replace hazardous chemicals like for instance phosgene. It is also a raw material useful for producing again polycarbonate resins. Also Dongpil et al. (2009) studied PC methanolysis mechanism in the temperature range 160-220 °C and with reactions time until 180 min. The increase of molar ratio between methanol and PC has been found to improve both DMC and BPA yields but, of course, it demands larger capital and energy costs.

Hu et al. (1998) studied alkali catalysed methanolysis using a mixed solvent of methanol and toluene. They found that by using more than a stoichiometric amount of methanol, DMC was produced in quantitative yields, highlighting the importance of adopting also an optimized ratio between PC and methanol.

Piñero et al. (2005) used methanol-water mixtures and developed (Piñero et al., 2006) a shrinking particle model to describe the reactive dissolution of the BPA-PC particles in semicontinuous de-polymerization of polycarbonate. Jie et al. (2006) studied decomposition in ethanol that has a critical point practically at same temperature and a lower pressure than that of methanol, allowing lower operating temperatures and pressures. Comparing the use of methanol and ethanol as solvents, it is reported that PC completely decomposes in supercritical methanol at 290°C and 9.96 MPa, in supercritical water above 374°C and pressure higher than 22.1 MPa, while in ethanol this is possible above 243 °C and 6.38 MPa producing BPA and diethylcarbonate (DEC). The mechanism consists in the random reaction along the polymer chain of the ester linkage with the solvent , that produces two smaller polymer chains, which can still react by ester exchange reaction until the polymer is completely converted to BPA and another product depending on the solvent.

In all the reported examples of alcoholysis yields of 90% of BPA (in terms of weight of obtained BPA divided the weight of initial PC) were obtained. The activation energy deduced from experimental data are resumed in table 5 (paragraph 6).

4. Hydrolysis near the critical point

In order to extend the results obtained by Tagaya et al. (1999), several experiments have been performed by adopting liquid water in the more convenient subcritical conditions. The results obtained in decomposing PC and producing BPA, will be reported in the following.

4.1 Experimental

4.1.1 Materials

The reagent grade Poly(bisphenol A carbonate) (average MW 64000) [CAS 25037-45-0], Bisphenol A (>99%) [CAS 80-05-7], Phenol (>99%) [CAS108-95-2] and other chemical used were all purchased from Sigma-Aldrich. Water was twice distilled. Commercial Recordable Compact Discs crashed for de-polymerization tests were Verbatim Datalife CD-R.

4.1.2 Apparatus and methods

De-polymerization tests were carried out in a 316 stainless steel tubular batch reactor (internal diameter 7.8 mm, length 150 mm) having an internal volume of 7.1 mL. The tests were performed by first weighting the empty reactor and then charging it with 1 g of BAPC and 1 g of water. The reactor, exactly weighted after charge, was put into a laboratory fan assisted furnace (Heraeus M110 electronic), preheated at the temperature set point, over a support disposed along the symmetry axis of the oven. A thermocouple fixed on the external wall of the reactor measured temperature level. Both horizontal and vertical disposition were studied. At the end of the experiment the reactor was recovered from the oven, rapidly cooled and newly weighted at ambient temperature. Not more than ±0.2 mg of weight difference from initial and final total weight was accepted as a probe of no spill and good capping for the test, otherwise the test was repeated. The reactor was unhead and the evolved gas collected and GC analyzed. The degassed reactor was finally weighted and the difference was assumed as CO_2 produced. The yield was evaluated from this latter information. A Mettler Toledo analytical precision balance (model B154-S) was employed.

By cooling the reactor, the resulting content (at room temperature) is constituted only by condensed phases. The liquid and solid internal material was discharged, identified and quantified by FTIR and GC.

4.1.3 Some analytical aspects

The solid sample obtained from the tests was characterized by Shimadzu FTIR: IRAffinity-1 in the 500 - 4000 cm^{-1} range (KBr disc). Gas chromatographic analyses of solid products were carried out (using methanol as solvent) on a GC-FID HP 6890plus with SLB-5ms capillary SUPELCO column (30 m length, 1 μl injection volume, split ratio 1:10, Helium carrier 1.4 mL/min, constant flow). The temperature was held at 65°C for the first 2 minutes, then increased at 255°C at a heating rate of 10°C/min and kept at this temperature for 15 minutes. The main products were identified and quantified by comparing the retention time with standard compounds.

Figure 3 shows a typical gas chromatographic analysis of the condensed phase discharged at the end of a test at high conversion. As it can be observed BPA is the main product. Gas chromatographic analyses of evolved gas were performed with a column 0.53 mm ID, Molecular Sieve 5A as stationary phase, GC-T as detector, isothermal at T=25°C. Permanent gases and CO_2 were detected.
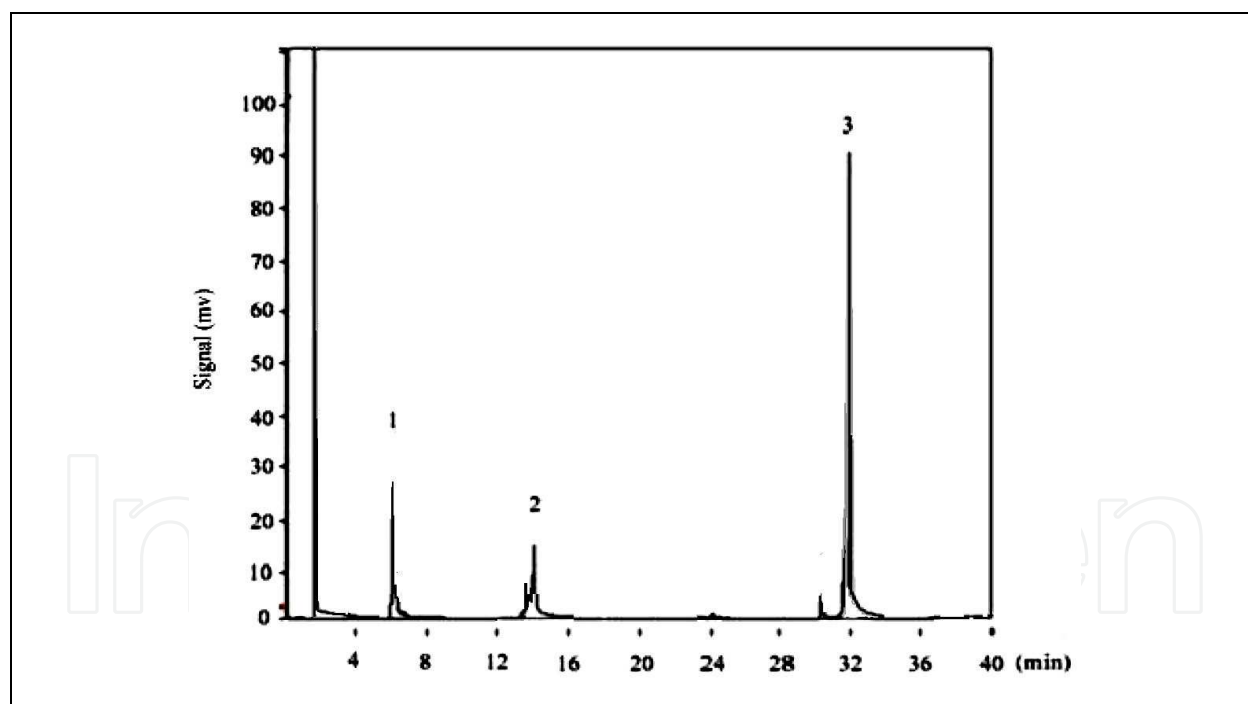

Fig. 3. Typical gas chromatographic analysis of solid product obtained by the tests.

Figure 4 shows FT transmittance plot showing the FTIR analyses of commercial poly(bisphenol A carbonate): (A) starting material obtained from a CD crash, (B) low conversion depolymerization solid discharged material, (C) medium conversion material, (D) solid material discharged at complete depolymerization. The FTIR spectra of reagent grade BPA, p-isopropylphenol and phenol are also reported. The figure 4 D shows the same shape as pure BPA.

4.2 Results and discussion

The experimental tests on hydrolysis have been performed at temperatures ranging from 240 to 290 °C (corresponding to a pressure range of 3.5-8 MPa). The latter temperature has been selected as a maximum, because it is known that BPA, obtained by hydrolysis of PC, starting from 300°C decomposes giving place to phenol (Tagaya et al., 1999).
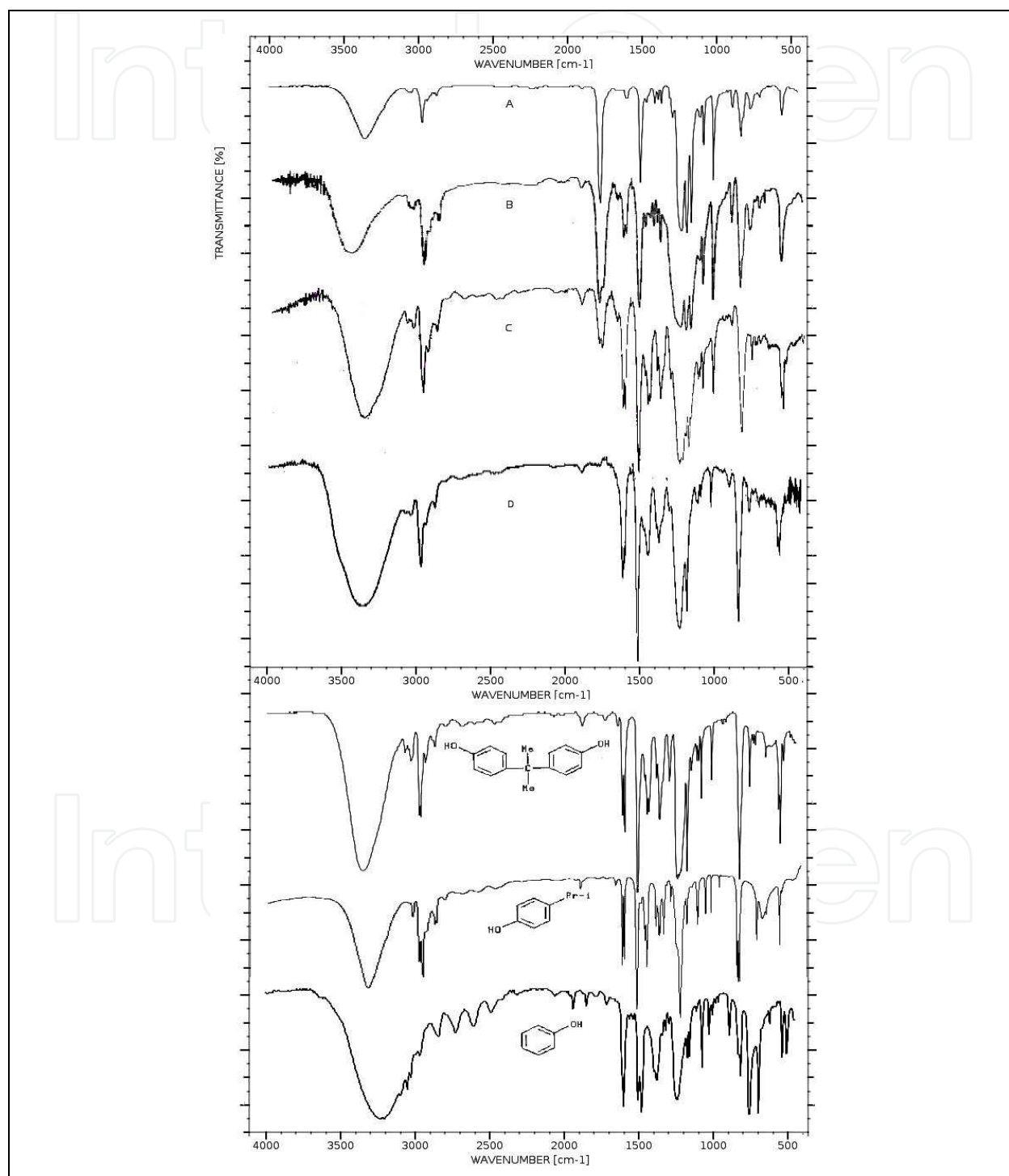

Fig. 4. FT transmittance plot from starting material until 100% conversion compared with BPA, p-isopropylphenol and phenol FTIR spectra.

This was also confirmed by some preliminary tests that have been performed. Different residence times have been adopted. Because of the competition existing among the concerted path hydrolysis reactions and the radical path (non selective) reactions, the selected temperature range has to be considered optimal. In facts the apparent activation energy of the pyrolysis is quite higher (40-80 kJ/mol more). The hydrolysis yields have been evaluated by means of both the amount of CO_2 released and the weight loss of the sample (of course the last one is comprehensive of all the gaseous matter produced). In the preliminary tests it has been verified that the horizontal position of the reactor inside the furnace is largely preferable. In fact the reaction takes place starting from the contact surface between the molten and swollen polymer and the water, producing fractures and pores that favor the further penetration of water (as also reported by Dongpil et al., 2009 in the case of methanolysis). It is important to point out that the horizontal configuration allows enhancing the surface contact between the molten immiscible polymer and the water and, therefore, the apparent global reaction rate.

Figure 5 reports the conversion versus time at different temperatures. One test has been performed for a time as long as 4 h. There is an apparent induction time for the process that can be essentially attributed to the time required for the heating of reagents inside the reactor. In order to understand whether some autocatalytic effect can be related to the products, it has been decided to perform also some tests by adding small amounts of BPA: practically no significant effect has been observed. The result obtained by Kitahara et al. (2009) in subcritical conditions are also reported in the figure.

The obtained data have been used for deducing the reaction rate and the apparent activation energy of the reaction. Figure 6 reports the experimental reaction rate constant as a function of 1/T. This diagram incidentally can be considered preliminary to deduce in a simple way the activation energy of the reaction that results to be about 80 kJ/mol (in agreement with other experiences).

The gases produced by the hydrolysis reaction was evaluated not only in terms of their total amount but, periodically, they were also analyzed by GC in terms of their composition. First of all the analyses have clearly shown that N_2/O_2 ratio, in the effluent gases, were practically the same of the original air inclusion. This result simply means that no oxidative degradation was taking place during hydrolysis. Indirectly, the last considerations are also showing that practically no extra components are entering during the periodical filling and emptying of the reactor. In the experiments with the highest de-polymerization degree the products obtained have been analyzed after mixing with methanol. The results show always a high purity in BPA in comparison with byproducts like phenol, p- propyl and propylidene phenols. This confirms that the polymer decomposition through breakage of the bond C aromatic-C isopropylic (i.e. pyrolysis) is negligible in practice and that this parasitic radical mechanism doesn't occur significantly in the selected operating conditions.

The FTIR analysis on the reaction residue after evaporation of the water shows a spectrum that is coherent with a progressive hydrolysis of the carbonate bond, without appreciable evidences of de-alkylation followed by formation of terminal propylidene and phenol. The IR spectra at higher conversion are practically coincident with those of standard BPA.

On the basis of these evidences, it can be affirmed that the de-polymerization reaction proceeds in the condensed phase and, under the preferred conditions, it regenerates the

monomer. It is important to point out that after the tests at the highest conversion level (i.e. BPA yield >90% wt), the melting point of the product resulted over 145-150 °: this is another excellent indication of the substantial purity of the obtained raw monomer.
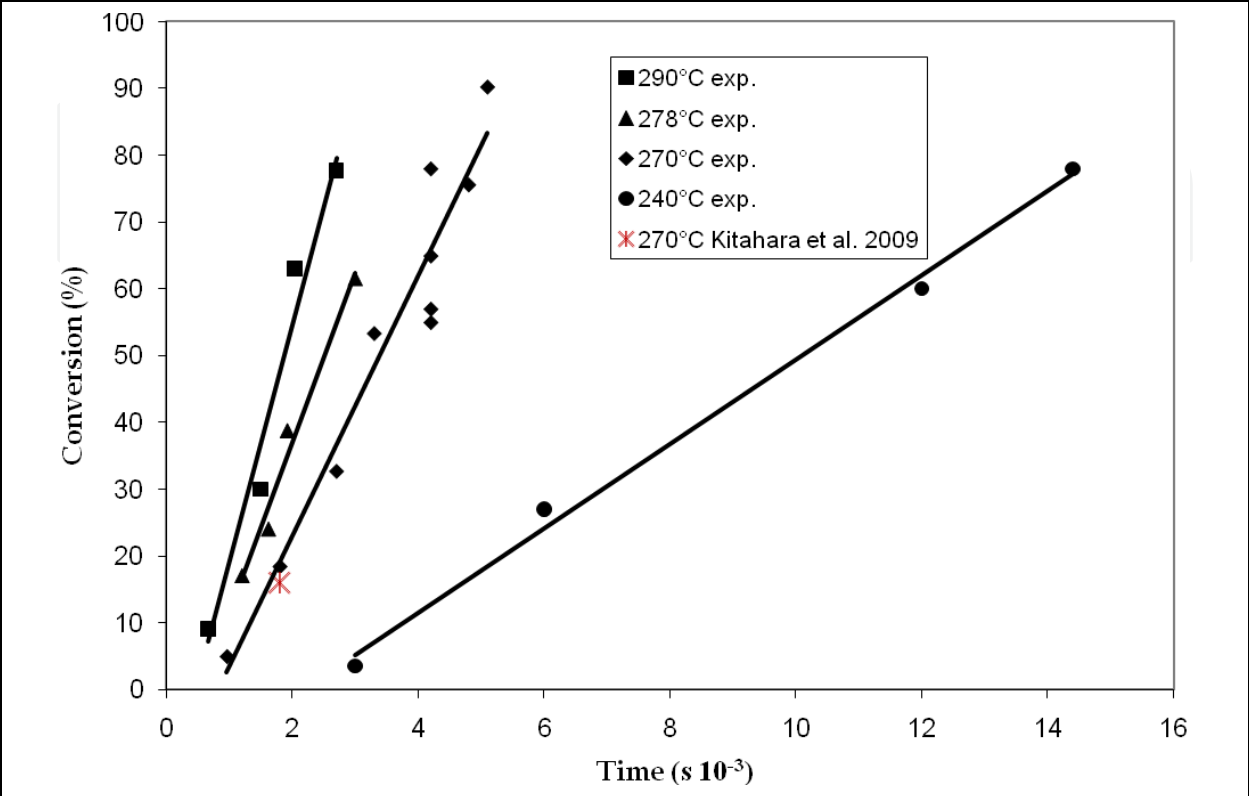

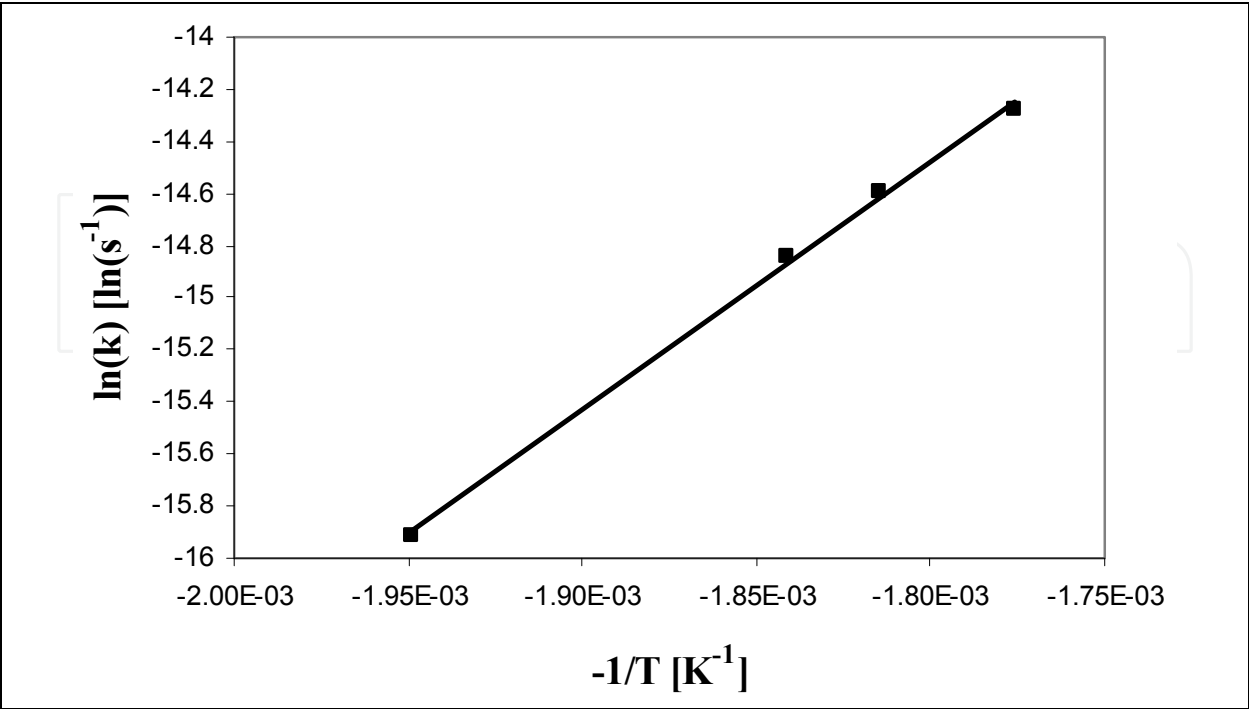Fig. 5. Yield of BPA versus time at different temperatures.

Fig. 6. Experimental kinetic constant (s^{-1}) as a function of $-1/T$ [K^{-1}].

These results seem to be in partial contradiction with some of those obtained by Tagaya et al. (1999) indicating low BPA yields (around 35%) after 2 h reaction at 300°C . In that paper no indication was given on modalities of contact between molten polymer and water. A hypothesis on the difference of the obtained results can be related to a non adequate surface contact in their experiments. On the contrary other data supports our results (Kitahara et al., 2009, see figure 5). In facts, after hydrolysis of PC with water for 30 minutes at 270°C, they obtained a BPA yield of 16% that is substantially in line with our results.

Regarding the experiments performed with pure PC or with crashed CDs, essentially no difference was observed.

5. Hydrolysis kinetic mechanism

It is interesting to observe that PC hydrolysis is mainly dominated by a six center concerted path reaction mechanism. By analogy with other reactions following the same mechanism, involving hydrolysis of esters, the kinetic constant suggested for every elementary de-polymerization act is:

$$k = 10^9 \exp\left(-\frac{84000}{RT}\right) \quad 1/\text{mol/s} \tag{1}$$

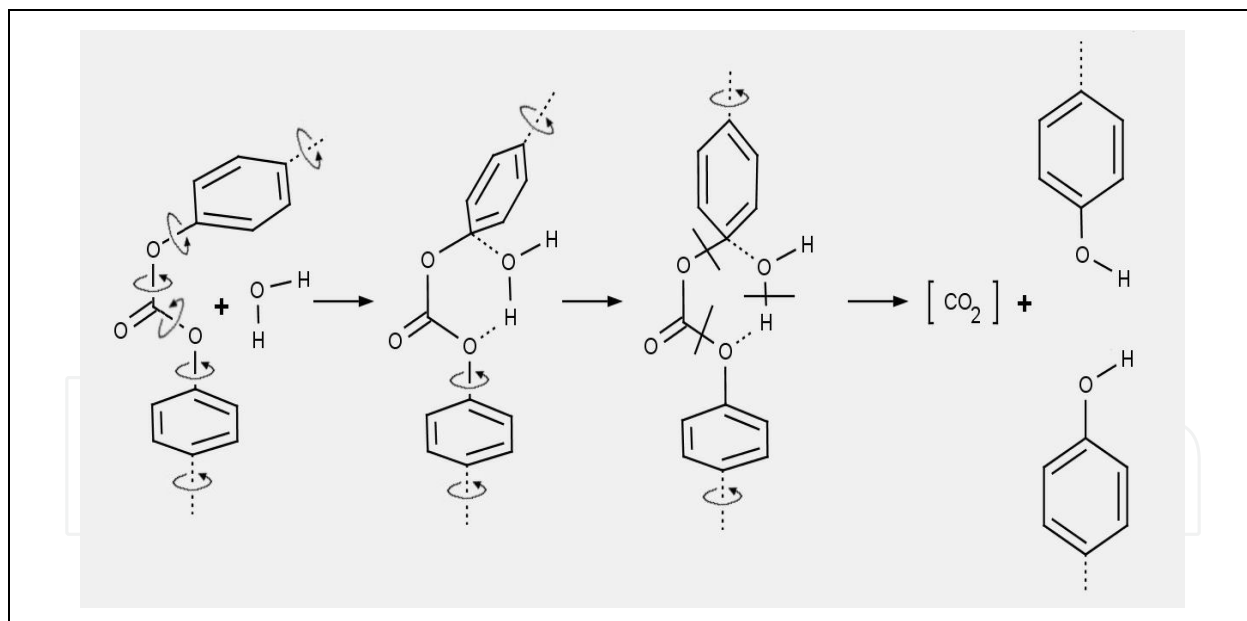This figure is coherent also with other activation energies as represented in Table 5.

Fig. 7. Hydrolysis mechanism.

Of course the radical reactions path becomes more important at higher temperatures (and of course in practical absence of water). In our conditions water becomes a powerful reactant. It has also to be pointed out that water approaching critical conditions has an increased solubility. Moreover, in this range of temperatures (>230-250 °C), the swelling of the molten polymer offers a large increase of diffusion coefficient into the polymer phase. Formally the homogeneous reaction can be schematized as shown in figure 7.

6. Process parameters

Now it is useful to observe Table 5. In this table are resumed the conditions of the different processes used for recovering BPA from waste PC by using alcoholysis or hydrolysis.

Authors	Reactant	BPA yield	T [°C]	P [MPa]	Time [min]	Activation Energy [kJ/mol]
Piñero et al., 2005	$CH_3OH/NaOH$	80-90%	70-180	2-25	45-130	87.58
Hu et al., 1998	CH_3OH/C_7H_8	7-96%	40-60	0.1	15-330	107.5
Dongpil et al., 2009	CH_3OH	90-96%	160-220	n.a.	40-180	79.5
Jie et al., 2006	C_2H_5OH	20-90%	240-290	n.a.	10-60	97.2
Chen et al., 2004	CH_3OH	20-90%	230-265	7.8-10	10-30	75.72
Bozzano et al., 2010	H_2O	80-90%	240-290	4-8	20-240	84

Table 5. Comparison among obtained results in recovering BPA from PC by alcoholysis or hydrolysis (n.a. = not available, BPA yield=kg BPa/kgPC).

The hydrolysis or methanolysis process can be performed at a temperature level that avoid pyrolysis. It can be observed that, with exception of the paper of Hu et al., 1998, were toluene is used, all the activation energies are very close. This means that the elementary processes and the reaction mechanisms are extremely similar. Most probably they are dominated by mass diffusion limitation. The BPA yield indicate that about complete decomposition of the polymer occurs with water.

Essentially in order to make some observations regarding a possible process that adopts the hydrolysis method, it can be observed that it has to comprise the following aspects: the chopping of the solid materials and the particles dispersion into water; the compression of the suspension till the proper pressure (e.g. 4-8 MPa); the heating of the mixture till the maximum temperature (280-290°C), possibly by superheated pressure steam; the cooling of the reacted mixture by flashing after the convenient reaction time (recovering the steam), till a relatively low pressure (0.5 MPa) allowing the recovery of the molten monomer for the decantation of the suspended inert solid particles; the clean liquid monomer (at 140-160°C) is separated from the remaining small amount of the practically immiscible water and then sent to subsequent conventional purification steps.

Some processes have been already patented by important societies. A list is following: General Electric (Fox D.W. & Peters E.N., 1989; Shaffer S.J., 1994; Caruso A.J. & Lee J.L., 1996; Eijsbouts P. et al., 1997), Bayer AG (Buysch H.J. & Schoen N., 1993; Buysch H.J. et al., 1994; Buysch H.J., 1995), Teijin Chemicals LTD (Kiyoshije K. & Matsumoto K., 1994; Suzuki M. & Matsumoto K., 1995; Suzuki M., 1995, Ogasawara K. & Matsuura T., 2004, Takemoto H., 2005), Mitsubishi Heavy Ind. LTD (Hishihara N. et al., 1999; Hishihara et al., 2001), Victor Company of Japan (Takahashi T. et al., 2001; Tsujita K. et al., 2001a; Tsujita K. et al., 2001b; Tsujita K. et al., 2001c; Tsujita K. et al., 2001d; Kawai N., 2002; Tsujita K. & Kawai N., 2004; Tsujita K. & Kawai N., 2005), Kansai Res. Inst. (Kawashima F. et al., 2003).

7. Conclusions

In this chapter the experimental results of the hydrolysis of poly(bisphenol A carbonate) with water have been presented together with a description of existing methods for recycling PC. Both pure PC and CDs waste have been treated. The adopted temperature levels are subcritical and pressures inside the reactor allow to hydrolyze with liquid water. The tests have shown the feasibility of the process that in these conditions is mainly based on real molecular concerted path reactions. Secondary reactions, requiring a radical path and leading to parasitic byproducts, are characterized by quite higher apparent activation energy and require higher temperature levels than those here adopted. For this reason in the presented process they are negligible.

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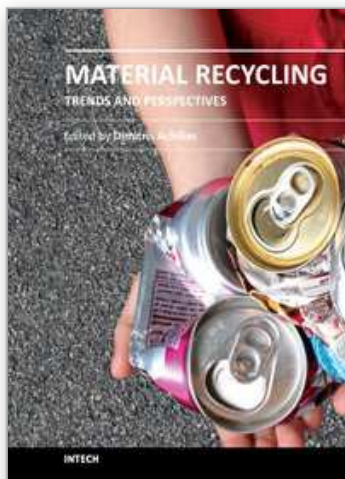
Material Recycling - Trends and Perspectives

Edited by Dr. Dimitris Achilias

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

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