

Full Length Research Paper

Hydrolysis degradation of polycarbonate under microwave irradiation by using design of experiment software

Nayeleh Deirram^{1*}, Abdul Razak Rahmat¹, Saba Rashidi¹, Taravat Ghanbari¹ and Mona Moradpour²

¹Faculty of Chemical Engineering, Universiti Teknologi Malaysia (UTM) 81310, Skudai, Johor, Malaysia.

²Faculty of Science, Islamic Azad University, South Tehran Branch, Tehran, Iran.

Accepted 7 June, 2012

Depolymerization of polycarbonate (PC) is one of the important issues in environment especially in industry field. In this project degradation of PC is done by employing the hydrolysis method using microwave irradiation. PC degradation was carried out under constant amount of tetrahydrofuran (THF) as co-solvent and by using various amount of water (H₂O) as main solvent and different concentration of sodium hydroxide (NaOH) as catalysts in a microwave reactor for low power and different time. The solid main product bisphenol A (BPA) was analyzed by FTIR and HPLC. It was found that PC degradation is favored by increasing amount of H₂O, concentration of NaOH and time duration of process. Complete depolymerization was found to occur in 12.5 min when the amount of water was 3.5 g and concentration of NaOH was 0.5 g at 110°C.

Key words: Hydrolysis, polycarbonate, microwave irradiation, bisphenol A.

INTRODUCTION

Polycarbonate (PC) is an interesting and important class of polymer and has very useful properties such as high heat capability, incredible transparency, excellent thermal stability and best impact strength (Sala et al., 2010). Extensive use of PC in the environment means that there are huge amount of PC waste in environment that should be recycled by using different techniques. The techniques of polymer recycling can be classified into four categories: primary recycling, mechanical recycling, chemical recycling and energy recovery (Achilias et al., 2010). Among these recycling techniques, chemical recycling is the only technique that can decompose polymer to its raw materials (monomer). This technique also is the most suitable technique concerning to the environmental issues. Furthermore, chemical recycling do not need extra resources to reproduce polymer (Sinha et al., 2008). The chemical recycling can be carried out using glycolysis, methanolysis, hydrolysis and aminolysis

methods (Shukla et al., 2008; Lorenzetti et al., 2006).

In glycolysis method, Polymer degradation can be carried out by ethylene glycol (EG), diethylene glycol, propylene glycol and dipropylene glycol. The glycolysis of PC with microwave irradiation was reported by Mohammad (2011). This method was done by using EG as recycling agent and NaOH as catalyst. The process was carried out at various times of 100, 200, 300, 400, 500 and 600 s and the yield of bisphenol A (BPA) were 15, 40, 76, 84, 93 and 93%, respectively. At the end of the experiment the pure BPA was analyzed by FTIR, H-NMR and C-NMR. Liu et al. (2009) Reported using of water, co-solvent and NaOH as a catalyst for hydrolysis degradation of PC. They used co-solvents such as tetrahydrofuran, 1,4-dioxane and N-methyl-2pyrrolidone in the hydrolysis process. The main product of their research was BPA. According to their study the yield of BPA had reached up to 94% in 8 h when the concentration of NaOH was 0.5 g. In addition, they recorded the significant effect of concentration of water (H₂O) on the yield of BPA. With increasing the concentration of water, the yield of BPA was increased too. In their study

*Corresponding author. E-mail: n.deyrram@gmail.com.

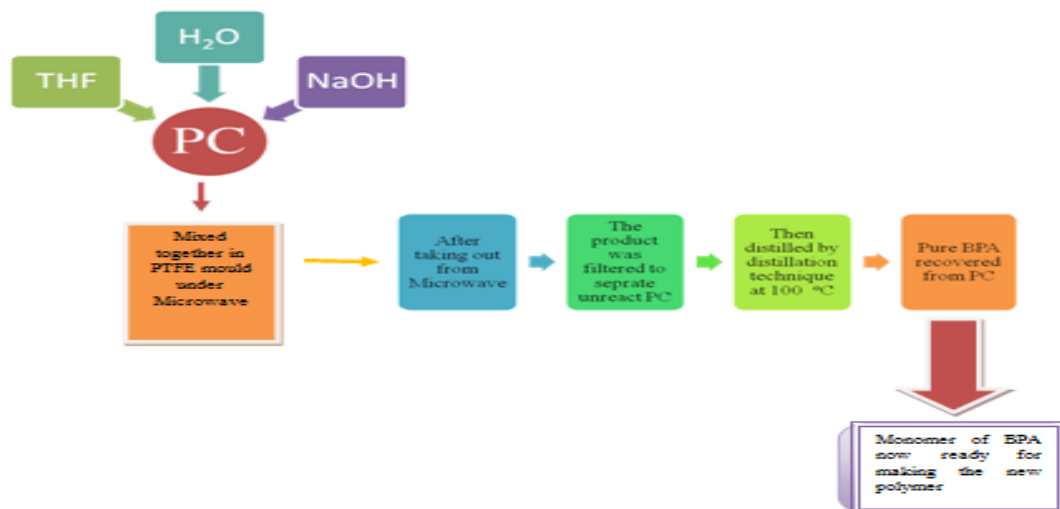


Figure 1. Process diagram of Pc degradation to BPA.

the maximum yield of BPA occurred when amount of water was 3.5 g and after that increasing the amount of water leads to decrease in yield of BPA. The yield of BPA was raised with increasing the concentration of co-solvent from 10 to 20 g. The maximum yield of BPA achieved 94% when 20 g of co-solvent was used.

Depolymerization of PC with alkali catalyses methanolysis was done at temperature of (40-60°C) in 330 min in the batch reactor by (Hu et al., 1997). The yield of BPA for this experiment was 7%. They also used mixed solvent and methanol, to increase the yield of BPA up to 90-96%. The new method of methanolysis degradation of PC was done in ionic liquid without acid or catalyst base by Liu et al. (2011). The main products of this method were bisphenol A and dimethyl carbonate with high yields over 95 % in 2.5 h at 105°C. Reusing the ionic liquid after experiment without any change in the yield of products is the main advantage of this method

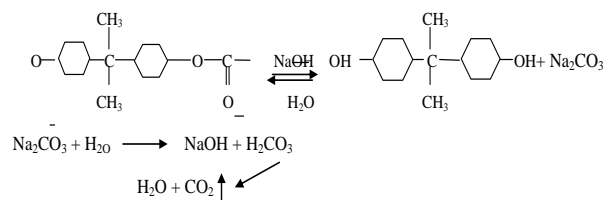
Microwave reactor for degradation of PC could be one of the best alternative techniques. Using microwave irradiation as a heating technique has many advantage over conventional heating. The main advantage of this technique is its ability to quick heating of the bulk materials. Getting more trustable results in shorter time in more comfortable situation are the other advantages of using microwave irradiation (Siddiqui et al., 2010).

In this study, we have explored the application of microwave irradiation as a powerful and “green” energy source in the chemical recycling of PC wastes for the first time. The hydrolysis method is quick and simple and BPA is recovered from pure PC pellet at short reaction times. The hydrolysis degradation of plastics is done by using water as a solvent. The low price of water and also plenty amount of water in the environment cause to decrease the cost of this method in comparison with other chemical methods.

MATERIALS AND METHODS

Pure polycarbonate (Makrolon-Bayer) as main polymer, Commercial available tetrahydrofuran (Merk, .Wt: 72.11 g/mol- Assay: 99.8%) as co-solvents, water as solvent and impure Sodium hydroxide (grade AR .Wt: 40, 00 g /mol- Assay: 99%) as catalyst were used in this study.

The polycarbonate degradation process was carried out in a grill microwave oven (brand: Panasonic MN-GF560M with maximum power of 1000 watt). Small pellets of sodium hydroxide (0.25, 0.5 and 0.75 g) as a catalyst were dissolved in different amount of water (2, 3.5 and 5 g) as a main solvent in a PTFE mould (25 ml). After mixing, the polycarbonate pellets (5 g) and 20 g tetrahydrofuran as co-solvent were added to the mould. The mixture was heated in a low microwave power during different times (10, 12.5 and 15 min). By taking the PTFE mould out from the microwave, the product was filtered to separate the solid unreacted PC and the remaining liquid phase materials. These liquid phases are consisting of the BPA (main monomer of PC), sodium carbonate as a byproduct (Na_2CO_3) which is soluble in water, THF (co-solvent) and water (H_2O). They were then distilled by distillation technique at 100°C to remove the THF and water (the boiling point of THF and H_2O are 66 and 100°C, respectively). Mohammad (2011) and liu et al. (2009) were reported about glycolysis degradation of PC by microwave and hydrolysis degradation of PC by thermal methods. The process of them is explained in introduction. Equation 1 shows the reaction mechanism for hydrolysis degradation of polycarbonate to bisphenol A.

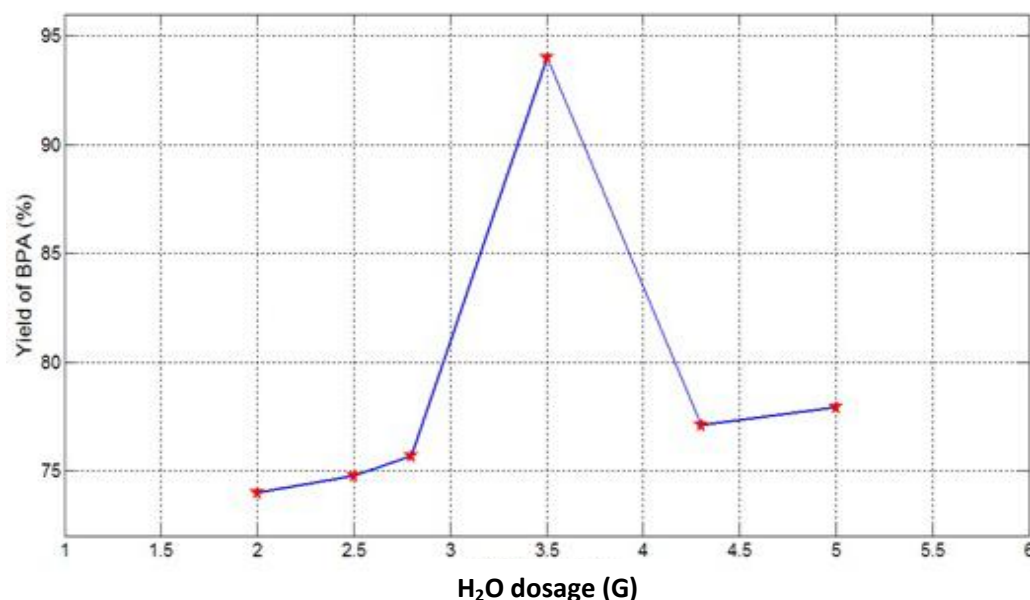


The process diagram of hydrolysis degradation of PC under microwave irradiation to achieve the pure BPA is shown in Figure 1.

By introducing the experiment effective parameters (H_2O , NaOH, time) as the variables in Design of Experiment software (full factorial) and inserting their corresponding values, DOE software

Table 1. Different experimental samples and their corresponding yield of BPA by using hydrolysis degradation method under microwave irradiation.

Number of samples	PC (g)	THF (g)	NaOH (g)	H ₂ O (g)	Time (min)	Yield of BPA (%)
1	5	20	0.25	2	15	72
2	5	20	0.75	5	15	78
3	5	20	0.25	2	10	60
4	5	20	0.5	3.5	12.5	94
5	5	20	0.75	2	15	74
6	5	20	0.25	5	15	70
7	5	20	0.5	3.5	12.5	92
8	5	20	0.75	5	10	62
9	5	20	0.5	3.5	12.5	93
10	5	20	0.25	5	10	64
11	5	20	0.75	2	10	66

**Figure 2.** The relationship between BPA yield and H₂O dosage: temperature 110°C, PC 5 g, THF 20 g, NaOH 0.5 g and reaction time 12.5 min.

suggests set of samples for experiment. The number of suggested samples by DOE software is less than the actual samples which must be achieved by variation of effective parameters. This significant reduction in the number of experiment samples saves the time and materials.

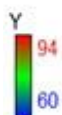
Bisphenol A was analyzed by Fourier transform infrared (FTIR) in the range of 4000- 400 cm⁻¹ by using KBr powder containing ca. 1 Wt% of sample. The analysis was carried out on Perkin-Elmer (1600 series). High performance liquid chromatography (HPLC) technique was then used to identify, quantify and purification of the individual components of the mixture. The solid sample (BPA) was diluted 25 times with methanol (25 g of BPA dilution in 1 g methanol) and then centrifuged. At the end, 5 µl of sample was injected into HPLC system (the software version was 6.3.1.0504). The column which was used for this sample was LC column waters C-18 (5 µm particle size, 4.6 × 250 nm). The mobile phase used methanol solution (45: 55, v/v) at 40°C.

RESULTS

Table 1 illustrates the eleven samples which DOE software determined for experiment to achieve the yield of BPA in percent. Doing these eleven experiments, yield of BPA achieved for each sample separately. According to the table sample number 4 has the highest yield of BPA (94%) when using 5 g polycarbonate, 3.5 g water as main solvent, 0.5 g NaOH as catalyst, 20 g tetrahydrofuran as co-solvent during 12.5 min time processing.

Figure 2 shows the effect of different concentration of water on the yield of BPA. It can be seen that increasing the amount of water leads to increase the yield of BPA

Design-Expert® Software



X1 = B: H₂O
X2 = C: Time

Actual Factor
A: NaOH = 0.50

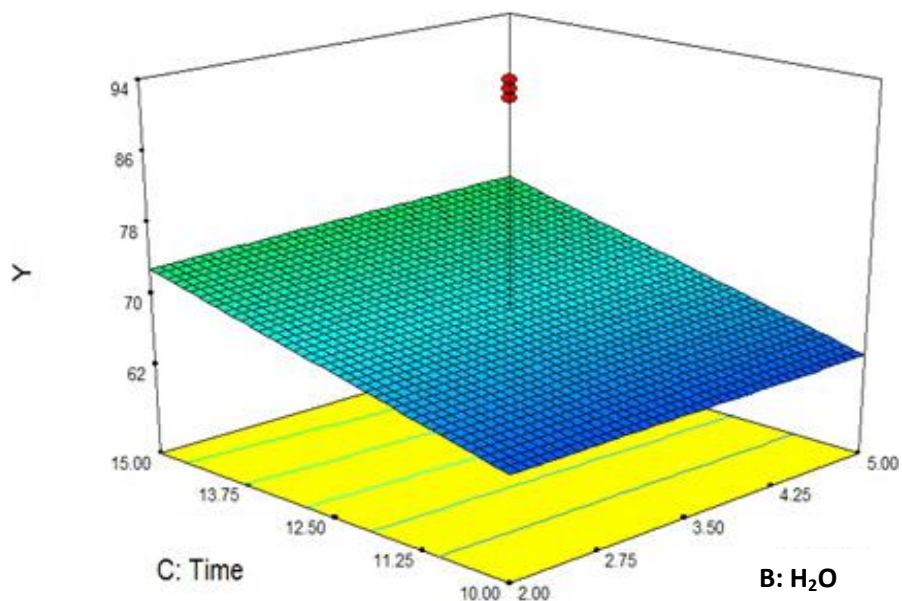


Figure 3. Relationships between different concentrations of water at various times when the amount of NaOH was constant (0.5 g).

gradually. The maximum yield of BPA (kg product/ kg PC) was achieved in present of 3.5 g H₂O and after that the yield of BPA decreased. This phenomenon happened due to significant deduction in concentration of NaOH and dissolubility of PC in solvent at the present of too much amount of water. Since all the variable parameters in experiment are influencing the yield of BPA simultaneously, determining the effect of each parameter on the yield of BPA is too difficult. The effect of water as a single parameter has been studied in this research and shown in Figure 2 to determine the accuracy of the experiment and also to be compared with the literature result as the benchmark.

Figure 3 shows the yield of BPA in constant concentration of NaOH (0.5 g) at various time and different amount of water. According to Figure 3, yield of BPA increased in direct proportion to the increase in amount of water. This phenomenon continued till the yield of BPA reached to its maximum value at 12.5 (min) processing time and present of 3.5 g water. The maximum value for yield of BPA is shown by red points in Figure 3. Since the experimental sample which leads to maximum yield of BPA is chosen three times by the DOE software there are three red points on figure which belongs to maximum yield. Although this selected sample had the same variable parameters during the experiments, its corresponding yield of BPA varied (92, 93 and 94%) due to change in environment and experiment condition. By increasing the amount of water, the BPA yield decrease after this peak due to discussed

reason.

Figure 4 shows the yield of BPA at constant time (12.5 min) for the variation of concentration of NaOH and amount of water. Increasing the amount of NaOH leads to increase in rate of hydrolysis of BPA. The highest yield of BPA (94%) occurred when the concentration of NaOH was 0.5 g. this peak is shown by red points in figure again. Look like the water concentration effect, after the peak increasing the amount of catalyst leads to sudden decrease in the yield of BPA. This phenomenal happens due to significant amount of NaOH. Therefore present of too much NaOH in mixture leads to decrease in dissolubility of PC and also decrease the rate of hydrolysis degradation.

One of the most important factors in degradation of PC is reaction time. Researchers put lots of effort to decrease the duration of PC degradation. Using microwave irradiation method can decrease the time duration of the PC degradation. This remarkable decrease in the time of the process can be seen clearly in Figure 5. According to the figure, when reaction time was 11.25 min and the concentration of NaOH was 0.30 g the yield of BPA was 50%. Highest yield of BPA was achieved during 12.5 min reaction time when the concentration of NaOH was 0.5 g. After that when the time was increased to 15 min the yield of BPA decrease.

Based on Figure 5 the effect of variation in time process is quite look like the water concentration effect. In another word, increase in time process lead to increase in yield of BPA before the peak (red points) and

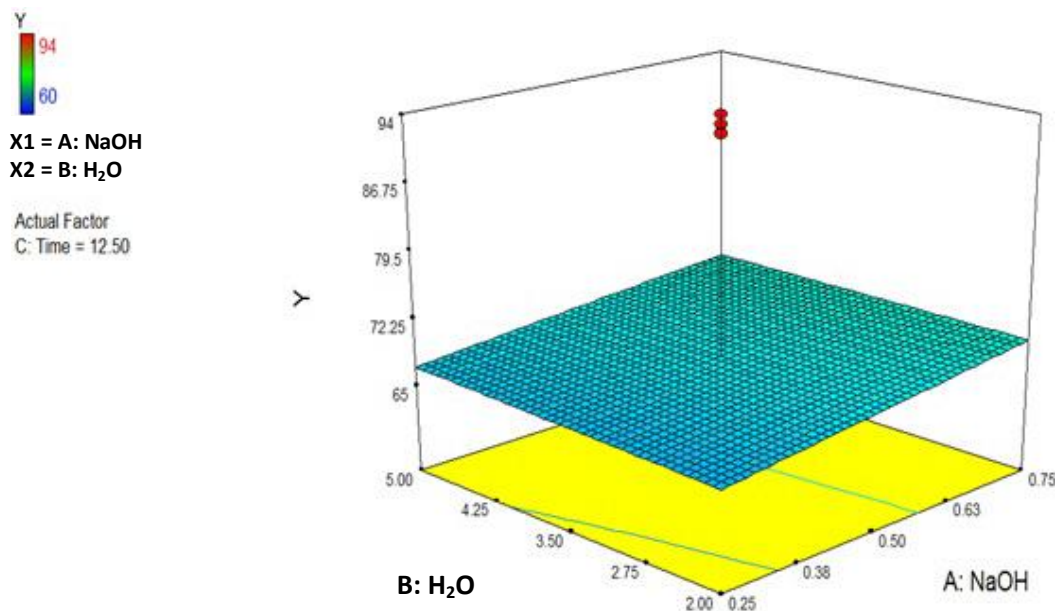


Figure 4. Relationship between different amount of water and concentration of NaOH when the reaction time was constant (12.5 min).

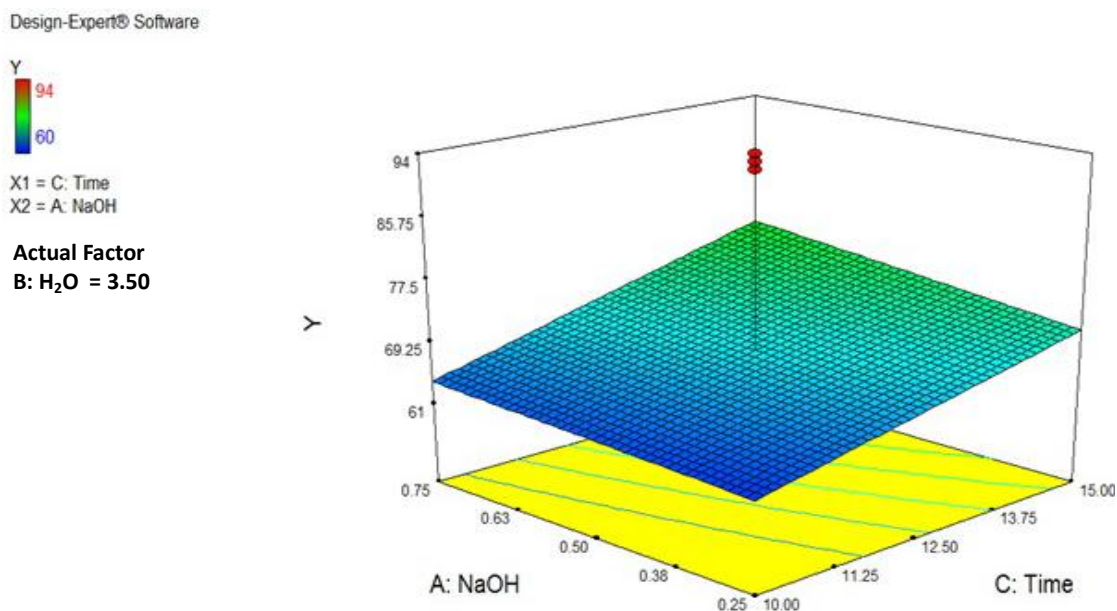


Figure 5. Relationships between BPA yields and reaction time at different concentration of NaOH dosage. Temperature 110°C, PC 5 g, H₂O 3.5 g and THF 20 g.

after that increase in time process cause a significant drop in BPA yield.

The structure of the recovered BPA was determined using spectroscopic methods and the results were then compared with the standard. The FTIR spectrum of recovered BPA is presented in Figure 6. A broad peak observed at 3379.90 cm⁻¹ is related to O – H cm⁻¹ phenol

group. The peak of C- H cm⁻¹ aromatic can be found at 2965.10 which is little and near the O – H cm⁻¹ group. The peak at 1362.75 cm⁻¹ is related to CH₃ while the sharp peak observed at 1238.20 is due to the C – O. The peaks at 1177.39 cm⁻¹ and 827.06 can be related to C – C alkanes in the structure of BPA. The peak at 552.35 cm⁻¹ is related to benzene rings. Figure 7 shows the suitable

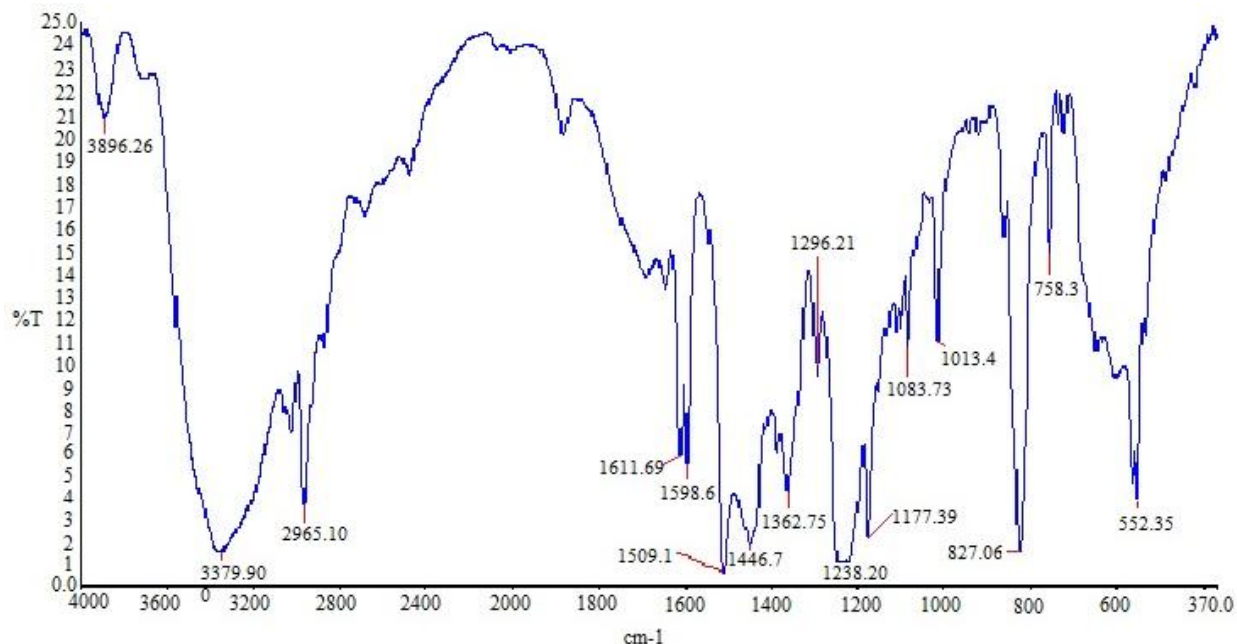


Figure 6. FTIR spectrum of recovered pure BPA.

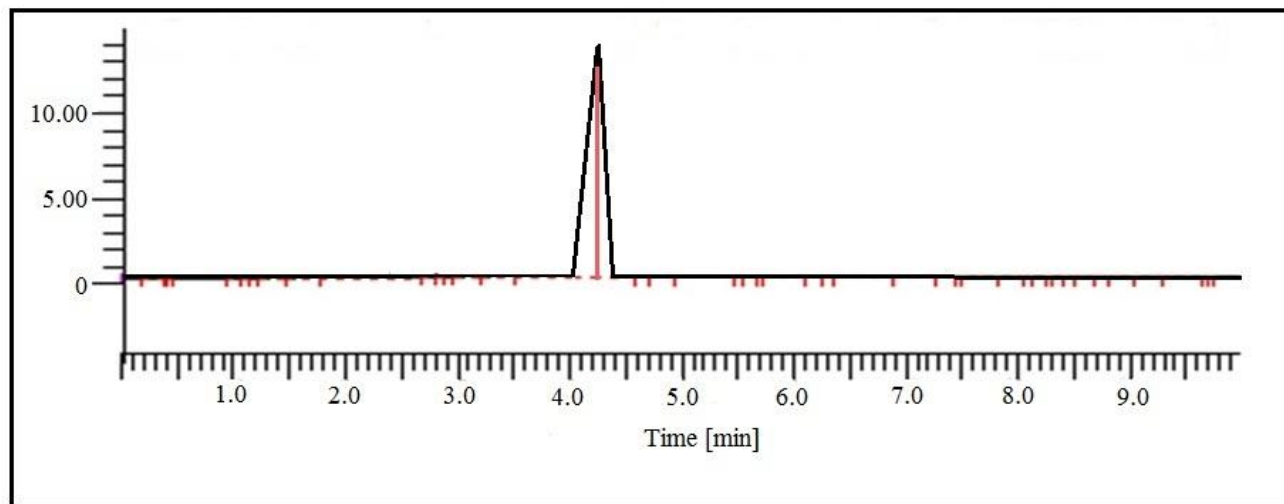


Figure 7. HPLC chromatogram of sample of the reaction mixture when methanol is used as solvent-reagent.

gas chromatography (HPLC) method to detect the presence of BPA in the reaction mixture of any other volatile compound.

DISCUSSION

The obtained graphs in the results showed the significant and undeniable effect of the operating parameters on yielding Bisphenol A such as amount of water as solvent, concentration of sodium hydroxide as catalyst and time

processing. As discussed in results and according to the Figures 1 and 2, variation of amount of water caused fluctuation in yield of BPA. This fluctuation has a great similarity with parametric study which had been done by liu et al. (2009). As another effective parameter the effect of the concentration of NaOH as catalyst on yielding of BPA has also been studied. As maintained in the results and based on Figure 3, the highest yield of BPA achieved at the present of 0.5 g NaOH. This achievement proved previously by (Mohammad, 2011; Fusheng et al., 2009). As the main advantage of this research, the highest yield

of BPA achieved in significantly shorter time processing compare with previous studies (Tagaya et al., 1998; Jie et al., 2006) however, the effect of time processing variation on yield of BPA had a completely same manner with literatures (Mohammad, 20011; Jie et al., 2006; Pan et al., 2006; Liu et al., 2009 a,b). The obtained FTIR spectroscopy of BPA in the results showed that the chemical structure of pure BPA. Based on the comparison of these peaks with previous studies (Mohammad, 2011; Liu et al., 2009; Pinero et al., 2005; Jang and Wilkie 2004) it is observed that there are high similarities between them and the formation of BPA can be confirmed. According to the result, HPLC system was used to determine the presence of specific chemicals (analyses) in a sample. Pinero et al. (2005) have used the HPLC to separate the aromatic compounds, in particular bisphenol A and phenols. The data acquisition and joining was similar to Figure 6 in the result.

Conclusion

Hydrolysis degradation of PC under microwave irradiation to its monomer of BPA was done by using NaOH as catalyst in presence of tetrahydrofuran as co-solvent in which PC can substantially dissolve. PC was almost completely degraded to give 94% yield of BPA by using 20 g THF, 3.5 g H₂O as main solvent and 0.5 g NaOH at 110°C during 12.5 min at lower power of microwave.

REFERENCES

- Achilias D, Redhwi H, Siddiqui M, Nikolaidis A, Bikiaris D, Karayannidis G (2010). Glycolytic depolymerization of PET waste in a microwave reactor. *Appl. Polymer. Sci.* 118: 3066-3073
- Hu L, Oku A, Yamada E, Tomari K (1997). Alkali – decomposition of poly (ethylene terephthalate) in mixed media of nonaqueous alcohol and ether. *Polymer* 29:708-712.
- Jang B, Wilkie C (2004). A TGA/FTIR and mass spectral study on the thermal degradation of bisphenol A polycarbonate. *Degrad. Stab.* 86:419-430.
- Jie H, Ke H, Qing Z, Yougqiang W, Zibin Z (2006). Study on depolymerization of polycarbonate in supercritical ethanol, *Polymer Degrad. Stab.* 91:2307-2314.
- Lorenzetti C, Maaresi P, Berti C, Barbiroli G (2006). Chemical recovery of useful chemicals from polyester (PET) waste for resource conservation: A survey of state of the art. *Polymers Environ.* 14:89-100.
- Liu F, Li Z, Yu S, Cui X, Ge X (2009a). A new route to recover bisphenol A and dimethyl carbonate from waste polycarbonate in ionic liquids: college of Chemical Engineering, Qingdao University of Science and Technology, Qingdao, China pp.261-271.
- Liu F, Li Z, Yu S, Cui X, Xie C, Ge X (2009b). Methanolysis and Hydrolysis of Polycarbonate Under Moderate Conditions. *Polymers Environ.* 17: 208-211
- Liu F, Li L, Yu S, Lv Z, Ge X (2011). Methanolysis of polycarbonate catalysed by ionic liquid [Bmim][Ac]. *Hazard. Mater.* 189:249-254.
- Mohammad A (2011). Glycolysis of polycarbonate wastes with microwave irradiation. *Polymer* pp.381-384.
- Pinero R, Garcia J, Cocero M (2005). Chemical recycling of polycarbonate in a semi-continuous lab-plant. A green route with methanol and methanol–water mixtures. *Green Chem.* 7:380-387.
- Pan Z, Bao Z, Chen Y (2006). Depolymerization of poly (bisphenol A carbonate) in subcritical and supercritical toluene. *Chinese Chem. Lett.* pp.545-548
- Sinha V, Patel M, Patel J (2008). Pet waste management by chemical recycling: A review. *Polymer Environ.* 18:8-25.
- Shukla S, Palekar V, Pingale N (2008). Ziolite Catalyzed glycolysis of poly (ethylene terephthalate) bottle wastes. *Appl. Polymer. Sci.* 110: 501-506.
- Sala M, Kitahara Y, Takahashi S, Fujii T (2010). Effect of atmosphere and catalyst on reducing bisphenol A (BPA) emission during thermal degradation of polycarbonate. *Chemosphere* 78:42-45.
- Siddiqui M, Achilias D, Bikiaris D, Katsogiannis K, Karayannidis G (2010). Hydrolytic depolymerization of PET in a microwave reactor. *Macromol. Mater. Eng.* 295:575-584.
- Tagaya H, Katoh K, Kadokawa J, Chiba K (1998). Decomposition of Polycarbonate in subcritical and supercritical water. *Polymer Degrad. Stab.* 64:289-292.