

Recovery of phenols from bisphenol A polycarbonate in the presence of MgO

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Abstract

Polycarbonate was hydrolyzed and pyrolyzed in the presence of MgO as bed material of a fluidized bed reactor. Pyrolysis was carried out at 480 °C and hydrolysis between 350 and 500 °C. Pyrolysis resulted mainly in residue, while significant amounts of phenols were obtained from hydrolysis. The highest BPA yield (26 wt%) was achieved at 400 °C. At lower temperatures more phenol and IPP were obtained as products from the fission of BPA, probably because of the reduced hydrolysis rate. At higher temperatures, BPA was degraded and high phenol yields were obtained. At any temperature, about 40 wt% of high boiling products were observed, indicating the volatilization of oligomeric material.

Keywords: Chemical recycling; Monomer recovery; Fluidized bed

1. Introduction

Poly(bisphenol A carbonate) (PC) is the most used polymer within the family of polycarbonates. PC is produced in large volumes and in Japan alone made up for 3.4% of the total thermoplastic resin production for the first four months of 2012 [1]. PC is generally used for its transparency, strength, and heat resistance. It is used e.g. in the production of optical storage media, reusable water bottles, and automobile headlights.

PC can be recycled by both mechanical and chemical methods. Mechanical recycling is applicable for controlled and cleaned waste streams, but falls short if the waste is of a more inhomogeneous type. Due to the ester bonds of PC, hydrolysis is a common approach for chemical recycling. However, water as a solvent in the hydrolysis of PC requires subcritical conditions at high pressure, making the process uneconomical. The use of organic solvents often lead to problems in the separation stage and solvent treatment requires special efforts. Also, the use of solvents in the case of impurities might result in contaminated recycle.

As an alternative to liquid systems, this work focuses on high temperature steam and MgO as a catalyst. MgO was previously found to be effective in promoting the degradation of PC into compounds such as isopropenylphenol (IPP), bisphenol A (BPA), and phenol [2] using a fixed bed reactor. In order to investigate the reaction under real processing conditions, a fluidized bed reactor was used. In contrast to a fixed bed, a fluidized bed is characterized by high heat transfer, ensuring more stable reaction conditions and a uniform temperature profile.

2. Materials and Methods

The materials used for this investigation were PC (Panlite® AD-5504, Teijin) and MgO (beads 98%, Sigma-

Aldrich). The PC was ground and sieved to obtain a particle size of less than 0.5 mm, while the bed material (MgO) was ground and the fraction with a particle size between 0.3 and 0.5 mm was used.

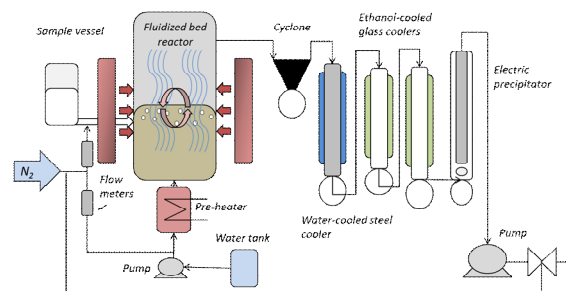


Fig. 1. Fluidized bed plant.

Experiments under hydrolysis conditions were performed between 350 and 500 °C in a laboratory scale fluidized bed plant (Fig. 1). One experiment under pyrolysis conditions was carried out at 480 °C in the same plant. Under hydrolysis conditions the fluidizing gas was made up from steam. A small side stream of N₂ (0.5 l min⁻¹, room pressure and temperature) was used to keep reaction gas from entering the feeders. Under pyrolysis conditions the reaction was performed in N₂ atmosphere. An overpressure of around 5 kPa was maintained in both experiments in order to prevent air from entering the plant. PC was fed at a speed of 100 g h⁻¹ and the products were condensed in a series of coolers.

Solid products from the hydrolysis were separated into organic and inorganic compounds by continuous extraction using diethyl ether; distillation at reduced pressure was used for pyrolysis products, resulting in a low (bp < 290 °C) and a high boiling fraction (bp > 290 °C). Liquid and gaseous products were analyzed by GC-FID, while the H₂ content of the gaseous fraction was determined by GC-TCD. For the qualitative analysis, the

retention times of compounds from the GC-FID were compared with those from GC-MS equipped with the same type of column, using the same temperature program.

3. Results and Discussion

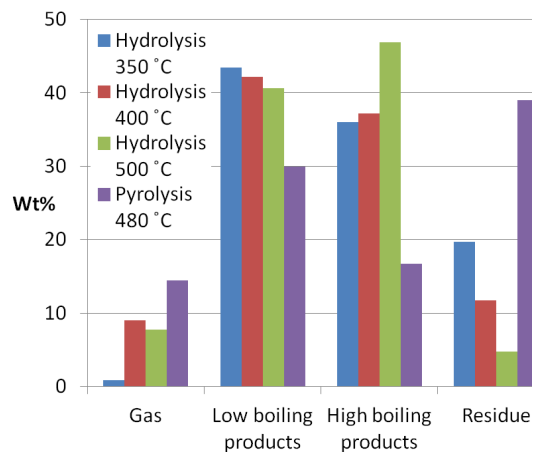


Fig. 2. Product distribution.

3.1 Fluidized bed pyrolysis

The pyrolysis reaction at 480 °C yielded 14.4 wt% gas, 29.9 wt% low boiling oil, 16.7 wt% high boiling oil and 39 wt% solid residue (Fig 2). The gas mainly consisted of CO₂ and CO. Other gaseous products were methane, hydrogen, ethylene, ethane, propylene, propyne and butenes. All were found in levels of less than 0.5 wt% of the total organic input.

More than one hundred different products were found in the low boiling oil (Fig. 3a). However, only a few were found in a significant amount. Main products were phenols. Small amounts of other aromatic compounds were also found. The amount of heavy oil and residue was problematic as the high viscosity of the oil caused plugging in coolers, resulting in problems in the reactor operation. The residue also had a strong negative effect upon the reaction as it caused defluidization of the bed material.

3.2 Fluidized bed hydrolysis

Compared with the pyrolysis, far less residue was obtained from the hydrolysis of PC (Fig. 2). Almost 20 wt% of unreacted material was found in the reactor at 350 °C, suggesting a low reaction rate at that temperature. About 40 wt% of low boiling products was found at any temperature, consisting of phenols. The highest BPA recovery (26 wt%) was achieved at 400 °C. At 350 °C, BPA was degraded to phenol and IPP, probably because of the slow hydrolysis rate, resulting in a longer residence time of PC in the reactor. At higher temperatures, the degradation of BPA was accelerated and more phenol was found. Also IPP was degraded, resulting in a rising phenol yield [2]. The tert-butylphenol yield was independent from the temperature. It can be assumed that tert-butylphenol was present as

polycondensation modifier, indicating a average molar weight of about 10,000 g mol⁻¹. At any temperature, about 40 wt% left the reactor in the form of high boiling products. It can be assumed that volatile oligomeric material left the reactor before the hydrolysis was completed. Only CO₂ was observed in the gas phase at any temperature.

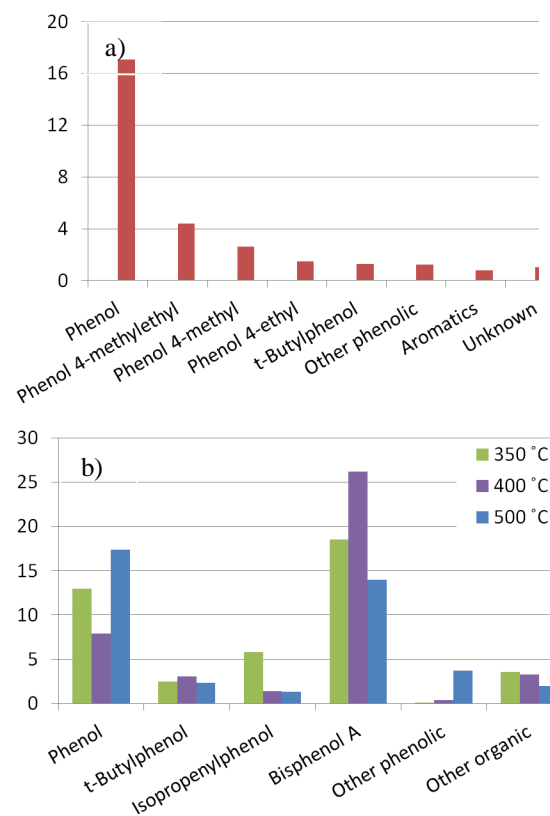


Fig. 3. Composition of the low boiling phase: a) pyrolysis at 480 °C, b) hydrolysis.

4. Conclusions

The use of steam hydrolysis in a MgO filled fluidized bed reactor for the chemical recycling of PC showed a promising way to increase the amount of phenolic products. The reduced amount of residue produced in the reactor allows a long utilization of the catalyst before deactivation. In contrast, pyrolysis of PC caused defluidization and large amounts of high boiling products and residue were produced. 400 °C was found to be the most promising temperature for PC hydrolysis. At a lower temperature, the hydrolysis rate is too slow and BPA fission occurs before hydrolysis. At higher temperatures, BPA is degraded before it can leave the reactor.

References

- [1] http://www.jpif.gr.jp/english/statistics/monthly/2012/2012_production_materials_e.htm, accessed 120719.
- [2] G. Grause, K. Sugawara, T. Mizoguchi, T. Yoshioka. *Polym. Degrad. Stab.* 94 (2009) 1119–1124.