Fluidized bed hydrolysis of poly(bisphenol-A)carbonate

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1. Introduction
Poly(bisphenol-A-carbonate) (PC) is the most produced polymer in the family of polycarbonates. It is used for applications which require high optical quality such as car head-lights, CDs and DVDs, but also for other injection molding applications as casings for electrical appliances. Solvolysis is considered the best way for the after-life treatment and high yields of bisphenol-A (BPA) can be achieved [1]. However, fillers and additives interfere with the process or reduce the product quality. Therefore, we proposed a process in steam atmosphere in the presence of MgO as a catalyst [2,3]. Earlier experiments were carried out in the mg-scale using a fixed bed reactor. In the present work, up-scaling was conducted in a fluidized bed reactor with a nominal though-put of 100 g h$^{-1}$ of organic material.

2. Experimental
All experiments were carried out with virgin PC. The efficiency of the MgO catalyst was compared with quartz sand. For comparison, pyrolysis in the absence of steam was carried out with MgO as bed material. The fluidized bed plant used for these experiments consisted of a reactor with a diameter of 52 mm fluidized by either nitrogen or steam. Input was maintained by a two-feeder system. Product gases left the reactor passing a cyclone. Then high-boiling phenols were condensed in an air-cooled steel cooler and separated in an impact precipitator. Water and low boiling products were recovered in ethanol-cooled glass coolers. Residual mist was removed from the gas flow by an electrostatic precipitator. Gas samples were taken in certain intervals. Pyrolysis was carried out at 480 °C and hydrolysis between 350 and 500 °C. Experiments were characterized by defluidization effects, making temperature control challenging.

Gaseous products were analyzed by GC-FID and GC-TCD. The bed material was burnt at 900 °C for the determination of the organic residue content and investigated by SEM.

The liquid product from the pyrolysis experiment was distilled. The light fraction was analyzed by GC-MSD and GC-FID. The residue was burnt in order to determine the heavy fraction and the inorganic fraction.

The condensed product fraction from the hydrolysis experiments comprised of an aqueous phase and an organic solid phase, which was separated by filtration. An organic liquid phase was not observed. Both organic phase and liquid phase were separately extracted by diethyl ether after acidification with hydrochloric acid. The organic phases were analyzed by GC-MSD, GC-FID, HPLC, and MALDI-ToF.

The water content of the original product was determined by Karl-Fischer analysis.
3. Results and discussion

Pyrolysis at 480 °C resulted mainly in residue and high boiling compounds. Light oil (30 wt%) comprised mainly of phenols with a high content in phenol. BPA was not observed as a product. The gas fraction (14 wt%) consisted mainly of CO₂.

The addition water in form of steam in the presence of MgO caused the hydrolysis of the carbonic acid ester bond and phenols were released more readily. Compared with pyrolysis, the yield of low boiling compounds increased. Between 350 and 450 °C, their yield was even doubled. BPA became the main product with a product fraction of 40 wt% compared with the original PC input (Figure 1). The highest BPA yield was observed at 400 °C. At higher temperatures, BPA was degraded to phenol and isopropenyl phenol (IPP) (Scheme 1).

Interestingly, using quartz sand instead of MgO resulted in unexpected changes in the behavior. Experiments with quartz sand at 500 °C and MgO at 400 °C gave very similar results, suggesting that both materials supported the hydrolysis of PC, even if MgO was the stronger catalyst. However, when the reaction temperature with quartz sand was reduced to 400 °C, the phenol recovery was barely affected, though; the impact on the product distribution was enormous. While at 400 °C in the presence of MgO the highest BPA yield was achieved, only one fourth of the BPA was obtained with quartz sand. BPA was efficiently degraded giving high yields of phenol and IPP. The IPP weight fraction reached with 17 wt% by far the highest yield in any experiment conducted.

4. Conclusion

Fluidized bed hydrolysis with MgO or quartz sand as bed material proved to be applicable for the treatment of PC. Depending on the conditions, different target compounds are accessible. Especially thermal labile IPP can be obtained with quartz sand at 400 °C.

References