

ABSTRACT OF DOCTORAL DISSERTATION

Producing of propylene carbonate and dimethyl carbonate via a double urea-glycol loop

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The subject of the doctoral dissertation was the development of a method for obtaining propylene carbonate and dimethyl carbonate via a double urea-glycol loop. The method of obtaining the above-mentioned chemical compounds is two-step. The first step of the synthesis involves the alcoholysis of urea with propylene glycol, which produces propylene carbonate and ammonia. The ammonia produced during the synthesis can be returned to the process of obtaining urea from carbon dioxide. Propylene carbonate can be a commercial product after purification or a substrate in the synthesis of dimethyl carbonate. Obtaining of dimethyl carbonate involves transesterification of propylene carbonate and methanol. During the process of dimethyl carbonate synthesis propylene glycol is also produced, which can be recycled to the synthesis of propylene carbonate by urea alcoholysis.

A review regarding the methods of propylene carbonate and dimethyl carbonate synthesis was carried out. On its basis, the choice of the method of obtaining propylene carbonate and dimethyl carbonate via urea-glycol double loop was justified. An in-depth literature study on the synthesis of PC by urea alcoholysis and DMC by transesterification of propylene carbonate with methanol was performed. On the basis of the literature review, it can be concluded that in the case of the synthesis of PC from PG and urea, the best catalysts are oxides and salts of zinc and magnesium. In the case of DMC synthesis by transesterification of propylene carbonate and methanol, the process is carried out in the presence of homogeneous sodium methanolate, but it is also possible to use heterogeneous anion resins or aluminosilicates with Lewis acid centers as catalysts. Ionic liquids are also active catalysts for the synthesis of dimethyl carbonate.

The first stage of the research was the selection of a catalyst for the synthesis of propylene carbonate. Among the zinc, magnesium, calcium, tin, aluminosilicate and silica catalysts used, the highest yield of propylene carbonate was obtained in the presence of basic zinc carbonate (79%) and zinc oxide (77%). However, these catalysts were homogeneous, which made their recovery difficult. Therefore, for further studies on the synthesis of propylene carbonate, a heterogeneous catalyst MgO:SiO₂ sol-gel 4:1 was selected, which was characterized by satisfactory activity and

selectivity in the studied reaction. Using MgO:SiO₂ sol-gel 4:1, the yield of PC was 68% and the yield of by-products 4-MOD and 5-MOD were 5 and 1%, respectively.

Then, research on the influence of the amount of catalyst, molar ratio of substrates, time and temperature on the propylene carbonate synthesis was carried out. It was revealed that the synthesis of PC in the presence of MgO:SiO₂ sol-gel 4:1 is preferably carried out for 2 h at 170°C using a 2-fold excess of PG relative to urea and using 0.3% wt. of catalyst. The yield of the PC reaction under these conditions was 93%. A kinetic model of the reaction was proposed and the dependences of the reaction rate constants on temperature were determined. Subsequently, catalyst recycle tests were successfully performed and it was proven that the MgO:SiO₂ sol-gel 4:1 maintained activity for 7 reaction cycles. It was also shown that the developed method of obtaining propylene carbonate is repeatable.

The next steps of the research were to scale-up of the process (from a 250 mL reactor to a 1-liter reactor) and purify propylene carbonate by distillation. The synthesis of PC was successfully carried out on a larger scale, and the obtained crude product was used for research on the purification of propylene carbonate by distillation under reduced pressure. As a result of vacuum distillation of the post-reaction mixture, two fractions were obtained, the first of which was a mixture of propylene glycol and propylene carbonate, and the second one contained PC with a purity of >99%, which was the final product of the process. The first fraction, containing the PG-PC mixture, was distilled at atmospheric pressure to obtain purified propylene glycol, which could be recycled for subsequent PC synthesis. Purified PG recycle to the synthesis allowed to achieve the same high reaction yield as in the case of using only fresh propylene glycol. Thus, the concept of obtaining propylene carbonate via urea alcoholysis method on a laboratory scale was positively verified. The obtained research results allowed to determine the assumptions for the design of the PC production technology.

Then, research on the synthesis of dimethyl carbonate was carried out. First, a test of catalysts was performed. For this purpose, the organic bases 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,1,3,3-tetramethylguanidine and 1,5,7-triazabicyclo[4.4.0]deca-5-ene, as well as their salts, and ionic liquids, which are salts of sulfuric acid and N,N-dimethylaminopropylamine or 1-(3-aminopropyl)imidazole, were used. High reaction yields (55-57%) were achieved using organic bases (DBU, TMG and TBD) as well as [DBUH]OFP and [HTMG]OFP. The catalyst [HTMG]OFP was selected for further studies on dimethyl carbonate synthesis.

Then, studies on the effect of the molar ratio of substrates, temperature, time and catalyst amount on the synthesis of dimethyl carbonate were carried out. Due to the fact that on the one hand the synthesis of DMC was carried out in a batch reactor and on the other hand the reaction studied is equilibrium, the molar ratio of the substrates had a great influence on the reaction yield.

The highest reaction yield was achieved with a methanol:PC molar ratio of 15:1 (79%). The DMC yields for the initial methanol:PC molar ratio of 5:1 and 2:1 reached 52-58% and 27-32%, respectively. The kinetic equation of the reaction was proposed and the dependence of reaction rate constants on temperature was determined. Further research also showed that the developed method of dimethyl carbonate synthesis is reproducible.

The next step of the research was the purification of dimethyl carbonate. Dimethyl carbonate with a purity of >98% was obtained using distillation methods. However, the method of obtaining DMC turned out to be complicated. Moreover, during the purification process, many waste streams were created and an attempt to recycle the [HTMG]OFP catalyst together with unreacted PC was unsuccessful.

The final result of the work was the preparation of a technological concept for the process of propylene carbonate synthesis by urea alcoholysis. The assumed capacity of the installation was 300 tons per year of propylene carbonate. The mass balance, block and technological schemes, description of the process, work schedule and specifications of the equipment were prepared.