

## The Industrial Production of Dimethyl Carbonate from Methanol and Carbon Dioxide

Frank F.T. de Groot\*, Roy R.G.J. Lammerink, Casper Heidemann,  
 Michiel P.M. van der Werff, Taiga Cafiero Garcia, Louis A.G.J. van der Ham,  
 Henk van den Berg

University of Twente, Faculty of Science and Technology, Drienerlolaan 5, 7522NB Enschede, Netherlands  
[f.t.degroot@student.utwente.nl](mailto:f.t.degroot@student.utwente.nl)

This work discusses the design of a dimethyl carbonate (DMC) production plant based on methanol and CO<sub>2</sub> as feed materials, which are a cheap and environment-friendly feedstock. DMC is a good alternative for methyl-tert-butyl ether (MTBE) as a fuel oxygenating agent, due to its low toxicity and fast biodegradability. Based on the MTBE demand of a general gasoline plant, the annual production capacity of the process design is stipulated to be 86 kt DMC, with a purity of 99 wt%.

Three routes are proposed to form DMC: 1) direct synthesis from methanol and CO<sub>2</sub>, 2) reaction of CO<sub>2</sub> and ammonia to urea, which can be converted to DMC with methanol, 3) reaction of ethylene oxide with CO<sub>2</sub> to a cyclic carbonate, which can be converted to DMC by transesterification with methanol. From a black box cost analysis based on raw material prices, it is concluded that the ethylene oxide route is the least profitable. Because of higher single-pass conversions found in literature, smaller recycles and easier separations, it is concluded that the urea route would be the most feasible.

The required process functions for the urea route have been determined in the conceptual design phase. A detailed design of the most important process operations is made and an overall technical and economic evaluation of the process has been carried out. In the first step of this DMC synthesis, urea is produced from carbon dioxide and ammonia with the ACES21 process. After separation and purification steps, urea is fed to a reactor with methanol (150 °C, 20 bar), where methyl carbamate (MC), an intermediate of DMC production, and ammonia are formed in the absence of a catalyst. Subsequently, MC and methanol are converted to DMC and ammonia (190 °C, 40 bar) over a ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst in a fixed-bed reactor. Methanol and DMC form an azeotrope; extractive distillation with methyl isobutyl ketone (MIBK) as entrainer is used to separate the azeotropic mixture.

The reactor model for the reaction towards DMC based on kinetic rate expressions, showed that a long residence time (>10 h) and a relatively high MeOH:MC molar feed ratio of 6 are required to achieve reasonable single-pass conversions (15 %). This resulted however in an unrealistically large reactor volume and a large methanol load on the process. A feasibility study was done in order to improve the performance of the process. It was calculated that with a MeOH:MC ratio of 2 and a single-pass conversion of MC of 30 % the process would become technically feasible; the reactor volume decreased from 5,000 m<sup>3</sup> to 600 m<sup>3</sup> and the energy consumption of the process was decreased from 238 MW to 50 MW. A Pinch analysis showed that maximally 6 MW could be saved with heat integration, which corresponds to approximately 2 M\$/y savings on energy costs.

To produce 86 kt/y of DMC, the required amounts of raw materials are 80 kt/y of methanol and 58 kt/y of CO<sub>2</sub>, which results in an overall DMC yield from methanol of 38 %. The required total capital investment of the process is 110 M\$. Economic feasibility depends on the DMC selling price. A price range between 800 and 1,100 \$/t was assumed. For 800 \$/t it is not possible to repay the capital investment within an assumed lifetime of 10 years and the process would therefore not be profitable. The break-even point is at 845 \$/t. For a selling price of 1,100 \$/t the gross profit becomes 22 M\$/y, with a payback period of 3 years and a return on investment of 20 %.

## 1. Project scope

The need for cleaner fuels from cheap feedstock has raised interest in the use of dimethyl carbonate (DMC) as a fuel additive. Since DMC has a low toxicity and is quickly biodegradable, it is an interesting alternative for methyl-tert-butyl ether (MTBE) as fuel oxygenating agent. The traditional way to produce DMC used highly toxic phosgene as raw material, but nowadays DMC is mainly produced by oxidative carbonylation of methanol (non-phosgene). In this work, a new process route is proposed to produce DMC by using only methanol and CO<sub>2</sub> as starting materials, giving the process a cheap and environment-friendly feedstock.

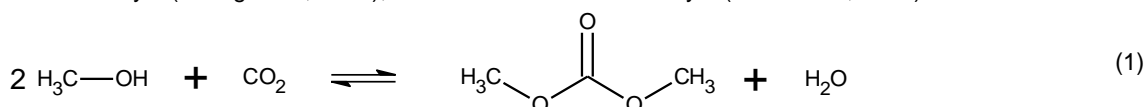
The oxygen content of DMC is approximately 3 times higher than of MTBE, which means that less DMC is required to meet the oxygen content specification for gasoline. The average production capacity of existing MTBE plants in the United States is 4,000 bbl/d with a purity of 99 %; assuming that the requirement of DMC production is one third of MTBE based on the difference of oxygen content, the required capacity of a DMC plant is assumed to be 1,333 bbl/d. Considering an operational time of 8,000 h/y, the annual production capacity upon which the design is based will be 86 kton with 99 % purity.

## 2. Process selection

There are three routes proposed to produce DMC from methanol and CO<sub>2</sub>, which will be described below: 1) direct synthesis route, 2) urea route 3) ethylene oxide route. In order to favour the equilibrium reaction towards DMC, methanol is in all cases added in a surplus and the unconverted methanol is recycled.

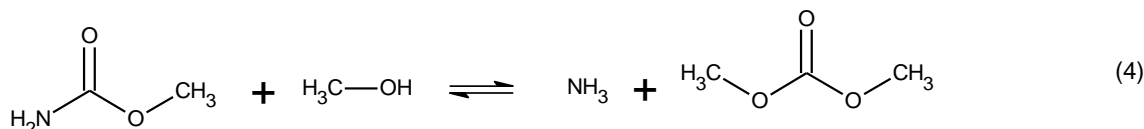
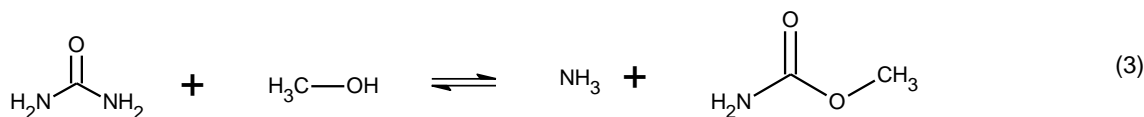
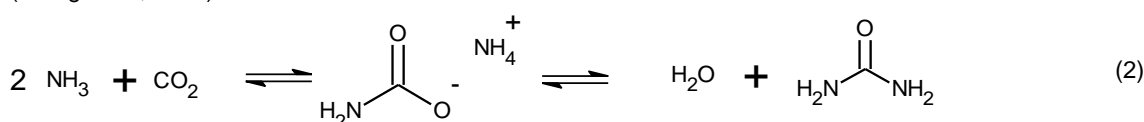
### 2.1 Direct synthesis route

This route is described with Eq(1) which directly converts methanol and CO<sub>2</sub> to DMC without any intermediates. Reported single-pass conversions are in the range of 5-10 %, using a Cu-based catalytic membrane reactor (Li and Zhong, 2003), basic compounds as catalyst (Cai et al., 2009), ceria-zirconia-based catalyst (Zhang et al., 2011), and a Cu-Ni bimetallic catalyst (Chen et al., 2012).



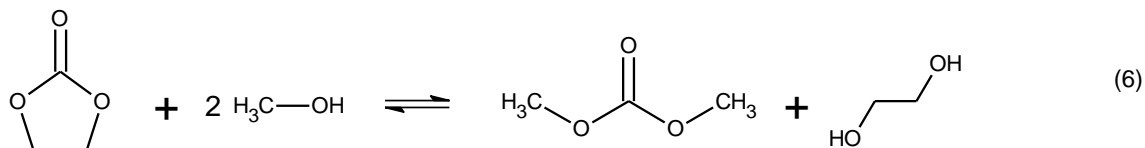
### 2.2 Urea route

The first step of the urea route is the uncatalysed reaction of ammonia and carbon dioxide to form urea, according to Eq(2) (Meessen, 2000). The second step is the uncatalysed reaction of urea with methanol by which an intermediate, methyl carbamate (MC), is formed according to Eq(3). MC reacts over a ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst with methanol producing DMC and ammonia, as shown in Eq(4). The reaction conditions are in the range of 160-190 °C and 20-40 bar; reported single-pass conversions of DMC are up to 30 %, using a ZnO catalyst (Wang et al., 2005), solid base catalysts (Wang et al., 2006), and by reactive distillation (Wang et al., 2007).



### 2.3 Ethylene oxide route

The use of ethylene oxide for synthesis of DMC is possible via its carbonylation at 190 °C and using a heterogeneous anion exchange resin catalyst to obtain a cyclic carbonate, according to Eq(5), followed by a transesterification with methanol to produce DMC, Eq(6) (Cao et al., 2006).



From an overall cost analysis based on raw material prices, it is concluded that the ethylene oxide route is the least profitable. Material balances showed far better results for the urea route compared to the direct synthesis route, which is due to the lower conversions reported in literature. Conversions per pass above 10 % are hardly reported, whereas a sensitivity analysis showed that a conversion to DMC of at least 20 % should be achieved to be competitive with the urea route. Low conversions result in large recycle flows, and hence high costs. Therefore the urea route is selected based on the fact that the recycle streams are much smaller than for the direct synthesis route. Moreover, the direct synthesis route poses a more difficult challenge in separations. Where the DMC reactor effluent in the urea process contains only a binary azeotropic mixture (DMC/methanol), the direct synthesis route contains a ternary azeotrope (water/methanol/DMC). This would result in a more advanced and more expensive separation section, and therefore the urea route is preferred. Furthermore, for the urea process more consistent literature data on catalysts is available. There is one type of catalyst that shows the best results in terms of DMC yield ( $\text{ZnO}-\text{Al}_2\text{O}_3$ ), which is already commercially available as well. In contrast, for direct synthesis a range of experimental catalysts are still under investigation showing comparable results, without one that stands out. The entire process of making decisions is schematically displayed in Figure 1.

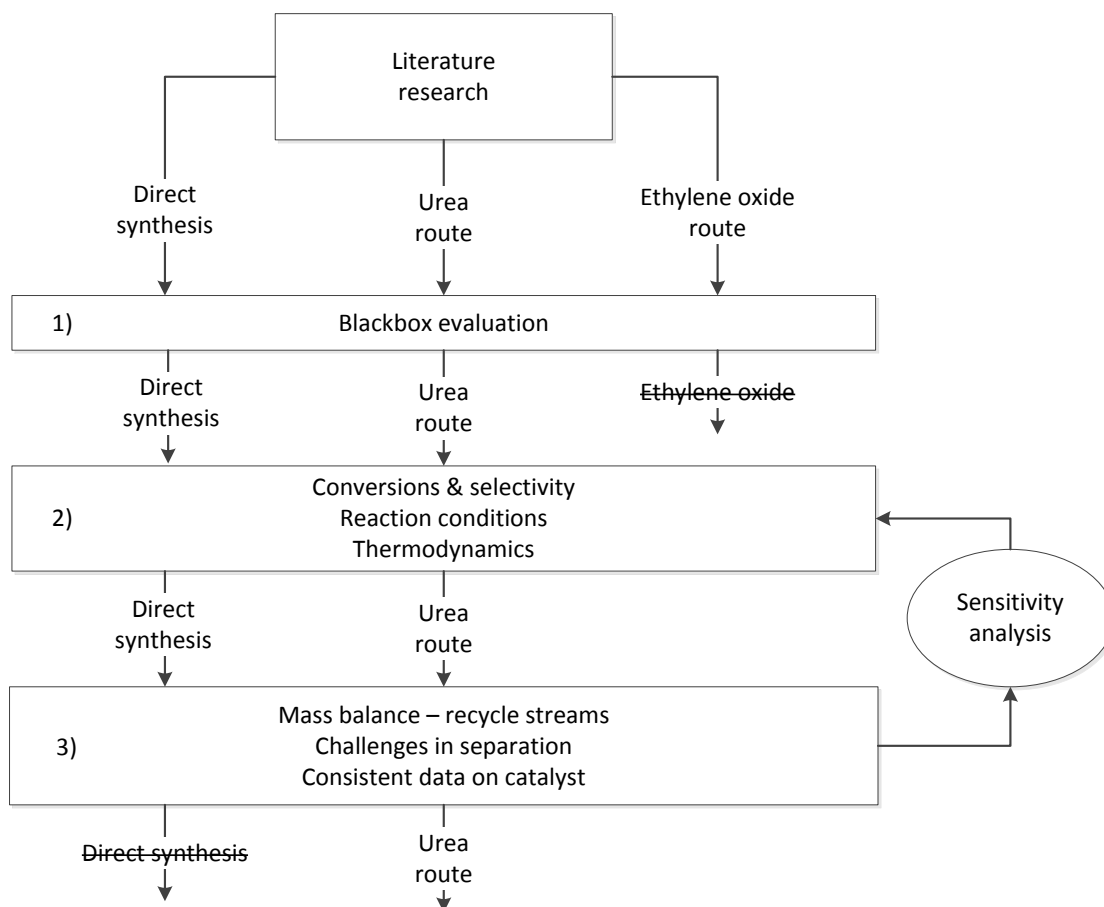


Figure 1: Decision tree of process selection

### 3. Conceptual design

In the conceptual design of the process, several process sections are defined: urea production, MC reactor, DMC reactor (Eqs(2), (3), (4), resp.) and separation section. The design of the urea production section is based on the existing ACES21 process, which is the most energy and cost-efficient commercially applied urea production process (Meessen, 2000). For the other process sections, several options are considered as shown in Figure 2, with the selected option highlighted.

Figure 2 shows that for the reactor section three possibilities are considered: carrying out reaction Eq(3) and Eq(4) in a single reactor (option 1a), in two separate reactors (option 1b), in two separate reactors while removing the side-product in-between (option 1c). Since high conversions of urea to MC in the absence of a catalyst (150 °C and 20 bar) are observed in literature (Sun et al., 2004), it can be assumed that reaction Eq(3) with complete urea conversion to MC can be achieved in a simple heated vessel. Since the ammonia that is produced in this reaction drastically decreases the conversion of MC to DMC, removal of ammonia is required and therefore option 1c is selected. Based on kinetic and equilibrium data from literature (Lin et al., 2004), a reactor was designed to model reaction Eq(4) towards DMC. Based on this study, a fixed-bed type reactor is proposed, which gives reasonable single-pass conversions (~13.6 %) and N-methyl methyl carbamate (N-MMC) as only major byproduct (~1.7 %) at optimized operation conditions of  $T=190$  °C and  $P=40$  bar.

The reactor effluent, containing DMC, MC, methanol,  $\text{NH}_3$ ,  $\text{CO}_2$  and N-MMC, has to be purified in order to obtain DMC with 99 % purity. Based on rules of thumb, it is decided that non-condensable gases have to be separated first, and that the most difficult separation (azeotropic methanol/DMC mixture) has to be carried out as last; this results in the selection of option 2a for the separation section in Figure 2. Methanol and DMC form an azeotrope (Matsuda et al., 2011) and can therefore not be separated by conventional distillation. Several possibilities to overcome this azeotrope were investigated. The methanol content of the stream is too high to obtain pure DMC by pervaporation. Furthermore, it was shown that the difference in boiling points between methanol and the azeotropic mixture at atmospheric pressure was too small ( $\pm 1$  °C) to carry out pressure-swing distillation. Extractive distillation with methyl isobutyl ketone (MIBK) as an entrainer was found to be the most promising method.

### 4. Process evaluation

Since the conversion of MC to DMC is limited by an equilibrium reaction, a large excess of methanol is required to shift the equilibrium to the product side. This resulted in an excessively high methanol load on the process, by which unrealistically high separation energy cost and recycle streams were required. Moreover, due to the slow kinetics, the required residence times resulted in a too large reactor volume. These results were based on thermodynamic and kinetic data found in literature (Lin et al., 2004), and the preliminary conclusion could be drawn that this "base-case" scenario is not technically feasible. Therefore, in order to develop a technically feasible process, different scenarios with faster kinetics and more favorable equilibrium conditions than reported in literature were evaluated. The goal of this feasibility study was to obtain realistic values for the energy consumption and recycle streams, by varying the conversion to DMC and the MeOH:MC ratio in the feed. Additionally, it is assumed that in the future the kinetics can

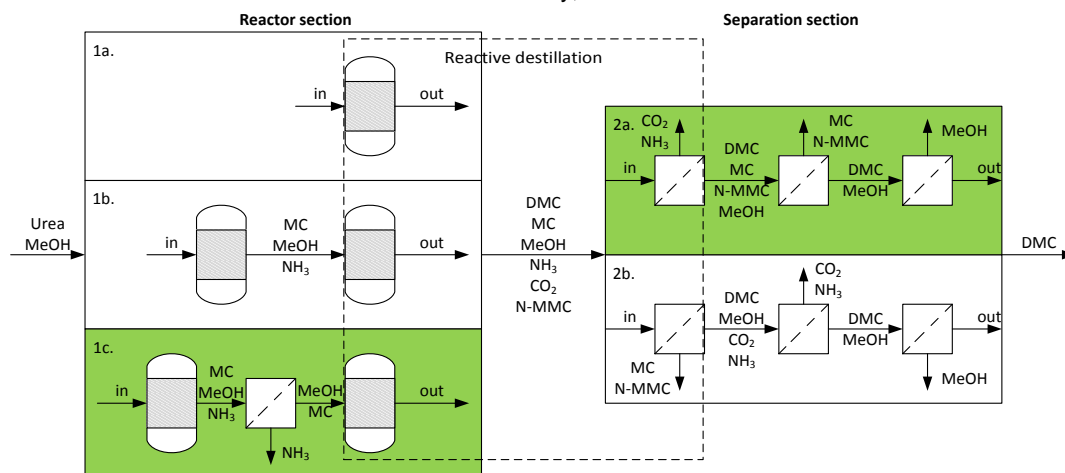


Figure 2: Conceptual design options and selection of DMC reactor section and separation train

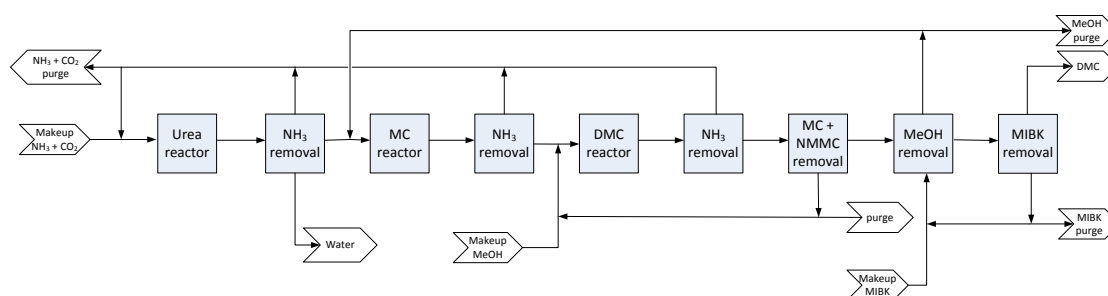


Figure 3: Block diagram of the process

be increased with a factor 5 due to better catalysts and that one of the products is selectively removed (i.e. membrane reactor, reactive distillation, etc.), so that the backward reaction cannot occur. For each scenario the energy consumption and the reactor volume were calculated. From this feasibility study, the scenario with a MeOH:MC ratio of 2 and a single-pass conversion of MC of 30 % was calculated to be most feasible; the energy consumption of the process was decreased from 238 MW to 50 MW, and the reactor volume from 5,000 m<sup>3</sup> to 600 m<sup>3</sup>.

Based on the selected reactor and separation design, a Process Flow Diagram is constructed, which is schematically displayed in Figure 3. Simulation of the process is carried out using UniSim®. The Wilson model is selected as thermodynamic property set, since it is recommended for simulating azeotropic separations. To produce 86 kt/y of DMC, the required amounts of raw materials are 80 kt of methanol and 58 kt of CO<sub>2</sub>, which results in an overall DMC yield from methanol of 38 %. The total energy consumption of the process is 50 MW. To evaluate the savings on energy that could be achieved, a heat integration study is carried out based on Pinch technology. A reduction of 6 MW is possible when heat integration is considered, which will save approximately 2 M\$/y on energy costs. This means that it is an investment well worth considering in future studies of the process. However, the capital investment for the plant will increase due to the heat exchangers. To which extent a heat exchanger network will be profitable is not evaluated, since it is outside the scope of this project.

## 5. Process economics

For the basic sizing of the major equipment the methods discussed in Chemical Engineering Design (Sinnott and Towler, 2009) are used. Based on this equipment list with major sizes the sum of bare equipment costs is estimated and multiplied by the Hand factor to obtain an estimate of the ISBL cost. The total CAPEX is calculated with a factor method based on the ISBL (see Table 1).

Operating costs are calculated based on market prices of raw materials, utilities, consumed catalyst and waste disposal. The gross profit is calculated by subtracting the operating costs from the revenues, see Table 2. The main contributor to the revenues of the process is the selling price of DMC. A reliable market price of DMC could hardly be found in literature, and therefore a price range between 800 and 1,100 \$/t was assumed. For 800 \$/t it was determined that it is not possible to repay the capital investment within its life time and the process would therefore not be profitable. The break-even point is at 845 \$/t, and for a selling price of 1,100 \$/t the gross profit becomes 22 M\$/y. At the highest selling price, the payback period is 3 y with a return on investment of 20 %.

Table 1: Estimation of total capital investment based on factorial method

Inside Battery Limits (ISBL) cost		M\$58
Offsite (OSBL)	0.3	M\$17
Design and Engineering (D&E)	0.3	M\$17
Contingency (X)	0.1	M\$6
Total fixed capital cost		M\$100
Working capital	0.1	M\$10
Total capital investment		M\$110

Table 2: Summary of process characteristics

Production DMC	86	kt/y
Raw materials		
- Methanol	80	kt/y
- CO <sub>2</sub>	58	kt/y
DMC yield	38	%
Energy consumption	50	MW
Reactor volume	600	m <sup>3</sup>
Total capital investment	110	M\$
Gross Profit	22	M\$/y
Return on Investment	20	%
Payback Period	3	y

## 6. Conclusions

The aim of this project was to design a process for producing DMC from methanol and CO<sub>2</sub> at industrial scale. A summary of the process characteristics that were obtained is shown in Table 2. Under the assumptions that have led to these results, the process seems to be technically feasible and economically viable. The main considerations that should be taken into account are 1) reaction conditions with a more favorable equilibrium and faster kinetics, 2) the price of DMC of 1,100 \$/t.

## References

- Cai Q., Lu B., Guo L., Shan Y., 2009, Studies on synthesis of dimethyl carbonate from methanol and carbon dioxide, *Catalysis Communications*, 10, 605-609.
- Cao M., Meng Y., Lu Y., 2006, Synthesis of dimethyl carbonate (DMC) from CO<sub>2</sub>, ethylene oxide and methanol using heterogeneous anion exchange resins as catalysts, *Reaction Kinetics and Catalysis Letters*, 88, 251-259.
- Chen H., Wang S., Xiao M., Han D., Lu Y., Meng Y., 2012, Direct Synthesis of Dimethyl Carbonate from CO<sub>2</sub> and CH<sub>3</sub>OH Using 0.4 nm Molecular Sieve Supported Cu-Ni Bimetal Catalyst, *Chinese Journal of Chemical Engineering*, 20, 906-913.
- Li C.-F., Zhong S.-H., 2003, Study on application of membrane reactor in direct synthesis DMC from CO<sub>2</sub> and CH<sub>3</sub>OH over Cu-KF/MgSiO catalyst, *Catalysis Today*, 82, 83-90.
- Lin H., Yang B., Sun J., Wang X., Wang D., 2004, Kinetics studies for the synthesis of dimethyl carbonate from urea and methanol, *Chemical Engineering Journal*, 103, 21-27.
- Matsuda H., Takahara H., Fujino S., Constantinescu D., Kurihara K., Tochigi K., Ochi K., Gmehling J., 2011, Selection of entrainers for the separation of the binary azeotropic system methanol/dimethyl carbonate by extractive distillation, *Fluid Phase Equilibria*, 310, 166-181.
- Meessen J.H., 2000, Urea, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, Germany.
- Sinnott R.K., Towler G., 2009, *Chemical Engineering Design*, Elsevier, Oxford, UK.
- Sun J., Yang B., Lin H., 2004, A Semi-continuous Process for the Synthesis of Methyl Carbamate from Urea and Methanol, *Chemical Engineering & Technology*, 27, 435-439.
- Wang M., Wang H., Zhao N., Wei W., Sun Y., 2007, High-Yield Synthesis of Dimethyl Carbonate from Urea and Methanol Using a Catalytic Distillation Process, *Industrial & Engineering Chemistry Research*, 46, 2683-2687.
- Wang M., Wang H., Zhao N., Wei W., Sun Y., 2006, Synthesis of dimethyl carbonate from urea and methanol over solid base catalysts, *Catalysis Communications*, 7, 6-10.
- Wang M., Zhao N., Wei W., Sun Y., 2005, Synthesis of Dimethyl Carbonate from Urea and Methanol over ZnO, *Industrial & Engineering Chemistry Research*, 44, 7596-7599.
- Zhang Z.-F., Liu Z.-W., Lu J., Liu Z.-T., 2011, Synthesis of Dimethyl Carbonate from Carbon Dioxide and Methanol over CexZr1-xO<sub>2</sub> and [EMIM]Br/Ce0.5Zr0.5O<sub>2</sub>, *Industrial & Engineering Chemistry Research*, 50, 1981-1988.