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Reactive rectifying for producing dimethyl carbonate

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Abstract

A process for producing dimethyl carbonate (DMC) from methanol and urea, using polyphosphoric acid (PPA) as the catalyst, has been carried out by conducting the reaction continuously under reactive rectifying conditions on a laboratory scale. Several operational variables which have an influence on the yield of DMC, such as the total feed flow rate, bottom temperature, pressure, reflux ratio, mass ratio of the reactants, the concentration of the catalyst and the stirring speed, were investigated to achieve an optimum operation. Under these optimized settings, the highest yield of DMC obtained was 92.2%. A high concentration and purity of DMC in the overhead products, more than 17%, was gained in the reactive rectifying conditions.

Keywords: Reactive rectifying; Dimethyl carbonate; Polyphosphoric acid; Urea; Methanol

1. Introduction

Dimethyl carbonate (DMC) has been considered as an environmentally benign chemical and applied widely during the last few years because of its the low toxicity and quick biodegradation [1,2]. DMC is typically synthesized by either phosgenation of methanol, oxidative carbonylation of methanol, and transesterification of ethylene carbonate with methanol [3–8]. Each of the aforementioned processes has either commercial or technical disadvantages. For example, phosgenation is a complicated and expensive process, phosgene is a highly toxic chemical; the oxidative carbonylation process requires expensive technology for handling carbon monoxide under high pressure and avoidance of flammable mixture in the reactor and the transesterification of ethylene carbonate with methanol is operationally and economically unfavorable since the production of dimethyl carbonate always accompanies the simultaneous production of a stoichiometric amount of glycol and ethylene carbonate is expensive.

The alcoholysis of urea for the synthesis of DMC as shown in Eq. (1) is a newly developed technology. Urea and methanol are used as starting materials having abundant resource and low cost. Since there is no water formed, the reaction mixture (in the overhead product) does not form a ternary azeotrope (methanol–water–DMC). Hence the subsequent separation and purification of DMC is easy.

$$NH_2CONH_2 + 2CH_3OH \leftrightharpoons CH_3OCOOCH_3 + 2NH_3 \qquad (1)$$

In this process, DMC is synthesized in two steps from urea and methanol via a methyl carbamate (MC) intermediate in the presence of various heterogeneous and homogeneous catalysts [9–12].

$$NH_2CONH_2 + CH_3OH \leftrightharpoons NH_2COOCH_3 + NH_3 \qquad (2)$$

$$NH_2COOCH_3 + CH_3OH \leftrightharpoons CH_3OCOOCH_3 + NH_3 \qquad (3)$$

These reactions are reversible and accompany the production of ammonia. Moreover, the DMC can react with methyl carbamate or urea, and the *N*-methyl by-products such as *N*-methyl methyl carbamate (*N*-NMC) and *N*-methylurea (*N*-MUrea) are produced as described by Eqs. (4) and (5):

$$CH_3OCOOCH_3 + NH_2COOCH_3 \leftrightharpoons CH_3NHCOOCH_3 + CH_3OH + CO_2 \qquad (4)$$

$$CH_3OCOOCH_3 + NH_2CONH_2 \leftrightharpoons CH_3NHCONH_2 + CH_3OH + CO_2 \qquad (5)$$

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Although this approach has many advantages, few reports are written about it. The most active catalysts reported in the prior literatures are organotin derivatives and metal oxides. However, there exist some problems such as low DMC yields and slow rates of the reaction according to the results reported by the authors and other researchers [13–19].

To accomplish a high yield of DMC, it is important (a) to choose a new catalyst with an high activity and selectivity to DMC, (b) to avoid the formation of *N*-methyl by-products during the DMC synthesis process and (c) to accelerate the equilibria of Eqs. (2) and (3) shifts to the right, therefore DMC and ammonia produced in the reactions need to be removed from the reactor as quickly as possible.

Via the thermodynamics calculation, the enthalpy change of Eq. (1) is $\Delta H_R^0 = +47.11\,\text{kJ/mol}$, and the change of Gibbs free energy is $\Delta G_R^0 = +4.3\,\text{kJ/mol}$. One can notice this reaction cannot take place spontaneously and some chemical or physical means must be induced to make it possible.

In a previous research, we investigated a number of catalysts, such as zinc oxide, calcium oxide, magnesia, 1,1,3,3-tetrabutyl-1-methoxy-3-isocyanatodistannoxane, zinc stearate, calcium stearate and polyphosphoric acid (PPA). Among these catalysts, the PPA shows a remarkable high activity and selectivity to DMC [20]. PPA can also be used as an adsorbent to remove ammonia from reactive liquid and to form ammonium hydrogen phosphate shown in Eq. (6):

$$\begin{aligned}&NH_2CONH_2 + 2CH_3OH + 2H_3PO_4\\&\rightleftharpoons CH_3OCOOCH_3 + 2NH_4H_2PO_4\end{aligned} \tag{6}$$

The change of Gibbs free energy of Eq. (6) is $\Delta G_R^0 = -30.2\,\text{kJ/mol}$ and the reaction equilibrium constant is 1.95×10^5 in 298.15 K. These prove that this reaction can take place spontaneously.

The process combined reaction and separation can be considered as an effective method to shift the equilibria of reversible reaction and to increase the yield of target product. Therefore, the reactive rectifying was employed for effectively removing DMC from the reaction zone to increase the DMC yield in this work. As shown in Table 1, the boiling point of azeotrope formed from methanol and DMC is lower than that of methanol and DMC. In other words, the operation of reactive rectifying is reasonable and the azeotrope can be concentrated in the overhead of reactive rectifying column. Because of the low concentration of DMC in the autoclave, the synthesis reaction of DMC will be enhanced and the formation of *N*-methyl by-products can thus be minimized.

Table 1
Summary of azeotropic DMC–methanol mixture

NBP	Boiling point (K)	Molecular weight
Binary azeotrope (70% methanol + 30% DMC)	336.2 K	–
Methanol	337.6	32.04
DMC	363.3	90.01

2. Experimental

2.1. Materials

Methanol, urea, *p*-dimethylaminobenzaldehyde (PDAB), *N*-methylurea and *N*-methyl methyl carbamate were purchased from Xi’an Chemical Reagent of China. PPA ($P_2O_5 \geq 85\%$, high viscosity colorless liquid, $\rho = 2.1$) was purchased from Shanghai Chemical Reagent of China. The standard sample DMC was purchased from Fluka Chemie GmbH CH-9471 Buchs (Germany). All the chemicals were of analytical grade and were used without further purification. N_2 (>99%) was purchased from Xi’an Chemical Corporation of China.

2.2. Experimental procedure and apparatus

The scheme of reactive rectifying system is shown in Fig. 1. The reactions were carried out in a stainless steel 750 mL autoclave with electric heating and dynamoelectric stirring. The distillation column, packed with ceramic saddles, was 0.025 m in diameter and 1.5 m in length.

Urea, methanol and PPA were premixed with a fixed ratio in the feed vessel 2 and 300 mL mixture was pumped to the autoclave 5. The whole system was then flushed with nitrogen to replace air before the start-up of operation. When the mixture in the autoclave was heated to the selected temperature, the feed mixture was pumped into the autoclave continuously and the operation was started. The reaction products were removed from the autoclave and condensed in condenser 10. Then the ammonia was released as gas via line 11 and the mixture of DMC and methanol was liquefied and left the system via cooler 12 to the products vessel. Small samples (approximately 1 mL each) were periodically withdrawn from the overhead and the autoclave during the experiment, and then analyzed by gas chromatograph.

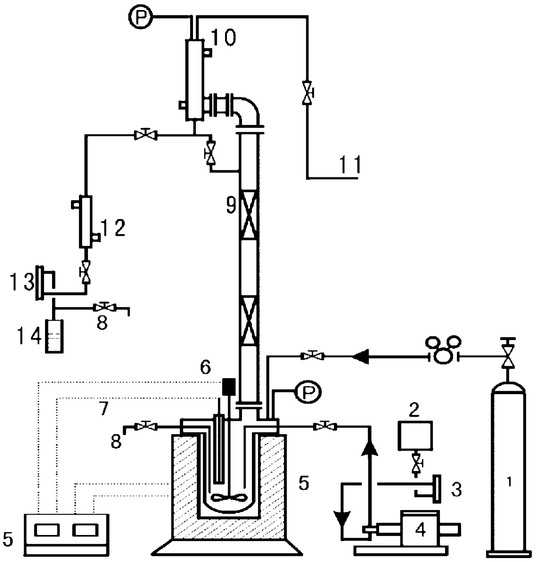

Fig. 1. Schematic diagram of the experiment apparatus. 1, N_2 cylinder; 2, feed vessel; 3, rotometer; 4, ram-type pump; 5, autoclave; 6, stirrer; 7, thermocouple; 8, sampling port; 9, packing column; 10, condenser; 11, overhead gas product absorption vessel; 12, cooler; 13, rotometer; 14, overhead liquid product vessel.

The temperature was monitored in six locations along the column 9, and the pressure of the autoclave and the overhead was also measured.

The reaction was carried out for 6 h in each run. Then, the unit was shut down and immediately cooled down in order to stop the reactions. All composite from overhead liquid product, the inventory materials in the autoclave and column were removed, collected from the system and weighed. The yield of DMC thus can be calculated.

2.3. Analysis

2.3.1. DMC analysis

The small samples withdrawn from the reactor were distilled. The distillated part that involved DMC and methanol were analyzed by a gas chromatograph (HP 4890D) using a HP-5 capillary column (15 m × 0.530 mm × 1.5 μm), column temperature: 433 K and a thermal conductivity detector (TCD). The external standard method was used to carry out the quantitative analysis of DMC.

2.3.2. N-MUrea and N-MMC analysis and identification

Actually, the Ehrlich reaction occurred when *N*-MUrea, *N*-MMC, MC and urea reacted with *p*-dimethylaminobenzaldehyde in acidic solution, which yielded lemon-yellow derivatives. They have stronger absorption at 420 nm. Therefore, the quantitative analysis for them can be done by HPLC using UV–vis detector at 420 nm.

N-MMC and *N*-MUrea were identified by retention time comparing with the standard samples. Retention times of colored derivatives of MC, *N*-MMC, Urea and *N*-MUrea were 8.5, 9.7, 12.8 and 13.4 min, respectively, when using a Hypersil C18 column with mobile phase comprised of 15% acetonitrile in water, flow rate 1.0 mL/min and column temperature 303 K.

2.4. Calculations

The yield of DMC was calculated by formula (7). The yield of *N*-MUrea and *N*-MMC were calculated using formula (8). The total moles DMC, *N*-MUrea and *N*-MMC means the cumulative amount of DMC, *N*-MUrea and *N*-MMC formed over the 6 h duration of the experiment, respectively. The total moles urea means the sum of urea introduced into the autoclave in the whole operation.

$$Y_{\mathrm{DMC}} = \frac{\text{Total moles DMC}}{\text{Total moles urea}} \times 100\% \qquad (7)$$

$$Y_{N\text{-MUrea or }N\text{-MMC}} = \frac{\text{Total moles }N\text{-MUrea or }N\text{-MMC}}{\text{Total moles urea}} \times 100\% \qquad (8)$$

3. Results and discussion

3.1. Two representative experiments results

Great deals of experiments were done in order to investigate the influence of several operational variables on the yield of DMC. Two representative experiments results are listed in Table 2. For running 1, the final overhead products contained 15.6% DMC, 84.4% methanol and trace ammonia; the bottom products contained 4.8% DMC, 2.3% *N*-MMC, 3.4% *N*-MUrea, 85.4% methanol and 4.6% others, respectively. For running 2, the overhead products contained 17.9% DMC, 82.1% methanol and trace ammonia; the bottom products contained 2.8% DMC, 2.1% *N*-MMC, 2.4% *N*-MUrea, 89.3% methanol and 3.4% others, respectively. The mass ratio of all the products to the total feed is larger than 95%, and the mass balances of the reactive rectifying column thus can be verified.

Table 2
The operational conditions and results of two representative experiments

Running	1	2
Precharged feed mix in autoclave	40 g urea/200 g methanol/40 g PPA	25 g urea/200 g methanol/20 g PPA
Total feed flow rate (mL/h)	150	200
Autoclave temperature (K)	417	403
Overhead product rate (mL/h)	150	200
Yield of DMC (%)	42.3	89.2
DMC recovered as overhead product (g)	99.44	182.8
DMC content in the overhead product (%)	15.6	17.9
Mass balance (%)	95.9	98.7

3.2. Effect of pressure on the operation

The pressure was an important operational variable in this system [21]. Table 3 shows the azeotropic temperature and composition at different pressure. As shown in this table, the DMC content in azeotrope decreased with the increase of the pressure, and thus lower pressure is preferred to increase the content of DMC in the overhead products. Therefore, the pressure in reactive rectifying was not pre-set with the inert gas; it was just autogenously about 0.5 MPa when the system attains the steady state.

3.3. Effect of total feed flow rate on DMC yields

The total feed flow rate varied from 140 to 270 mL/h with the mass ratio of feed and the temperature constant. The exit flow rate of the column varied with the variety of the total feed flow rate. But the yield of DMC had no significant change, hence,

Table 3
The azeotropic temperature and composition at different pressure

Pressure (MPa)	Temperature (K)	Azeotropic composition (wt%)	
		Methanol	DMC
0.1	337.15	70.0	30.0
0.2	355.15	73.4	26.6
0.4	377.15	79.3	20.7
0.6	391.15	82.5	17.5
0.8	402.15	85.2	14.8
1.0	411.15	87.6	12.4

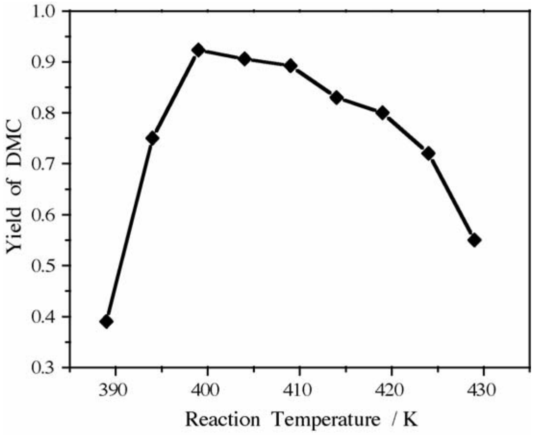

Fig. 2. The effect of reaction temperature on DMC yield. Reaction time, 6.0 h; methanol/urea mass ratio, 8:1; PPA/urea mass ratio, 0.8:1; reflux ratio, 4; the stirring speed, 600 rpm.

the further experiments were carried out in a total flow rate of 200 mL/h.

3.4. *Effect of reaction temperature*

The reaction temperature plays an important role in DMC synthesis reaction as shown in Fig. 2. It is obvious that the DMC yield increases rapidly in the range of 388–397 K, however, it decreases when reaction temperature exceeds 397 K. As an endothermic reaction, it has benefits for the synthesis of DMC from urea and methanol at a higher reaction temperature in thermodynamics. However, higher reaction temperature can result in thermal decomposition of urea and MC and the high rate of side reactions, which will decrease the DMC selectivity. It shows that 397 K was the optimal reaction temperature for the reactive rectifying of DMC synthesis.

3.5. *Effect of methanol/urea mass ratio*

The effect of methanol/urea mass ratio on DMC yield is shown in Fig. 3. One can notice that the DMC yield increases as the mass ratio of methanol/urea increases. When the mass ratio of methanol/urea is low and the reaction temperature is high, the decomposition of urea and MC will take place. When the mass ratio of methanol/urea is higher than 8:1, the DMC yield begins to decrease. Because the higher methanol/urea mass ratio will result in lower urea concentration and it will reduce the reaction rate. Hence, the methanol/urea mass ratio 8:1 is selected.

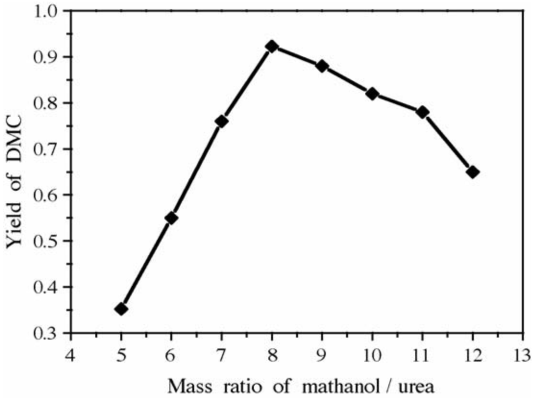

Fig. 3. The effect of methanol/urea mass ratio on DMC yield. Reaction time, 6.0 h; reaction temperature, 397 K; PPA/urea, 0.8:1; reflux ratio, 4; the stirring speed, 600 rpm.

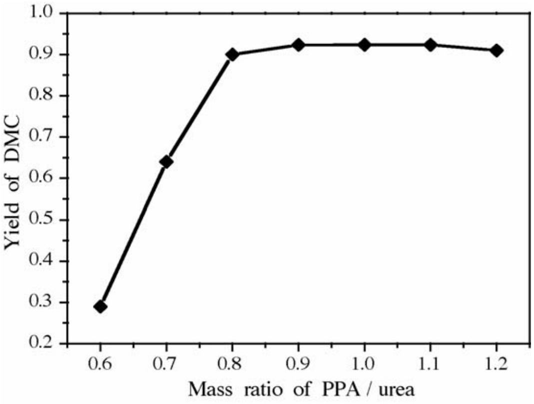

Fig. 4. The effect of PPA/urea mass ratio on DMC yield. Reaction time, 6.0 h; reaction temperature, 397 K; methanol/urea mass ratio, 8:1; reflux ratio, 4; the stirring speed, 600 rpm.

3.6. *Effect of the PPA/urea mass ratio*

Fig. 4 shows the effect of the PPA/urea mass ratio on DMC yield. From this figure, it can be seen that DMC yield increases with the increase of PPA/urea mass ratio. The change of DMC yield is little when the PPA/urea mass ratio exceeds 0.8:1. PPA is both catalyst and the ammonia absorbent in this process. When the mass ratio of PPA/urea is low, the ammonia emerging cannot be totally absorbed. Thus, the PPA/urea mass ratio of 0.8:1is selected in this process.

3.7. *Effect of the stirring speed*

The stirring speed has a light influence on DMC yield as shown in Fig. 5. With the increase of the stirring speed, DMC yield increases. In the case of homogeneous reaction, the stirring

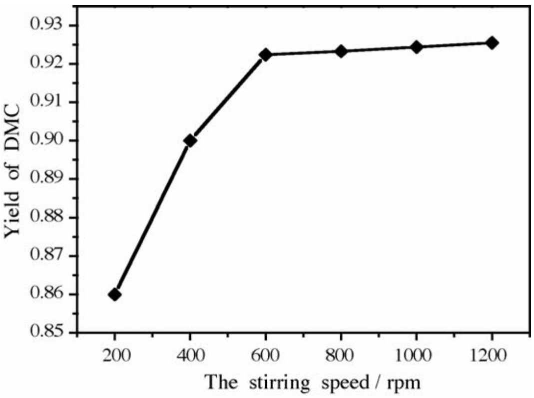

Fig. 5. The effect of the stirring speed on DMC yield. Reflux ratio, 4; reaction time, 6.0 h; reaction temperature, 397 K; methanol/urea mass ratio, 8:1; PPA/urea mass ratio, 0.8:1.

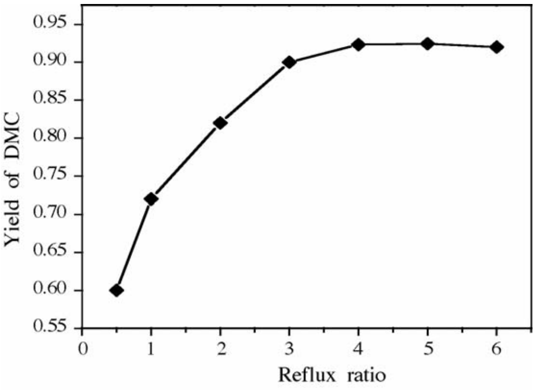

Fig. 6. The effect of reflux ratio on DMC yield. Reaction time, 6.0 h; reaction temperature, 397 K; methanol/urea mass ratio, 8:1; PPA/urea mass ratio, 0.8:1; the stirring speed, 600 rpm.

speed does not have a significant effect on DMC yield. Hence the stirring speed of 600 was maintained in the subsequent experiments.

3.8. Effect of reflux ratio on DMC yield

The reflux ratio is defined as the ratio of reflux flow rate and the overhead product flow rate in these experiments. Fig. 6 shows the effect of the reflux ratio on DMC yield obtained experimentally. In the range of low reflux ratio, the DMC yield increases steeply towards a maximum value of nearly 92.2%, which occurs at an optimal reflux ratio of 4. It is found that low DMC yield below the maximum was accompanied by a high content of methanol in the top products. This result is due to the poor separation of the reactant methanol and the product DMC in the rectifying section of the column. When increasing the reflux ratio up to values greater than 4, the DMC yield decreases slightly. Therefore, the reflux ratio of reactive rectifying is preferably with the range of 3.6–6, and the reflux ratio of 4 is the optimal reflux ratio for the reactive rectifying of DMC synthesis.

3.9. The difference of DMC concentration between the overhead and the bottom

The difference of DMC concentration between the overhead and the bottom under the optimum conditions is shown in Fig. 7. One can notice that the concentration of DMC in the overhead product is increased with the increase of reaction time, and it levels off after 4 h. It means that the whole operations can reach a steady state after 4 h run. A very low concentration of DMC at the bottom, no more than 2% (based on DMC and methanol solution), is observed due to the high rate of removing DMC and ammonia from the reactor. A high content and purity of DMC in the overhead products, more than 17%, is achieved and so reduces the costs of the subsequent separation.

3.10. Reactive rectifying versus batch system

As stated above, authors have reported some results for synthesis of DMC in batch mode [20]. In that paper, the influence of several manipulated variables on the yield of DMC was investigated and the set of individually optimized setting was attained too. To illustrate the efficiency of the combined process of reaction with separation, the result of the reactive rectifying is compared with that of the batch mode shown in Figs. 8 and 9.

From these two figures, it can be seen that the low concentration of DMC within the reactor can restrict the side reactions and

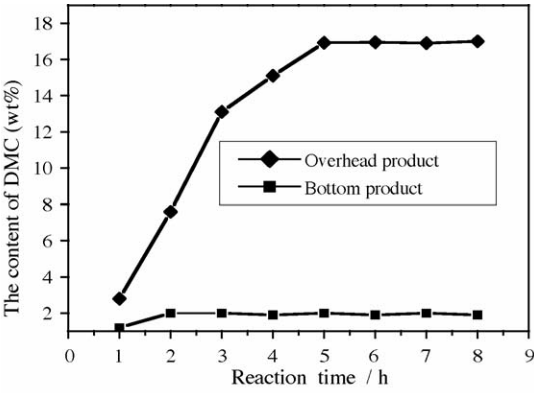

Fig. 7. Comparison of the content of DMC between overhead product and bottom. Reflux ratio, 4; reaction temperature, 397 K; methanol/urea mass ratio, 8:1; PPA/urea mass ratio, 0.8:1; the stirring speed, 800 rpm.

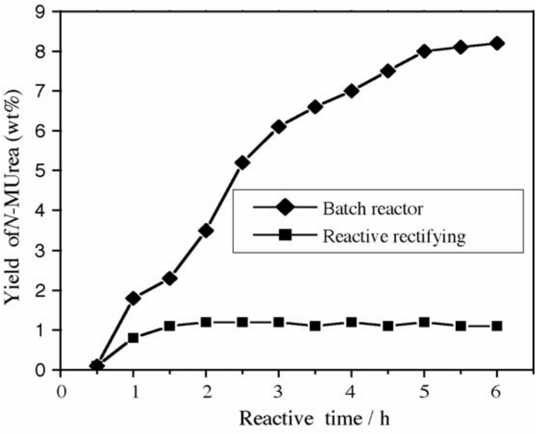

Fig. 8. Comparison of *N*-MUrea yield between batch reactor and reactive rectifying.

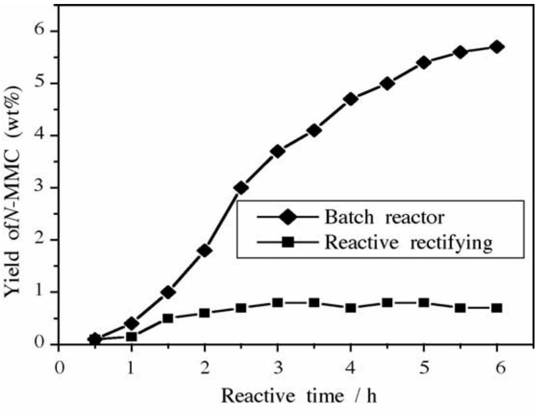

Fig. 9. Comparison of *N*-MMC yield between batch reactor and reactive rectifying.

Table 4
Reactive rectifying vs. batch system

Example	Batch reaction	Reactive rectifying
Reactor temperature (K)	413	397
Reactor pressure (MPa)	2	0.5
Reflux ratio	–	4
Methanol/urea mass ratio	7:1	8:1
PPA/urea mass ratio	1:1	0.8:1
Stirring speed (rmp)	800	600
The reaction time (h)	4	6
Yield of DMC (%)	67.4	92.2
Yield of *N*-MMC (%)	8.2	1.1
Yield of *N*-MUrea (%)	5.7	0.7

minimize the formation of *N*-methyl by-products in the reactive rectifying. The yield of *N*-MMC is maintained in the range of 0–0.8%, as well as *N*-MUrea yield in the range of 0–1.2% for this case. However, in the batch reactions, the reaction rates of side reactions became much higher and resulted in the rapid increase of *N*-MMC and *N*-MUrea. The yield of *N*-MUrea reached 8% under the optimized settings.

The operational conditions can be palliated by introducing the rectifying process. As shown in Table 4, the reaction temperature was 397 K in reactive rectifying, and 413 K in batch reactions. The reaction pressure was maintained at about 0.5 MPa after 2 h under the condition of reactive rectifying using, however, 2.0 MPa in batch reactions. The reason for this is that the operation of reactive rectifying can overcome the equilibrium limitation and allow the reaction to be carried out at a lower temperature and pressure than that of the batch method.

As stated above, since the distillation operation can remove the DMC from the reactor, the forward reactions can be enhanced and the yield of DMC will greatly increase. As shown in Table 4, the maximum yield of DMC, 67.4%, in batch mode is much lower than that 92.2% obtained in the reactive rectifying process. Furthermore, only a trace of ammonia was detected in the overhead liquid products. The higher purity of DMC in the methanol solution can be easily subjected to the subsequent extractive distillation to obtain pure DMC.

4. Conclusions

The reactive rectifying is employed for the synthesis of DMC from urea and methanol. The DMC formed in the reaction could be effectively removed. The concentration of DMC in the autoclave is held at a low level and it favored the minimization of *N*-methyl by-products. Since the DMC content of azeotrope in the overhead decrease with the increase of the pressure, the low pressure operation is preferred.

The set of individually optimized settings was total feed flow rate of 200 mL/h, bottom temperature of 397 K, reflux ratio of 4, methanol/urea mass ratio of 8:1, PPA/urea mass ratio of 0.8:1, stirring speed of 600 rmp, respectively. In the set of individually optimized conditions, the yield of DMC was 92.2%. A higher concentration of DMC product, more than 17%, was achieved. And the cost of subsequent separation and purifying would be reduced.

Acknowledgements

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