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Kinetics studies for the synthesis of dimethyl carbonate from urea and methanol

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Abstract

A new route was proposed for producing dimethyl carbonate (DMC) from urea and methanol catalyzed by the organotin and the high boiling electron donor solvent as a co-catalyst. The effects of methanol/urea initial molar ratio, the mass percent of catalyst and solvent, the reaction time and the reaction temperature on the DMC yield were investigated. Experimental results indicated that the temperature is more important to the reaction and the content of solvent has little effect on DMC yield. Furthermore, too higher reaction temperature results in the consumption of DMC to form the N-alkyl by-products due to the high activity of DMC. Removing DMC and ammonia from the reaction system in time is vital to improving DMC yield. The kinetics model for this reaction system was developed. The calculated results using the parameters obtained from the genetic algorithm (GA) agree well with the experimental data.

Keywords: Dimethyl carbonate; Urea; Methanol; Organotin; Kinetics

1. Introduction

Dimethyl carbonate (DMC) has been considered as the green chemical raw material of 21st century and registered as an innoxious chemical in Europe. Since the DMC molecule includes CH_3–, CH_3O–, CH_3O–CO–, –CO– groups, it shows excellent reaction activity. For example, DMC is used to replace the virulent carcinogen such as phosgene, dimethyl sulfate (DMS), chloromethane and methyl chloroformate, etc., as carbonylation, methylation, esterification or ester interchange agent to produce many kinds of chemical industry productions. Furthermore, DMC has been widely used at many fields such as medicine, pesticide, composite material, dyestuff, additive of gasoline, flavoring agent of foodstuff and electronic chemical, etc. [1–3]. Nowadays, DMC has become the new basic material of organic synthesis field.

Since the alluring industry application foreground with DMC, many researchers pay more attention to its development of the synthetic route. The process is towards route's simplification, process's innocuity and no pollution at the present time.

Presently, the DMC synthesis techniques reported internationally mainly consist of phosgenation of methanol, oxidative carbonylation of methanol, ester exchange, esterification of carbon dioxide methanol, etc. [4–7].

The alcoholysis of urea for producing DMC is one kind of new process developed recently. This process uses the urea and methanol, which have abundant resource and lower cost, as raw material under the definite temperature, pressure and existence of the catalyst. As there is no water formed during this process, the ternary azeotrope, methanol–water–DMC does not come into being, the subsequent separation and purification of DMC thus can be simplified. If the ammonia, the only by-product, is connected with the urea production line, it can achieve the duty cycle operation. Therefore, this process is one kind of environment-friendly technique.

Even this process is an interesting route, the interrelated reports especially the kinetics study about this process are relatively less. In this work, a semi-batch operation was designed to carry out the kinetics studies of this process. Several reaction factors such as the reaction time and the reaction

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Nomenclature

a, b	Van der Waal's constant ($\mathrm{Pa\,m^6\,mol^{-2}}$, $\mathrm{m^3\,mol^{-1}}$)
C	molar concentration ($\mathrm{mol\,m^{-3}}$)
C_{CAT}	catalyst concentration ($\mathrm{g/m^3}$)
$C_j(t_i)$	experiment molar concentration of jth component at i moment ($\mathrm{mol\,m^{-3}}$)
E_{a}	activation energy ($\mathrm{kJ\,mol^{-1}}$)
k	reaction rate constant
$\bar{K}$	pre-estimated rate constant vector (including four constants)
P	reaction pressure (MPa)
r	reaction rate ($\mathrm{mol\,m^{-3}\,s^{-1}}$)
R	universal gas constant 8.314 ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
R^2	variance of linear fitting (–)
$(t_i, \bar{K})$	calculated molar concentration of jth component at i moment by using the pre-estimated rate constant ($\mathrm{mol\,m^{-3}}$)
T	reaction temperature (K)
V	revised solution volume of reaction system ($\mathrm{m^3}$)
V_{m}	molar volume ($\mathrm{m^3\,mol^{-1}}$)
V_{T}	the total volume of reactor ($\mathrm{m^3}$)
Y_{DMC}	yield of DMC (–)
Z	compressibility factor (–)

Greek letters

α, β, χ	ratio of 2nd, 3rd, 4th to 1st reaction rate (–)
φ	degree of adaptability (–)

Subscripts

c	critical parameter
N-MUREA	*N*-alkyl urea
N-MMC	*N*-alkyl carbamate
j	urea, methanol, methyl carbamate and dimethyl carbonate

temperature were investigated, the reaction mechanism was explored and the reaction kinetics model was established. The reaction kinetics parameters had been found by using genetic algorithm (GA) based on the experimental results. Consequently, the activation energy of each reaction was obtained.

2. Experimental

2.1. Materials

Methanol (A.R.), urea (A.R.) and methyl carbamate (A.R.) were commercial reagents that purity was greater than 99.9 mass percent. Dibutyltin oxide (C.R.) and polyethylene glycol dimethyl ether (PGDE, average molecular weight: 250–270)) (C.R.) were also commercial reagents. All of them were purchased from Xi'an Chemical Reagent, in Xi'an, China. DMC was purchased as analytically pure reagents from Fluka Chemie GmbH CH-9471 Buchs (Germany).

2.2. Preparation of catalyst

The dibutyltin dimethyloxide catalyst is preferably formed from dibutyltin oxide and methyl carbamate (MC) at definite temperature (150–190 °C) and an autogenous pressure (1.5–3.0 MPa), i.e., the sum of the vapor pressure of the methanol, ammonia and MC at the reaction temperature [14,15]. The production can be separated by delamination.

$$\mathrm{Bu_2SnO + CH_3OH + NH_2COOCH_3}$$
$$\rightarrow \mathrm{Bu_2Sn(OCH_3)_2 + NH_3} \uparrow + \mathrm{CO_2} \uparrow$$

2.3. Apparatus and procedure

The scheme of reaction system is shown in Fig. 1.The reactor was a stainless steel V_{T} = 750 ml autoclave with an electric heating and a dynamoelectric stirring. This apparatus is equipped with a sampling line 9, a back-pressure regulator 6, a mass flow controller 13 and an overhead condenser 5. For each run, a mixture with methanol, urea, catalyst (dibutyltin dimethyloxide) and the solvent (PGDE) was placed in the reactor according to a definite ratio; the autoclave was flushed with nitrogen to replace air within the reactor, then, the autoclave was pressured with nitrogen at 1.0 MPa and rapidly heated to the desired temperature with stirring. During this period of time, valves 3 and 4 were shut off and no gas could be released from the reactor. When the reaction temperature reached at the desired value, valves 3 and 4 were opened. The analysis of the sample from the $\mathrm{NH_3}$ absorption vessel 11 can

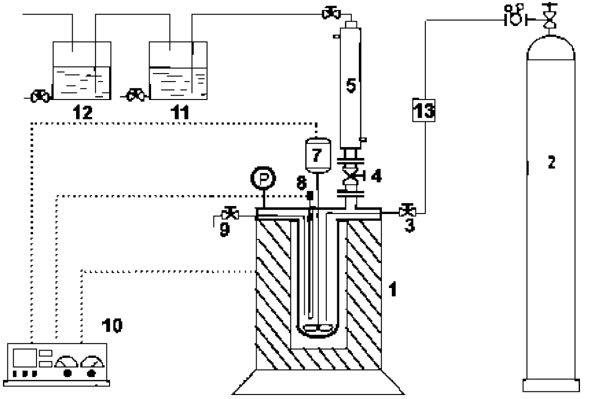


Fig. 1. Schematic diagram of the experimental apparatus. 1: Autoclave; 2: nitrogen cylinder; 3: nitrogen charge valve; 4: valve; 5: condenser; 6: back-pressure regulator; 7: stirrer; 8: thermocouple; 9: sampling valve; 10: temperature and stirring speed controller; 11: $\mathrm{NH_3}$ absorption vessel; 12: $\mathrm{CO_2}$ absorption vessel; 13: mass flow controller; P: pressure gauge.

be used to confirm that the reaction can be neglected during the heating time.

During the experiment, the nitrogen purged the reaction system from the autoclave bottom and the gas products (NH_3 and CO_2) were carried over by nitrogen. A mass flow controller 13 was used to purge the system with nitrogen at 100 ml/min and the reaction pressure was set at 2.0 MPa during the reaction each time by the back-pressure regulator 6. This gas mixture was cooled down through the condenser 5 to avoid other reactant (in particular, the methanol) to escape from the reactor. The expulsive gas mixture was first passed over the NH_3 absorption vessel 11 that was filled with an aqueous solution of boric acid, and then passed over the CO_2 absorption vessel 12 that was filled with an aqueous solution of sodium hydrate. These two absorption solutions were periodically analyzed by titration to, respectively, determine the molars amount of NH_3 and the CO_2 released with nitrogen. The console 10 controlled the autoclave temperature and the stirring rate.

After the reaction was complete, the total residual liquid reactant mixture was discharged from the autoclave and its cumulative volume was measured.

2.4. Analytic methods

Small samples (1 ml each) were withdrawn via sampling valve 9 from the reactor. They were first distilled to separate into two parts, one involved DMC and methanol, and another involved urea, MC, catalyst and the solvent. The first part contained DMC and methanol was analyzed by gas chromatograph (HP 4890D) using a HP-5 capillary column (15 m × 0.530 mm × 1.5 μm) with the thermal conductivity detector (TCD).

The second part contained mainly urea and MC was first added some water to a constant volume (2 ml), and the catalyst can be hydrolyzed to form into some solid production. Subsequently this suspending liquid was separated by centrifugal separation to remove the solid production. And then the solid production was washed three times by water (1 ml per time). The total left solution by centrifugal separation and washing involved urea, MC, and the solvent. Then this solution was added some water to constant volume (5 ml) again, urea and MC can be analyzed by ultraviolet spectrophotometry method based on the partial least-squares method.

2.5. Calculations

The yield of DMC was calculated using following formula:

$$Y_{\mathrm{DMC}} = \frac{\text{Moles DMC}_{(\text{existing in the solution at } t \text{ moment})}}{\text{Starting moles urea}} \times 100\%$$

The mass percent (wt.%) of each compound was calculated based on total compounds content of the reactor solution.

3. Result and discussion

3.1. Analysis of the reaction mechanism

The reaction actually contains two steps. First, methyl carbamate (MC) can be synthesized from urea and methanol without any catalyst.

$$NH_2CONH_2 + CH_3OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NH_2COONH_3 + NH_3\uparrow \quad (1)$$

And then MC can react further with methanol to form DMC in the presence of the novel organotin catalyst [8–13]. In this process, following steps as described by Scheme 1 are included: (I) dibutyltin dimethyloxide **1** reacts with MC to yield dibutyltin methoxycarbamato **2**; (II) an intramolecular or intermolecular nucleophilic attack of alcohol occurs on the carbonyl carbon of the carbamatotin species, resulting in elimination of the carbonate and formation of an aminotin intermediate **3**; (III) it involves the reaction of the carbamate with **3**, to regenerate **2** with concomitant elimination of ammonia [16].

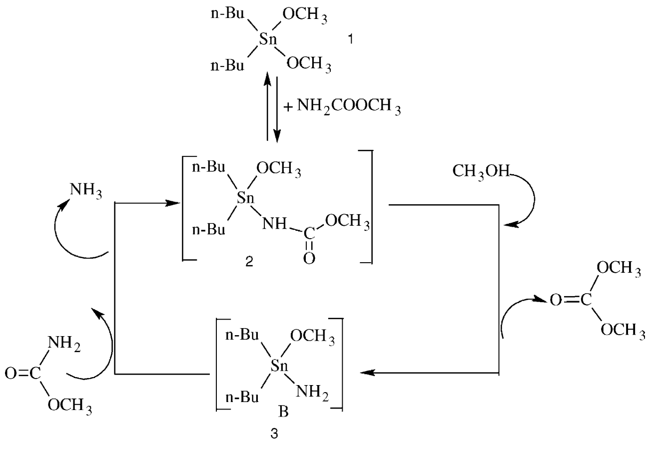
The stoichiometric equation can be written as follows:

$$NH_2COONH_3 + CH_3OH \underset{k_4}{\overset{k_3}{\rightleftharpoons}} CH_3OCOONH_3 + NH_3\uparrow \quad (2)$$

It is very important that ammonia produced in these two steps must be removed from the reactor in time. Otherwise, the conversion of urea and DMC yield would be relatively lower.

When the DMC concentration in the reaction solution is comparatively higher, the N-alkyl by-products can be formed during the DMC synthesis process as described by Eqs. (3) and (4):

$$CH_3OCOOCH_3 + NH_2CONH_2 \underset{k_6}{\overset{k_5}{\rightleftharpoons}} CH_3NHCONH_2 + CH_3OH + CO_2\uparrow \quad (3)$$



Scheme 1. Proposed catalysis mechanism for the formation of DMC from MC.

$$CH_3OCOOCH_3 + NH_2COOCH_3 \underset{k_8}{\overset{k_7}{\rightleftharpoons}} CH_3NHCOOCH_3 + CH_3OH + CO_2 \uparrow \quad (4)$$

From Eqs. (3) and (4), it can be known that using CO_2 to pressure the autoclave instead of nitrogen is efficient to restrain above side reaction.

3.2. Derivation of kinetics model

According to the above-mentioned reaction mechanism, the reaction rate equations of each above four equations can be listed as follows:

$$r_1 = k_1 \cdot C_{NH_2CONH_2} \cdot C_{CH_3OH} - k_2 \cdot C_{NH_2COOCH_3} \cdot C_{NH_3} \quad (5)$$

$$r_2 = k_3 \cdot C_{NH_2COOCH_3} \cdot C_{CH_3OH} - k_4 \cdot C_{CH_3OCOOCH_3} \cdot C_{NH_3} \quad (6)$$

$$r_3 = k_5 \cdot C_{CH_3OCOOCH_3} \cdot C_{NH_2CONH_2} - k_6 \cdot C_{CH_3NHCONH_2} \cdot C_{CH_3OH} \cdot C_{CO_2} \quad (7)$$

$$r_4 = k_7 \cdot C_{CH_3OCOOCH_3} \cdot C_{NH_2COOCH_3} - k_8 \cdot C_{CH_3NHCOOCH_3} \cdot C_{CH_3OH} \cdot C_{CO_2} \quad (8)$$

Material balance about each reactant based on total reaction system can be listed as follows:

$$C_{CH_3NHCOOCH_3} = \frac{1}{2}\left(\frac{2C^0_{CH_3OH} \cdot V_0}{V} - \frac{C^0_{NH_2CONH_2} \cdot V_0}{V} + C_{NH_2CONH_2} - C_{NH_2COOCH_3} - 3C_{CH_3OCOOCH_3} - 2C_{CH_3OH}\right) \quad (9)$$

$$C_{NH_3} = \left(\frac{C^0_{NH_2CONH_2} \cdot V_0}{V} - C_{NH_2CONH_2} + C_{CH_3OCOOCH_3} + C_{CH_3NHCOOCH_3}\right) - \frac{n_{NH_3}}{V} \quad (10)$$

$$C_{CH_3NHCONH_2} = \frac{1}{2}\left(\frac{C^0_{NH_2CONH_2} \cdot V_0}{V} - C_{NH_2CONH_2} - C_{NH_2COOCH_3} - C_{CH_3OCOOCH_3}\right) - C_{CH_3NHCOOCH_3} \quad (11)$$

$$C_{CO_2} = \frac{1}{2} \cdot \left(\frac{C^0_{NH_2CONH_2} \cdot V_0}{V} - C_{NH_2CONH_2} - C_{NH_2COOCH_3} - C_{CH_3OCOOCH_3}\right) - \frac{n_{CO_2}}{V} \quad (12)$$

Introducing some parameters:

$$\alpha = \frac{r_2}{r_1}, \qquad \beta = \frac{r_3}{r_1}, \qquad \chi = \frac{r_4}{r_1} \quad (13)$$

Then, following equations can be derived:

$$\frac{dC_{NH_2CONH_2}}{dt} = -C_{CAT} \cdot (1 + \beta) \cdot r_1 \quad (14)$$

$$\frac{dC_{CH_3OH}}{dt} = -C_{CAT} \cdot (1 + \alpha - \beta - \chi) \cdot r_1 \quad (15)$$

$$\frac{dC_{NH_2COOCH_3}}{dt} = C_{CAT} \cdot (1 - \alpha - \chi) \cdot r_1 \quad (16)$$

$$\frac{dC_{CH_3OCOOCH_3}}{dt} = C_{CAT} \cdot (\alpha - \beta - \chi) \cdot r_1 \quad (17)$$

Using the Runge-Kutta method, the concentration of NH_2CONH_2, CH_3OH, NH_2COOCH_3 and $CH_3OCOOCH_3$ can be calculated.

The volume of total reaction solution can be considered as constant one during the reaction since the dosage of methanol is largely excessive to the urea, but must be revised from idea solution. RK equation can be used to calculate the volume of gas-phase V_G at the initial of the reaction. With the result that the volume of reaction solution $V = V_T - V_G$. During the warming up, the nitrogen mol amount in the gas phase can be considered as the initial value due to the slightly solubility of nitrogen in the reaction solution. Then, the volume of reaction solution V revised can be impetrated.

For the sake of being calculated easily by computer, the RK equation can be rewritten as follows:

$$Z = \frac{1}{1-h} - \frac{A}{B}\left(\frac{h}{1+h}\right) \quad (18)$$

$$h = \frac{b}{V_m} = \frac{BP}{Z} \quad (19)$$

$$B = \frac{b}{RT}, \qquad \frac{A}{B} = \frac{a}{bRT^{1.5}} \quad (20)$$

These parameters a and b can be calculated as follows:

$$a = 0.4278\frac{R^2T_C^{5/2}}{P}, \qquad b = 0.0867\frac{RT_C}{P_C} \quad (21)$$

The initial value of the compressibility factor Z is set as $Z = Z_1 = 1$. When the value achieves $h = h_1$, the optimal Z can be impetrated, then $PV_m = ZRT$ is used to get the molar volume V_m of nitrogen. Thereby the volume of reaction solution V can be achieved.

Then Eqs. (5)–(21) are used to constitute the kinetics model of the process.

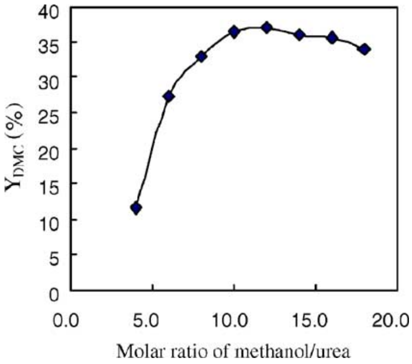


Fig. 2. The effect of methanol/urea initial molar ratio on DMC yield. Reaction temperature: 443 K, reaction pressure: 2.0 MPa, reaction time: 7 h, the mass percent of catalyst: 10 wt.%, the mass percent of solvent: 30 wt.%, the stirring speed: 600 rpm.

3.3. *Effect of methanol/urea initial molar ratio on DMC yield*

The effect of methanol/urea initial molar ratio on DMC yield is shown in Fig. 2. It can be known that DMC yield increases with increasing molar ratio of initial methanol/urea. When the molar ratio of methanol/urea is lower, the urea concentration will become higher and the decomposition of urea and MC will take place in a higher reaction temperature. When the molar ratio of initial methanol/urea is higher than 10:1, the DMC yield begins to fall. The reason is that the higher methanol/urea initial molar ratio would result in lower urea concentration and it will reduce the reaction rate. Hence, the methanol/urea initial molar ratio 10:1 was selected.

3.4. *Effect of catalyst concentration*

The effect of catalyst loading on DMC yield is shown in Fig. 3. As shown in this figure, DMC yield increases with increasing catalyst loading. However, when the catalyst loading reaches in 10 wt.%, the DMC yield increases slightly until at 15 wt.%. Then, DMC yield will decline with the increasing catalyst loading. The reason is that higher catalyst concentration can cause the consuming of DMC by secondary reaction earlier. Therefore, the mass percent of catalyst 10 wt.% was selected.

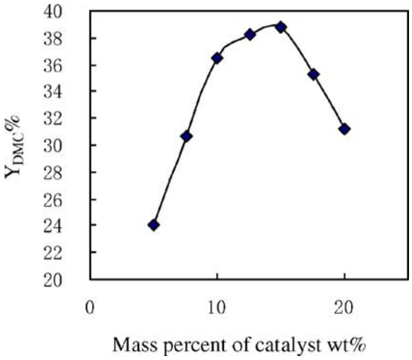


Fig. 3. The effect of catalyst loading on DMC yield. Reaction temperature: 443 K, reaction pressure: 2.0 MPa, reaction time: 7 h, methanol/urea molar ratio = 10:1, the mass percent of solvent: 30 wt.%, the stirring speed: 600 rpm.

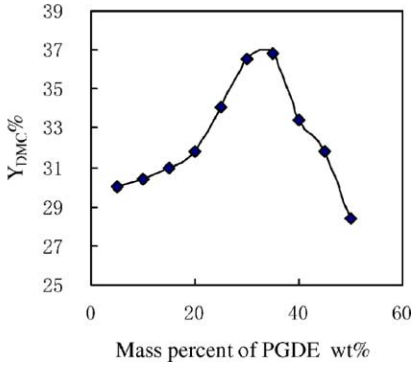


Fig. 4. The effect of PGDE concentration on DMC yield. Reaction temperature: 443 K, reaction pressure: 2.0 MPa, reaction time: 7 h, methanol/urea molar ratio = 10:1, the mass percent of catalyst: 10 wt.%, the stirring speed: 600 rpm.

3.5. *Effect of PGDE concentration*

The effect of solvent concentration on DMC yield is shown in Fig. 4. This high boiling electron donor compound can form one kind of co-catalyst with the organotin (dibutyltin dimethyloxide) catalyst, which will improve the DMC forming rate. The reason can be considered as the effective of removal ammonia. Also, this kind of co-catalyst can prevents the formation of by-products such as alkyl amine or decomposition of urea or MC at relatively high concentration of DMC in the reactor. When the mass percent of solvent is higher than 35 wt.%, the DMC yield begins to decline. It is because the higher solvent concentration will decrease the reactant concentration and reduce the reaction rate. Hence, the mass percent of solvent 30 wt.% was selected.

3.6. *Effect of reaction time on DMC yield*

The effect of reaction time on DMC yield is shown in Fig. 5. The DMC yield increases at a higher reaction rate to synthesize DMC due to the higher raw material concentration in the process of time before 7 h. Along with the increasing of DMC concentration, the side reaction will occurred to form the N-alkyl by-products owing to the higher reaction activity of DMC. Between 7 and 9 h, the forming rate of DMC is almost balanced with the consuming rate of DMC by its methylation reaction. After 9 h, the consuming rate is faster than the forming rate of DMC and DMC yield declines. Therefore, the reaction time 7 h was selected.

3.7. *Effect of reaction pressure on DMC yield*

According to preparatory experiments results, the reaction pressure was proved to have little effect on this synthesis reaction here when it ranges form 1.8 to 3.0 MPa. Under the

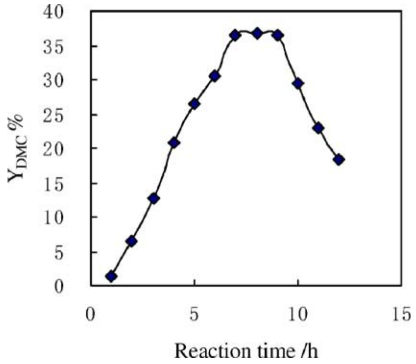


Fig. 5. The effect of reaction time on DMC yield. Reaction temperature: 443 K, reaction pressure: 2.0 MPa, methanol/urea molar ratio = 10:1, the mass percent of catalyst: 10 wt.%, the mass percent of solvent: 30 wt.%, the stirring speed: 600 rpm.

desired reaction condition, the reaction pressure is higher than the saturated vapor pressure of methanol in the reaction temperature to keep the reactant mixture in the liquid state. Therefore, the reaction pressure 2.0 MPa was selected for all the runs.

3.8. Effect of reaction temperature on DMC yield

Under the optimal reaction condition of this system (reaction pressure: 2.0 MPa, reaction time: 7 h, methanol/urea molar ratio=10:1, the mass percent of catalyst: 10 wt.%, the mass percent of solvent: 30 wt.%, the stirring speed: 600 rpm), the experiments were, respectively, carried out at 423, 433, 443 and 453 K. The effect of reaction temperature on DMC yield is shown in Fig. 6. From this figure, it can be known that the DMC yield increases with increasing temperature, and then decrease rapidly, the pick is in 443 K. Since the reaction is an endothermic reaction, it is benefits for the synthesis of DMC in a higher reaction temperature range from the thermodynamics viewpoint. However, the higher reaction temperature will result in the decomposition of MC and urea. And it will accelerate the by-reaction. The selectivity and yield of DMC will decline rapidly when the temperature is higher than 453 K. Hence the reaction temperature 443 K was selected.

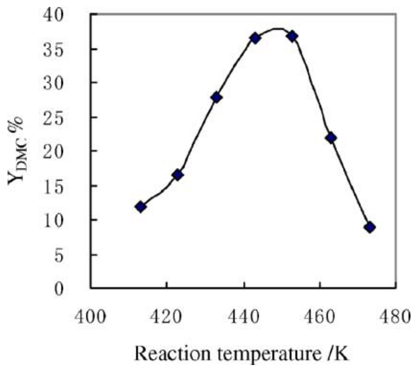


Fig. 6. The effect of reaction temperature on DMC yield. Reaction pressure: 2.0 MPa, reaction time: 7 h, methanol/urea molar ratio = 10:1, the mass percent of catalyst: 10 wt.%, the mass percent of solvent: 30 wt.%, the stirring speed: 600 rpm.

3.9. The development of the kinetics parameters

The genetic algorithm [17–20] was used to estimate kinetics parameters ($k_1 - k_8$) based on the experimental data.

1) The criterion function is defined as:

$$\phi(\bar{K}) = \sum_{j}^{q}\sum_{i=1}^{p}\left(\frac{\bar{C}_j(t_i,\bar{K}) - C_j(t_i)}{C_j(t_i)}\right)^{-2} \tag{22}$$

The criterion corresponds to the adaptation of the individual to “survive” in the new generations. The higher the criterion is, the more likely the individual will be kept during the selection step.

2) For the sake of simplicity, decimal coding was preferred. The length of the chains will state the necessary precision.
3) The roulette wheel selection was used as selection operator. The selection of parent generation is according to their adaptability. The adaptability is bigger, and the opportunity of being selected is greater.
4) The uniform crossover was selected as the crossover operator of GA. Two parents are chosen randomly from the individuals selected. The parents’ chains are combined to create a new child. The coding chains of the two parents are cut at certain points (the same for both parents) and the chain segments are interchanged between the two parents.
5) Each filial generation $\bar{K}$ selected by selection operator is divided into four segments, such as the symbol segment of the exponent part, the figure segment of the exponent part, and the fore-and-aft segments of the numerical value parts where the decimal point exists. Each character in the coding chain has a probability of changing randomly.

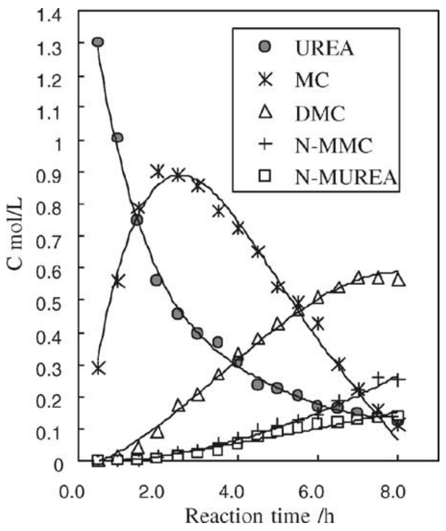


Fig. 7. Concentration profiles with reaction time. Reaction temperature: 443 K, reaction pressure: 2.0 MPa, methanol/urea molar ratio = 10:1, the mass percent of catalyst: 10 wt.%, the mass percent of solvent: 30 wt.%, the stirring speed: 600 rpm.

Table 1
The expressions of kinetics constants and activity energy

Expressions of the relationship between k and T	Unit of k	Activation energy, E_a (kJ mol^{-1})	Variance R^2
$k_1 = \exp(-1140.94/T + 2.457)$	g^{-1} mol^{-1} m^6 s^{-1}	98.1	0.987
$k_2 = \exp(-693.38/T + 0.738)$	g^{-1} mol^{-1} m^6 s^{-1}	47.2	0.975
$k_3 = \exp(-1565.60/T + 2.546)$	g^{-1} mol^{-1} m^6 s^{-1}	106.6	0.973
$k_4 = \exp(-684.21/T + 0.672)$	g^{-1} mol^{-1} m^6 s^{-1}	46.6	0.981
$k_5 = \exp(-1779.74/T + 2.906)$	g^{-1} mol^{-1} m^6 s^{-1}	121.2	0.979
$k_6 = \exp(-1501.37/T + 2.226)$	g^{-1} mol^{-2} m^9 s^{-1}	102.2	0.991
$k_7 = \exp(-1755.24/T + 2.899)$	g^{-1} mol^{-1} m^6 s^{-1}	119.5	0.985
$k_8 = \exp(-1188.19/T + 1.614)$	g^{-1} mol^{-2} m^9 s^{-1}	80.9	0.993

By minimizing the objective function $(\phi(\bar{K}))^{-1}$, the parameters $(\bar{K})$ of the kinetics model can be obtained. According to the Arrhenius equation, the activation energy E_a can be achieved by linear fitting with the $\bar{K}$ data. The expressions of kinetics constants and activation energies are represented in Table 1.

Fig. 7 is the relation between the concentration of five components and the reaction time under the desired conditions. The solid lines are the calculated concentration results by the above kinetics model with the kinetics constants $\bar{K}$ represented in Table 1. All the marks are the experimental concentrations of five components in the experiment at 443 K. It is obvious that the modeling results can fit the experiment points very well. The model with these kinetics constants also has been validated with the experimental concentrations at 423, 433 and 453 K. Therefore these kinetics constants $\bar{K}$ represented in Table 1 are the most probable ones.

4. Conclusion

1. The kinetics parameters of synthesis of DMC from urea and methanol using the organotin as catalyst and the high boiling electron donor compound as solvent are estimated by using the genetic algorithm. The rate constant values at different temperature are obtained. Calculated results agreed well with the experimental results.
2. The initial molar ratio of methanol/urea, the catalyst concentration, the solvent concentration, the reaction time and the reaction temperature show effects on the DMC yield, the temperature is more important to the reaction and the mass percent of solvent has little effect on DMC yield.
3. The activation energies of the secondary reactions are higher than those of the main reactions. Therefore, higher reaction temperature is in favor of the consuming of DMC by forming N-alkyl by-production due to DMC's high activity. Removing DMC and ammonia from the reaction system in time is vital to improving DMC yield.

Acknowledgments

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