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A Method to Predict Phosgenation Reaction Performance To Produce Toluene Diisocyanate in Jet Reactors

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ABSTRACT: Toluene diisocyanate (TDI) is a widely used intermediate in the production of polyurethanes. Phosgenation reaction is the most important operation in the process of producing TDI, which is commonly performed in a jet reactor. Because of the high toxicity of phosgene, it is unpractical to evaluate the performance of the reaction by sampling intermediate products. To overcome this difficulty, first, a mapping table was created for reaction path and temperature. Next, various parameters that affect temperature, such as reaction path, ratio of phosgene, diethyl iso-phthalate (DEIP), etc. were investigated by simulation studies. The results show that the ratio of phosgene is the most important parameter. On the basis of the mapping table, easily available experimental reaction temperature data can be utilized to infer the reaction path, and consequently the performance of jet reactor can be predicted. The method was validated after being used in an experimental setup of 1000 tons/annum TDI capacity.

INTRODUCTION

Toluene diisocyanate (TDI) is an important intermediate in the production of polyurethanes. Although TDI can be prepared by several methods, most of these methods are not applicable on an industrial scale.[1−4] TDI is commercially produced by reacting toluene diamine (TDA) with phosgene in the presence of a solvent, and this process is called phosgenation.[5,6] Thus, the raw materials for industrial TDI production are TDA and phosgene. TDA is prepared by catalytic reduction of dinitrotoluene under hydrogen pressure, which is subsequently treated with phosgene to give TDI.[8−12]

It is well-known that the process of producing TDI includes two steps, namely cold and hot reactions.[7] Further, each step consists of a series of reactions. The cold step is very crucial since the reaction rate is very fast, and the intermediates easily react with TDA leading to undesired side products. Therefore, a fast and effective mixing is extremely important to restrain undesired side reactions. Many reactor types were proposed in the past decade, most of them focused on improving the mixing performance of the reactors.[16] Among all these types of reactors, the jet reactor is most popular, and is now widely used in the TDI industrial process. The jet reactor is a high-intensity mixing equipment, and is widely used in the chemical industry. Many studies have focused on the mixing capacity and performance of the jet reactor in large-scale production.[13−15]

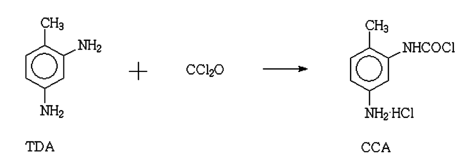
Meanwhile, during the phosgenation process, sampling of intermediates is unpractical due to two reasons: (i) the process time of cold reaction is very short, usually occurs within milliseconds, and (ii) the high toxicity of phosgene.[17] These factors make it difficult to investigate the cold reaction in detail, and evaluate the performance of the reactor.

In this study, we propose a method to evaluate the performance of the cold reaction without any sampling of the intermediates. The ratio of reactants, reaction conditions (e.g., temperature, pressure, etc.), heat of reaction, and vapor−liquid equilibrium model were used to determine the detailed reaction information and performance of cold reaction in jet reactors, by using the reverse deduction method.

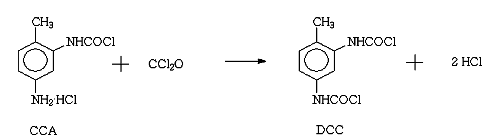
REACTION PROCESS

TDA is a 80:20 mixture of two 2,4-TDA and 2,6-TDA (structural isomers). For ease of understanding, we have used 2,4-TDA throughout the Schemes and text in this paper.

Cold Phosgenation. The cold phosgenation consists of mainly two reactions C1 and C2 as follows:



(C1)



(C2)

In the first step C1, the *p*-amino group of TDA reacts with phosgene to form carbamoylchloride and hydrochloric acid (HCl), and the formed HCl molecule is most likely kinetically trapped by the second *o*-amino group within the same molecule resulting incarbamoylchloride-aminohydrochloride (CCA) intermediate. In the second step C2, CCA reacts with phosgene to form dicarbamoylchloride (DCC). The first step is very fast but the second one is slower, because the CCA undergoes decomposition and HCl is removed. Both these reactions are highly exothermic.

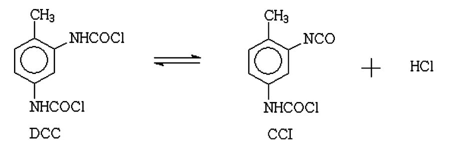
Hot Phosgenation. DCC undergoes two equilibrium reactions to form TDI H1 and H2 as shown in the reactions. First, DCC gets decomposed to toluene-carbamoylchloride-

Special Issue: NASCRE 3

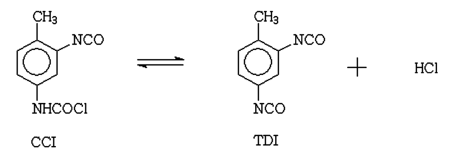
Received: February 26, 2013
Revised: May 20, 2013
Accepted: May 20, 2013
Published: May 20, 2013

dx.doi.org/10.1021/ie400626n | Ind. Eng. Chem. Res. 2013, 52, 15353−15358

isocyanate (CCI) and HCl, and then CCI gets decomposed to TDI and HCl. Both these reactions are endothermic.



(H1)



(H2)

Side Reactions. C1 is a very fast reaction, and generally goes to completion within 0.5 s, while C2 is a much slower reaction than C1. Often CCA cannot be completely converted to DCC in the cold reactor, and therefore unreacted CCA may be present in the hot reactor. This unreacted CCA reacts with TDI in the hot reactor to form undesired side products, and thereby reduce the yield and selectivity of TDA. In addition, CCA, DCC, and TDI easily react with TDA to form many undesired side products.[18,19] Therefore, it is important to confirm whether or not all of the TDA was converted to CCA or DCC.

In the entire phosgenation, the cold reaction mainly controls the yield and selectivity of the process. To restrain the undesired side reactions, phosgene and solvent are added in excess to the reactants. The lower is the TDA fraction in the reaction mixture, the higher the yield of TDI will be.

Another parameter affecting the yield is the mixing performance of the reactor. A fast and effective mixing is extremely important to ensure a high yield. Many reactor types have been proposed in the past decade, and most of them focused on improving the mixing performance of the reactors. Among all these types of reactors, the jet reactor is most popular and commonly used in TDI industry.

■ METHODS AND EXPERIMENTS SETUP

Methods Description. A jet reactor is a high-intensity piece of equipment commonly used in the TDI process. Because of the high toxicity of phosgene, it is very difficult to quantify the mixing performance in the experiment. Especially in the industrial scale, the temperature of the cold reaction is the only indicator that can be safely measured. We designed a method to study the reaction path, during the cold phosgenation as shown in Figure 1.

The method in Figure 1 is divided into two steps: simulation and experiment. In the simulation step, commercially available software from Aspen plus was used to simulate the cold phosgenation reaction. During the simulation studies, the thermodynamic data of reactants and the reaction conditions can be easily acquired from this software. The two uncertain parameters are: (i) the reaction path and (ii) temperature. If the reaction conditions (mainly the ratio of reactants) are fixed, then there is a one-to-one correspondence between the reaction temperature and reaction path. Therefore, a series of reaction paths, by considering all the possibilities in the industrial process, can be predefined. Next, corresponding temperatures can be simulated accordingly. Thus, we can establish a mapping table between the reaction path and temperature of the process. The reaction temperature data can

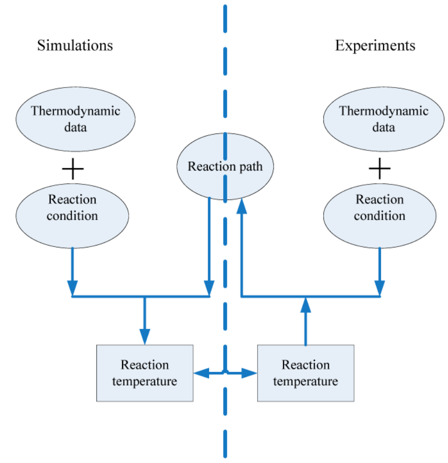
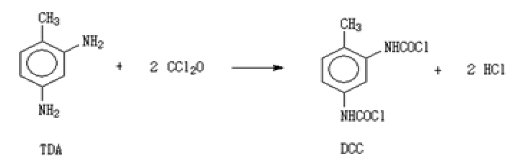


Figure 1. Design of experiments and simulations.

be safely and easily obtained during the experiments, whereas it is difficult to acquire the composition of the reaction mixture. Using the mapping table, the reaction path can be easily obtained from the temperature data. Thus, finally the composition of reaction mixture can be easily determined.

Reaction C3 simplifies the simulation process of the cold reaction. C3 is a virtual reaction that represents combined C1 and C2 reactions. Reaction C2 was used to represent the process for the production of DCC, and reaction C1 was used to represent the process that forms CCA, during the simulation studies.



(C3)

Experimental Equipment. Figure 2 shows the equipment and process used in a 1000 tons/annum TDI capacity plant. Phosgene, DEIP, and TDA are delivered to the jet reactor by the pumps. Before entering the reactor, the temperatures of the three reactants are adjusted to the optimum values. DEIP and TDA are premixed before entering the reactor. Thermometers, flow meters, and pressure meters are set up on the pipes going into and out of the jet reactor. A reaction tower (reactor) is set up outside the jet reactor to carry out the hot phosgenation, and then the reaction mixtures are finally sent for purification.

Base conditions of simulation and experiment. The reaction conditions for the simulation studies were as follows:

reaction pressure: 1.5 MPa
ratio of reactants (wt): TDA:DEIP:phosgene = 1:3:7
thermodynamics method: PR
phosgene temperature: −10 °C
TDA temperature: 120 °C
DEIP temperature: 80 °C

Reaction path: The ratio of reactants for C1 and C2 were set at 28% and 72%, respectively.

■ SIMULATION RESULTS AND DISCUSSION

Five factors affect the reaction temperature: (i) ratio of reactants, (ii) reaction conditions (e.g., temperature, pressure, etc.), (iii) heat of reaction, (iv) vapor–liquid equilibrium, and (v) reaction path. The change in reaction temperature can be

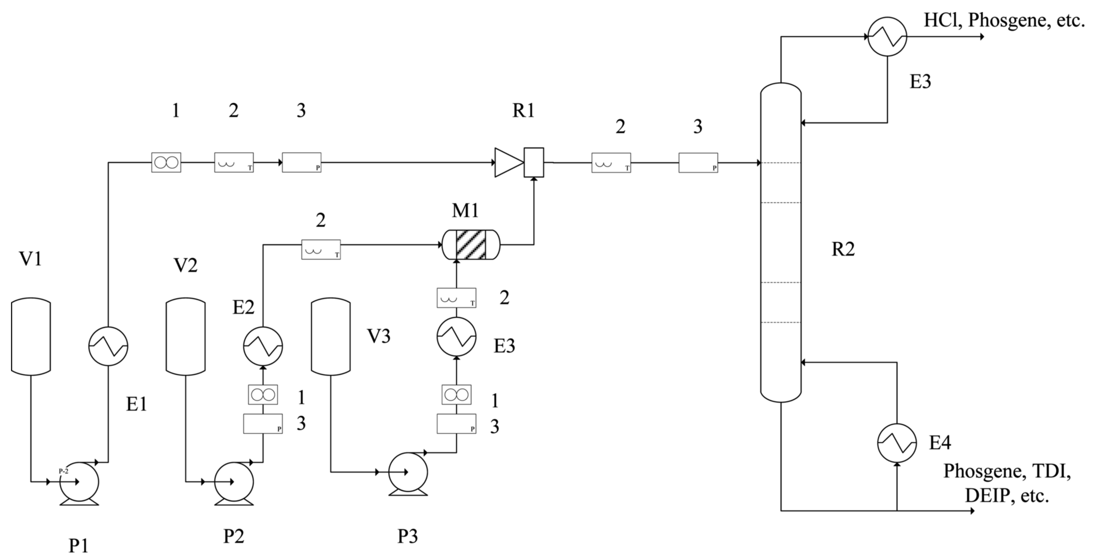


Figure 2. The flow sheet of the industrial process. V1, V2, and V3, storage tanks for phosgene, DEIP, and TDA, respectively; P1, P2, and P3, delivery pumps for phosgene, DEIP, and TDA, respectively; E1, E2, and E3,: heat exchangers of phosgene, DEIP, and TDA, respectively; M1, mixer for DEIP and TDA; R1, jet reactor for cold phosgenation; R2, reaction tower (reactor) of hot phosgenation; E3, condenser for R2; E4, reboiler for R2; 1, flow meters; 2, thermometers; 3, pressure meters.

studied by adjusting four of the above factors. Commercial software Aspen Plus10.2 was used to obtain the reaction path data (i.e., the details of reactions in the reactor), and these data were then used to evaluate the performance of the cold reaction.

Effects of Reaction Path. Reactions C1 and C3 represent the two limiting cases of the reaction path. Usually both the reactions C1 and C3 take place in the experimental or industrial equipment. Under a fixed reaction pressure and ratio of reactants, reactions C1 and C3 may lead to different reaction temperatures and vapor fractions. Under the basic operating conditions, the reaction temperature and vapor fraction change with the reaction path (Figure 3).

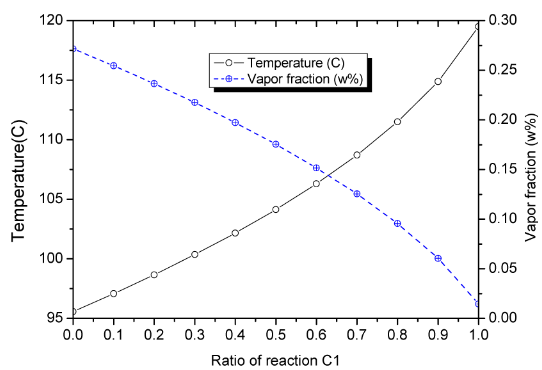


Figure 3. The change in reaction temperature with reaction path.

Figure 3 shows that when the ratio of first reaction increases from 0.0 to 1.0, the reaction temperature increases from 90.57 to 119.50 °C, and the vapor fraction decreases from 0.2715 to 0.0145. With the increase in the ratio of first reaction, more HCl was produced. Because of the low boiling point of HCl, the bubble-point temperature of the reaction mixture got decreased. In other words, when the temperature is fixed, existence of more HCl obviously leads to higher vapor fraction.

As previously mentioned, CCA is a hindrance in the production of TDI. Therefore, low temperature is preferred because less CCA is produced during the cold reaction. It is can be seen that under basic conditions, the ratio of first reaction is 28%, and the reaction temperature is approximately 100 °C.

Effects of Ratios of Reactants. To restrain the undesired side reactions, an excess of phosgene and solvent are added to the reactants. Excess of phosgene and solvent used requires more energy during the separation process, and the safety of the process is decreased. Therefore, an optimum value for phosgene and solvent has to be calculated to balance the risks and the benefits.

Ratio of Phosgene. The ratios of phosgene from 5.0 to 9.5 were simulated. The results obtained are presented in the Figure 4. With the increase in the mass ratio of phosgene, both

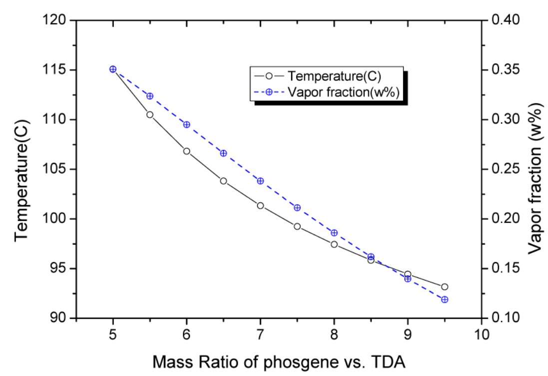


Figure 4. The change in reaction temperature change with ratio of phosgene.

the temperature and vapor fraction decreases. The vapor fraction has a linear relationship, while temperature has a nonlinear relationship, with the ratio of phosgene.

A higher amount of added phosgene usually enhances the mixing performance of reactants, and improves the yield of TDI. However, too much phosgene can lead to a much lower reaction temperature, which can increase the viscosity of the reactive mixture and cause problems such as blockage of the pipe or equipment.

dx.doi.org/10.1021/ie400626n | Ind. Eng. Chem. Res. 2013, 52, 15353−15358

Generally, there is an attempt to decrease the ratio of phosgene, both for the safety reasons and reduction in energy consumption. However, as shown in Figure 4, less phosgene use leads to high temperature leading to undesired side-reactions. To reduce the reaction temperature under a low ratio of phosgene, the mixing performance needs to be enhanced for efficient reaction C3.

Ratio of Reaction Solvent. Solvents are used to minimize the side reactions during the phosgenation reaction. The commonly used solvents are DEIP, chlorobenzene, *o*-dichlorobenzene, and dimethylbenzene. DEIP was used as the solvent in this study.

The ratio of DEIP to other reactants in the reaction ranges from 2.0−4.0 during the simulation studies, and the results are presented in Figure 5. As the ratio of DEIP increases, the temperature increases while the vapor fraction decreases. This is because the boiling point of DEIP is much higher than the other reactants, and the bubble-point of the reaction mixture becomes high in the presence of more DEIP.

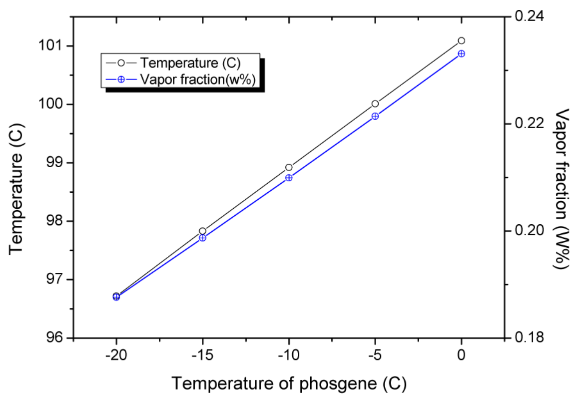


Figure 5. The change in reaction temperature with temperature of phosgene.

Although the ratio of DEIP affects the reaction temperature and vapor fraction, its effect was found to be much lower than that of phosgene.

Effects of Other Parameters. Other parameters which affect the temperature and vapor fraction, such as temperature of phosgene and reaction pressure, were also investigated. The results are presented in Figures 5 and 6.

Figure 5 shows the effects of the temperature of phosgene. Both the reaction temperature and vapor fraction are proportional to the temperature of phosgene. Figure 6 shows the effect of reaction pressure. As the pressure increases, the reaction temperature also linearly increases, while the vapor fraction linearly decreases.

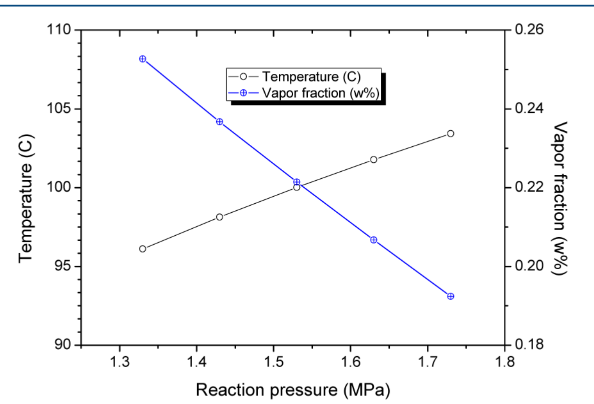


Figure 6. The change in reaction temperature with reaction pressure.

Although both the temperature of phosgene and reaction pressure affect the reaction temperature and vapor fraction, the effects are insignificant compared to reaction path (1 and 2) and ratio of reactants.

■ EXPERIMENTAL RESULTS AND DISCUSSION

Experimental Results. To validate the simulation results, we did some experiments using the industrial equipment (Figure 2). The results of this experiment are presented in Table 1.

Table 1. Experimental Results on Industrial Equipment

		temperature			
no.	ratio	TDA	phosgene	DEIP	reaction
1	1:6.0	120	−10.0	80.2	115.1
2	1:6.1	121	−10.2	78.5	112.0
3	1:6.3	118	−9.5	82.5	108.3
4	1:6.6	122	−10.2	79.6	105.6
5	1:7.0	120	−9.8	80.6	102.2
6	1:7.2	124	−12.0	81.6	100.5
7	1:7.3	120	−11.2	79.6	99.60
8	1:7.5	122	−10.5	80.1	99.22
9	1:7.8	119	−10.3	80.3	97.53
10	1:8.0	118	−10.6	82.1	97.02
11	1:8.2	123	−11.0	76.8	95.23
12	1:8.4	124	−11.5	78.0	94.12
13	1:8.5	122	−10.8	77.6	93.46
14	1:8.8	120	−10.6	79.0	92.85
15	1:9.0	120	−12.0	80.6	92.60
16	1:9.3	124	−11.6	80.4	91.85
17	1:9.4	120	−10.9	80.6	91.52
18	1:9.5	123	−10.5	81.6	91.4

Table1 shows that, as the ratio of reactants increases, the reaction temperature decreases.

Comparison of Temperature. We have presented the simulated reaction and experimental temperatures in Figure 7 for comparison. As the ratio of phosgene increases, the temperature of both experimental and simulation studies decreases. The graph in Figure 7 can be divided into three parts, and each part represents a condition which can be

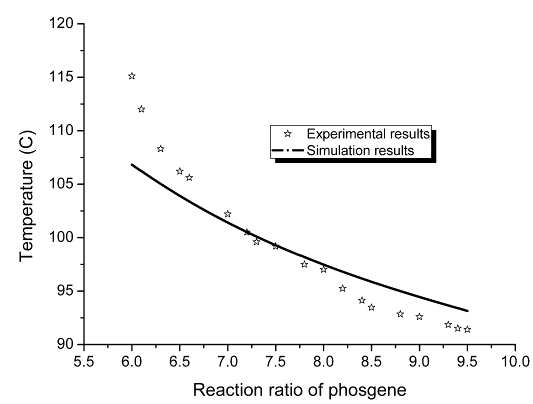


Figure 7. Comparison of experimental and simulation results.

interpreted from the characteristics of reaction and performance of reactor.

The first part shows a low ratio of phosgene in the reaction, that is, <7.0. In this section, the temperature of experiment is higher than that of simulation. The smaller the ratio is, the bigger the difference is. This suggests that in this period, more reaction (C1) was going on under the experimental conditions than simulation. As mentioned before, a higher percentage of reaction (C1) leads to a higher amount CCA being produced, and that ultimately results in a low yield of TDI. This is due to the bad mixing performance of the reactor.

The second part of the graph represents the middle ratio of phosgene in the reaction, that is, 7.0−8.0. In this period, the results obtained from the experiment are in good agreement with the simulation. Therefore, the reactions occurring in the experimental equipment are almost same as the simulation studies.

The final portion of the graph denotes the high ratio of phosgene in the reaction, that is, >8.0. The temperature readings from the experiments are lower than those of simulations in this part. This result suggests that more reaction (C2) occurred in the reactor than simulation studies. A higher ratio of phosgene indicates that a higher amount of phosgene was added to the reactor resulting in a better mixing performance of the reactor.

From the chart in Figure 7, it can be concluded that there is an optimal value for the ratio of phosgene in the reactor. As the ratio is moved lower than this optimum value, a bad mixing performance leads to a high reaction temperature. As the ratio is made close to this optimum value, a good mixing performance leads to an optimum reaction temperature. As the ratio is increased beyond this optimum value, a good mixing performance leads to lower reaction temperature; however, more energy would be needed to add more phosgene and purification, and thus the overall safety of the process would deteriorate.

The reaction temperature can be an indicator for the reactor's performance. On the basis of the reactor's operating conditions, the reactions occurring in the reactor can be deduced, and also the overall performance of the reactor can be evaluated.

Comparison of Reaction Path. Based on the temperature data obtained from these experiments, the ratio of reaction C1 to C2 during the cold phosgenation in the jet reactor can be computed using the simulation results. The ratio of reaction C1 to C2 occurring in the reactor is presented in Figure 8, with the change in the ratio of phosgene.

Figure 8 shows that as the ratio of phosgene to other reactants increases, the ratio of reaction C1 to C2 decreases. In the case of a low ratio of phosgene, the ratio of reaction C1 to C2 rapidly decreases. However, under a high ratio of phosgene, the changes in the ratio of reaction C1 to C2 are not significant. There is an inflection point in the curve, which represents the optimal operation conditions of the jet reactor. It is important to note that the inflection point varies for different jet reactors. But when the configuration of a jet reactor is fixed, the inflection point becomes a constant value. When the ratio of phosgene to other reactants is lower than this optimum value, the reactions in the equipment are not optimal. A higher ratio of phosgene leads to more consumption of power and energy, even though the reactions are almost similar to those in optimal conditions. As far as the jet reactor experiments are concerned, the optimal value for the ratio of phosgene to other reactants is approximately 7.0.

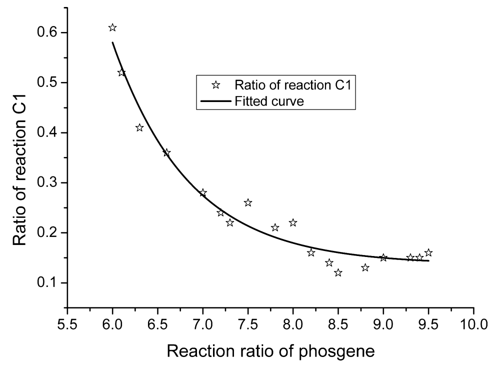


Figure 8. Ratio of reaction C1 to C2 based on the experimental temperature.

CONCLUSION

(1) A mapping table was obtained between the reaction path and temperature. On the basis of the mapping table, the reaction temperature can be seen as indicative of the reaction path or performance of the reactor.
(2) The effects of parameters such as ratio of phosgene, DEIP, etc. were also investigated. The ratio of phosgene to other reactants was found to be the most important parameter that affects the reaction path and temperature.
(3) A method to predict the phosgenation reaction performance, for the production of TDI in jet reactors, was proposed. The method utilizes easily obtained experimental reaction temperature data to predict the reaction performance in the jet reactor.
(4) Equipment with a capacity of 1000 tons/annum TDI was studied using the developed method, and the production department in the industry was advised accordingly.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the co-workers from Qingdao YKHY Process and Information Technology Co., Ltd. and Gansu Yinguang Chemical Industry Group Co., Ltd.

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