# Chemical Kinetics of the Alkylation of Xylenol for the Separation of Their Close-Boiling Isomers from Coal Tar

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Abstract—To support the industrial design and process development for the separation of xylenol isomers from coal tar, the present work was focused on 2,4/2,5-xylenol mixture as 2,4-xylenol and 2,5-xylenol have very close boiling points. Specifically, the kinetics of the alkylation of 2,4/2,5-xylenol mixture was investigated that formed the first step of the alkylation-distillation-dealkylation separation strategy. By quantifying the influence of various key factors on the reaction rate, the rate equations of 2,4-xylenol and 2,5-xylenol

alkylation were determined as  $r_{2,4} = 1538e^{-39360/RT}c_{2,4}^{1.1}P_{\text{PIB}}^{1.0}c_{\text{PTSA}}^{0.4}$  and  $r_{2,5} = 516e^{-32241/RT}c_{2,5}^{1.0}P_{\text{PIB}}^{0.8}c_{\text{PTSA}}^{0.7}$ , respectively. The alkylation rate of 2,4-xylenol was notably higher than that of 2,5-xylenol. The influence of temperature, xylenol concentration and isobutylene partial pressure on the reaction rate of 2,4-xylenol was also greater than that of 2,5-xylenol, whilst the influence of catalyst dosage on the alkylation rate of 2,5-xylenol was not also be greater than that of 2,4-xylenol. The results can be potentially used for reactor design and process development for the separation of 2,4/2,5-xylenol mixture from coal tar.

**Keywords:** 2,4-xylenol, 2,5-xylenol, alkylation, reaction kinetics, separation **DOI:** 10.1134/S0965544120110031

# INTRODUCTION

Xylenol (or hydroxyxylene) generally refers to any of the six isomers of dimethylphenol  $[(CH_3)_2C_6H_3OH]$  or to combinations thereof. Xylenols are naturally-occurring phenolic compounds, which are present in various sources such as coal, petroleum and tobacco [1, 2]. Individual xylenol isomers may be produced through separation, and/or synthetic processes. When extracted from coal tar, the products are typically in the form of mixtures of more than one isomers, which normally need further separation if pure xylenol isomers are required [3, 4]. Owing to their unique reactivity and solvency properties, xylenols are regarded as key raw materials in many products manufacturing, e.g. resins and polymers, antioxidants in fuels and plastics, and reactive solvents in applying insulation to electrical wires/cables [5, 6].

Overall, the technological development trend with time in the production of xylenols has followed that in the general chemical industry, showing heavy dependence on sources of raw materials [2, 7]. The interest in using coal tar as raw materials for xylenols production dates back to the 1930s [8–10], that was largely replaced by the natural gas- and oil-based resources for chemical synthesis of xylenols [11–13]. However, with the growing challenges faced by the petroleum-

based chemical industry, such as limited feedstock and increasing environmental concerns, more research efforts have been directed to either partial or complete replacement of chem-stocks of petroleum-based industries [2]. For example, coal- including coal tarbased chemicals are of particular relevance in China, mainly due to the significant coal reserves and production [14–16].

Coal tar is a byproduct in the production of coke or coal gas from coal, typically in form of brown/black viscous liquid. When obtained through the process in the low-medium temperature range (typically, 500– 900°C), the coal tar consists of mainly polyalkylene aromatic hydrocarbon, aliphatic chain alkane, alkene and phenols [17–19]. The content of phenols is about 20–30 wt %, while 2,4-xylenol and 2,5-xylenol account for about 13–15% of the total phenol content (for the tar produced in Shaanxi Province, China) [14, 20, 21]. The annual production of coal tar in this region is estimated to be over 3 million tonnes, thus regarded as a promising alternative source of 2,4-xylenol and 2,5-xylenol [15, 22].

With the rapid increase of demand for downstream fine chemical products, the market demand for single component 2,4-xylenol and 2,5-xylenol has also been growing steadily especially in the Chinese manufacture sector, while the price is rising. It was estimated in 2019 that the market price of mixed 2,4/2,5-xylenol was 2200 USD/ton, while single component 2,4-xylenol was 6100 USD/ton, and 2,5-xylenol was 8400 USD/ton [23]. Therefore, the development of deep separation technology of 2,4/2,5-mixed xylenol in coal tar can not only meet the market demand, but also increase the added value of coal tar and bring huge benefits economically [20–22]. However, no industrial process is currently available for the production of their individual isomers through separation, while they are mostly produced and sold in the form of 2,4/2,5-xylenol mixtures.

The key challenge in 2,4/2,5-xylenol separation is associated with their very close boiling points at 211.0 and 211.2°C, respectively, under normal pressure. That makes the conventional distillation economically unviable. To address this issue, the three-step process of alkylation-distillation-dealkylation provides a promising route to separation, based on the extensive studies on the separation of close-boiling cresols [3, 4, 24–29]. Furthermore, even without the last step of dealkylation, the alkylation product itself, e.g. 6-tertbutyl-2,4-xylenol (or TBX) has been widely used as an antioxidant agent [30, 31].

With an ultimate goal to provide fundamental understanding and data for industrial design and process development, the present work was focused on the kinetic and mechanistic studies on alkylation of xylenols, the first step of the process for close-boiling xylenols separation. Isobutylene was selected as alkylating agent which has been widely used for the alkylation of cresols [32-34]. p-Toluenesulfonic acid was used as catalyst mainly due to its capacity for high yield and good selectivity [35–37]. The reaction rate, the product yield and selectivity were investigated by varying the reactant concentration, partial pressure, catalyst amount and gas-liquid contact time. Based on the experimental results, a reaction kinetic model was established and the reaction orders were obtained with rate equations. Furthermore, with the rate constants determined at different temperatures, the activation energies and pre-exponential factors were calculated.

# **EXPERIMENTAL**

**Chemicals.** 2,4-Xylenol and 2,5-xylenol (Analytical grade) were obtained from Juye Runjia Chemical Co., Ltd) and isobutene (Analytical grade) was supplied by Shaanxi Baotashan New Material Co., Ltd. *p*-Toluenesulfonic acid, or PTSA (Analytical grade) was purchased from Nanjing Datang Chemical Co., Ltd. All chemicals were used as received without any further purification.

**Experimental methods.** Alkylation of 2,4/2,5-xylenol mixture. 50.0 g 2,4-Xylenol and 50.0 g 2,5-xylenol mixture were weighed into 250 mL 3-neck round-bottom glass flask that was placed in a water bath. With the mechanical agitator set at 800 rpm, and temperature raised slowly to the specified temperature, 2.5 wt % catalyst PTSA was added in after the solid phase of 2,4/2,5-xylenol mixture turned to liquid. Then gas isobutylene was introduced into the reaction vessel at the bottom where the gas bubbles were broken up by agitation. Both flow rates of the inlet and outlet tail gases were measured, respectively, by two gas flow meters (50-500 mL/min, Ningbo Dongchi Measurement and Control Technology Co., Ltd). When no measureable difference between and inlet and outlet gas flow rates was observed, the reaction was stopped. During the reaction, samples were taken at regular intervals and analyzed immediately by gas chromatography. All experiments were repeated in triplicate, and the average values are reported.

Products analysis. The alkylation products were analyzed by gas chromatography (GC6890, Agilent) with an FID detector, and a column (KB-CRESOL,  $50 \text{ m} \times 0.25 \text{ mm} \times 0.2 \text{ µm}$ ) supplied by Beijing Kerimai Technology Co., Ltd. The GC operated at a detector temperature of 250°C, and column box temperature of 140°C. The temperature rising procedure included; first to keep column temperature at 60°C for 3 min, then to raise temperature to  $100^{\circ}$ C at  $5^{\circ}$ C/min rate, and finally to continue to raise temperature to 180°C at 10°C /min for 3 min. The split ratio was 50 : 1, while the carrier gas flow rate was set at 1 mL/min, the airflow rate at 400 mL/min, and the hydrogen flow rate at 50 mL/min. Standard control and normalization methods were used for qualitative and quantitative analysis.

# **RESULTS AND DISCUSSION**

Reaction mechanism of alkylation of 2,4/2,5-xylenol mixture. The alkylation of dimethylphenol with isobutylene is an electrophilic substitution reaction on benzene ring, a classical Friedel-Crafts reaction. In a generally understood mechanism, the alkylation isobutylene produces alkylcarbocation reagent  $[^{+}C(CH_{3})_{3}]$  under the action of acid catalyst PTSA, which attacks benzene ring as electrophilic reagent to replace the hydrogen above, and then deprotons to generate alkylaromatics [38, 39]. Theoretically, for 2,4/2,5-xylenol, the hydroxyl group is an either orthoor para-orientation group, and the alkylation products may include 6-tert-butyl-2,4-xylenol, 5-tert-butyl-2,4-xylenol and 3-tert-butyl-2,4-xylenol from 2,4xylenol, whilst 4-tert-butyl-2,5-xylenol, 6-tert-butyl-2,5-xylenol and 3-tert-butyl-2,5-xylenol from 2,5xylenol, as illustrated in Fig. 1. As expected, the main alkylation products were 6-tert-butyl-2,4-xylenol and 4-tert-butyl-2,5-xylenol, with high selectivities of 98.75% and 93.91%, respectively. The GC-MS analysis results are summarized in Table 1, which are in line with the previous studies [38, 39].

Effect of reaction time on alkylation of 2,4/2,5xylenol mixture. The alkylation took place with 100.0 g

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Table 1. Selectivity of alkylation products

Materials	Alkylation products	Selectivity, %
2,4-Xylenol	6-tert-butyl-2,4-xylenol	98.75
	5-tert-butyl-2,4-xylenol	1.25
2,5-Xylenol	4-tert-butyl-2,5-xylenol	93.91
	6-tert-butyl-2,5-xylenol	6.09

of 2,4/2,5-xylenol mixture (1 : 1 wt) and 2.5 wt % of catalyst PTSA, at a stirring speed of 800 rpm, temperature 65°C, under atmospheric pressure, with an isobutylene flow rate of 100 mL/min, the composition and content of products were analyzed with GC at different reaction stages. The reaction percentage yield (%) was calculated by dividing the amount of the product actually produced by the theoretical amount of product expected. The yields (%) of both products and byproduct as a function of reaction time are plotted in Fig. 2.

As can be seen in Fig. 2a, the total yield of the target products of 6-tert-butyl-2,4-xylenol and 4-tert-butyl-2,5-xylenol began to rise with the increase of reaction time. At reaction time about 240 min, the total yield reached a maximum of 89.5%, which was followed by a slight decline when the reaction continued. It was also observed that the yield of the byproduct increased with time in an approximately linear way, up to 10% when the reaction was stooped after 360 min. It was found that the byproduct consisted of mainly light components through isobutylene oligomerization, including dimers and trimers [33].

Figure 2b compares the yields of two target products of 6-tert-butyl-2,4-xylenol and 4-tert-butyl-2,5xylenol at different reaction times. The production of 6-tert-butyl-2,4-xylenol increased rapidly within the first 120 min approximately in linear, and then at a slower rate of increase before reaching a yield of 97.3% when the reaction time was 360 min.

Overall, the yield of 4-tert-butyl-2,5-xylenol was lower (15–30%) than that of 6-tert-butyl-2,4-xylenol at any given time (Fig. 2b). The yield also increased rapidly before reaching a maximum of 82.3% at reaction time 240 min, which was followed by a slight decline. Further experiments confirmed the partial decomposition of 4-tert-butyl-2,5-xylenol (to 2,5xylenol and isobutene) at higher reaction temperature (above 65°C) in the presence of catalyst PTSA (data not shown). This suggested the reverse decomposition reaction to be largely accountable for the slight reduction in the product yield after 240 min.

Kinetic model development for the alkylation of 2,4/2,5-xylenol. In view of providing a chemical kinetic model for reactor design and process development, it is essential to quantify the influence of various operating factors, leading to the establishment of mathematical description of the course of the reaction for each reaction step as a function of components in the system [40]. The key factors include reactant concentration, reaction time, reaction temperature, and catalyst amount used.

According to the reaction scheme (Fig. 1), the reaction rates for the alkylation of 2,4/2,5-xylenol can be generally expressed by Eqs. (1) and (2).

$$r_{2,4} = -\frac{dc_{2,4}}{dt} = k_1 c_{2,4}^{a_1} p_{\text{PIB}}^{b_1} c_{\text{PTSA}}^{c_1}, \qquad (1)$$

$$r_{2,5} = -\frac{dc_{2,5}}{dt} = k_2 c_{2,5}^{a_2} p_{\text{PIB}}^{b_2} c_{\text{PTSA}}^{c_2}, \tag{2}$$

where  $r_{2,4}$  and  $r_{2,5}$  represent the reaction rates of 2,4xylenol and 2,5-xylenol, respectively.  $k_1$  and  $k_2$  are their reaction rate constants.  $c_{2,4}$  and  $c_{2,5}$  represent the molar concentrations of 2,4-xylenol and 2,5-xylenol, respectively.  $p_{\text{PIB}}$  and  $c_{\text{PTSA}}$  are the partial pressure of



Fig. 2. Yields of (a) product mixture and byproduct (light components), and (b) two individual products as a function of time.



**Fig. 3.** Dependences of concentration of 2,4-xylenol (a) and 2,5-xylenol (b) on alkylation reaction rate. Experimental conditions: 2,4/2,5-xylenol concentration, 2.73–8.20 mol/L; catalyst PTSA concentration, 0.145 mol/L; stirring speed, 800 rpm; temperature,  $65^{\circ}$ C; isobutylene flow rate, 100 mL/min with partial pressure 101.32 kPa; reaction time, 30 min.

isobutylene and the molar concentrations of catalyst PTSA, respectively.  $a_1$ ,  $b_1$  and  $c_1$  represent the reaction orders of 2,4-xylenol, isobutylene and PTSA during the alkylation of 2,4-xylenol, and  $a_2$ ,  $b_2$  and  $c_2$ , the reaction orders of 2,5-xylenol, isobutylene and PTSA, respectively.

In the reaction system of 2,4/2,5-xylenol alkylation, there were four main components at the start, i.e. 2,4-xylenol, 2,5-xylenol, isobutylene and PTSA. In order to determine the reaction order for a specific reactant, the concentrations of other components were set to be greatly excessive, reasonably regarded as a constant. Therefore, the reaction order of the tested component was obtained through the  $c \sim t$  relationship.

Determination of alkylation reaction order for 2,4xylenol and 2,5-xylenol. To determine the reaction order, the reaction initial rate is normally measured in order to eliminate the interference of the product. Based on the relationship between the yield and reaction time for the alkylation of 2,4/2,5-xylenol (Fig. 2), at the early stage of the reaction, the side reactions were insignificant along with the higher rate of alkylation main reaction, whilst the yield changed appropriately in linear with time. Therefore, the initial reaction time of 30 min was selected for characterizing reaction kinetics.

For the alkylation of 2,4/2,5-xylenol mixture, 10 times more isobutylene and catalyst were added, respectively, in the reaction vessel. The start concentration of xylenol was adjusted by adding nitrobenzene, and the reaction rates of 2,4-xylenol and 2,5-xylenol were determined at different start concentrations. Since the concentration of isobutylene and PTSA can be considered unchanged during the process, the reaction rate Eqs. (1) and (2) can be simplified as Eqs. (3) and (4), and then Eqs. (5) and (6).

$$r_{2,4} = -\frac{dc_{2,4}}{dt} = k_1 c_{2,4}^{a_1},\tag{3}$$

$$r_{2,5} = -\frac{dc_{2,5}}{dt} = k_2 c_{2,5}^{a_2},\tag{4}$$

$$\ln r_{2,4} = \ln \left( \frac{dc_{2,4}}{dt} \right) = a_1 \ln c_{2,4} + \ln k_1, \tag{5}$$

$$\ln r_{2,5} = \ln \left( \frac{dc_{2,5}}{dt} \right) = a_2 \ln c_{2,5} + \ln k_2.$$
 (6)

The initial reaction rates, obtained for five different xylenol concentrations, are plotted against xylenol concentration on a log-log scale (Fig. 3). By best-fitting straight lines to the experimental data, the reaction orders ( $a_1$  and  $a_2$ ) and the reaction rate constants ( $k_1$  and  $k_2$ ) were determined.

As can be seen in Fig. 3, with increase in the concentration of 2,4-xylenol and 2,5-xylenol, the reaction rate increased correspondingly with a good linear relationship. With the equation of the line of best fit, the reaction orders for 2,4-xylenol ( $a_1$ ) and 2,5-xylenol ( $a_2$ ) were found to be 1.1 and 1.0, respectively.

Determination of reaction order for isobutylene. Similarly, the effect of partial pressure  $(p/p^0)$  of isobutylene was quantified by diluting isobutylene with nitrogen, with excessive amounts of 2,4/2,5-xylenol mixture and catalyst. The corresponding reaction rates, measured at a temperature of 65°C, are plotted against partial pressure on a log-log scale, as illustrated in Fig. 4.

Both reaction rates of 2,4-xylenol and 2,5-xylenol had a good linear relationship with the change of isobutylene partial pressure on a log-log scale. The reaction rate increased with the rising of isobutylene partial pressure. Using the equation for a straight line



**Fig. 4.** Dependence of partial pressure of 2,4-xylenol (a) and 2,5-xylenol (b) on alkylation reaction rate. Experimental conditions: 2,4-/2,5-xylenol concentration, 8.20 mol/L; isobutylene flow rate, 100 mL/min with partial pressure form 25.43 kPa to 101.32 kPa; other conditions, same as those shown in Fig. 3.



**Fig. 5.** Dependence of the alkylation reaction rate of 2,4-xylenol (a) and 2,5-xylenol (b) from the amount of catalyst. Experimental conditions: catalyst PTSA concentration, 0.087-0.203 mol/L; concentration of 2,4-/2,5-xylenol, 8.20 mol/L; other conditions, same as those shown in Fig. 3.

of best fit, it was found that for the alkylation of 2,4xylenol, the reaction order of isobutylene was  $b_1 = 1.0$ , while for the alkylation of 2,5-xylenol, the reaction order of isobutylene was  $b_2 = 0.8$ .

Determination of reaction order for catalyst. The reaction rates of 2,4-xylenol and 2,5-xylenol were also determined by varying the amount of catalyst PTSA, with excessive amounts of 2,4/2,5-xylenol mixture and isobutylene at a reaction temperature of 65°C within 30 min of reaction time. The relationships of  $\ln r_{2,4}$  with  $\ln(\text{PTSA})$ , and  $\ln r_{2,5}$  with  $\ln(\text{PTSA})$  are depicted in Fig. 5.

It can be seen from Fig. 5 that, within the range of catalyst amount examined, the alkylation rate of 2,4/2,5-xylenol increased with the increasing concen-

tration of catalyst PTSA, as expected. From the equation for a straight line of best fit, it was determined that, for the alkylation of 2,4-xylenol and 2,5-xylenol, the reaction orders for catalyst PTSA were  $c_1 = 0.4$  and  $c_2 = 0.7$ , respectively.

It should be noted that the reaction order n of elementary reactions and simple reactions may be integer one, two and three (though three applies to only a few reactions), while the reaction order n of complex reactions is generally non-integer. The reaction order obtained in the present study is not an integer, indicating complex reactions occurring.

*Estimation of activation energy and Arrhenius constant A.* The temperature (T) dependence of the reac-

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**Fig. 6.** Dependence of the reaction rate constants of the alkylation of 2,4-xylenol (a) and 2,5-xylenol (b) on temperature in Arrhenius coordinates. Experimental conditions: concentration of 2,4/2,5-xylenol, 8.20 mol/L; temperature,  $60-75^{\circ}$ C; other conditions, same as those shown in Fig. 3.

tion rate constants k is defined according to the Arrhenius approach given in Eq. (7).

$$k = A e^{\frac{-E_a}{RT}},\tag{7}$$

where the kinetic parameters A and  $E_a$  describe the pre-exponential factor (collision factor) and the activation energy of the reaction, respectively, and R is the ideal gas constant. Then logarithm of both sides of Eq. (7) is expressed by Eq. (8).

$$\ln k = \frac{-E_{\alpha}}{RT} + \ln A.$$
(8)

By measuring the reaction rate constants of 2,4xylenol and 2,5-xylenol at different temperatures, and then plotting  $\ln k$  against 1/T, the values of  $E_a$  and Awere obtained from the equation for a straight line of best fit, as illustrated in Fig. 6.

Figure 6 shows a good linear relationship was observed between  $\ln k$  and 1/T in the temperature range investigated for the alkylation of both 2,4-xylenol and 2,5-xylenol. From these plots and the best-fitting equations, the activation energy  $E_{a1}$  and Arrhenius constant  $A_1$  for 2,4-xylenol alkylation were found to be 39.36 kJ/mol and 15389 mol<sup>-0.5</sup> L<sup>0.5</sup> min<sup>-1</sup>, respectively, while the activation energy  $E_{a1}$  and Arrhenius constant  $A_2$  for 2,5-xylenol alkylation were 32.24 kJ/mol and 516 mol<sup>-0.7</sup> L<sup>0.7</sup> min<sup>-1</sup>, respectively. To the best of our knowledge, there is no data reported in the literature on the activation energy for the xylenol alkylation reactions. For the alkylation of p-cresol with isobutylene catalyzed by sulfated zirconia the activation energy was found to be 95.73 kJ/mol [39], indicating the comparison of the kinetic data obtained in this study. The results indicated a very low activation energy for the alkylation of both 2,4-xylenol and 2,5-xylenol, demonstrating the effectiveness of the catalyst used for these two reactions, generally by providing an alternative pathway with lower activation energy requirements [39, 41].

Kinetic equations of the alkylation of 2,4/2,5-xylenol. As analyzed above, in the alkylation process of 2,4-xylenol and 2,5-xylenol, the reaction orders of 2,4-xylenol, isobutylene and PTSA were 1.1, 1.0 and 0.4, respectively, with a total reaction order of 2.5; the activation energy was 39.36 kJ/mol, and the Arrhenius constant, 15389 mol<sup>-0.5</sup> L<sup>0.5</sup> min<sup>-1</sup>. For the alkylation of 2,5-xylenol, the reaction orders of 2,5-xylenol, isobutylene, and PTSA were 1.0, 0.8 and 0.7, respectively, with a total reaction order of 2.5, and the activation energy was 32.24 kJ/mol, and the Arrhenius constant, 516 mol<sup>-0.7</sup> L<sup>0.7</sup> min<sup>-1</sup>. By inserting these values into the reaction rate Eqs. (1) and (2), the kinetic Eqs. (9) and (10) for the alkylation of 2,4/2,5-xylenol can be obtained.

$$r_{2,4} = k_1 c_{2,4}^{1.1} P_{\text{PIB}}^{1.0} c_{\text{PTSA}}^{0.4}$$
  
= 1538 $e^{-39360/RT} c_{2,4}^{1.1} P_{\text{PIB}}^{1.0} c_{\text{PTSA}}^{0.4}$ , (9)

$$r_{2,5} = k_2 c_{2,5}^{1.0} P_{\text{PIB}}^{0.8} c_{\text{PTSA}}^{0.7}$$
  
= 516e<sup>-32241/RT</sup> c\_{2,5}^{1.0} P\_{\text{PIB}}^{0.8} c\_{\text{PTSA}}^{0.7}. (10)

It is understood that the rate constant k is independent of concentration, whose value directly reflects the reaction rate. For example, at 65°C, the rate constants  $k_1 = 1.2 \times 10^{-2} \text{ mol}^{-0.5} \text{ L}^{0.5} \text{ min}^{-1}$ , and  $k_2 = 5.4 \times 10^{-3} \text{ mol}^{-0.7} \text{ L}^{0.7} \text{ min}^{-1}$ , thus  $k_1/k_2 = 2.22$ , indicating that the reaction rate of 2,4-xylenol alkylation was 2.2 times that of 2,5-xylenol. This was in good agreement with the experimental observation (Fig. 2).

As can be seen from Eqs. (9) and (10), the level of the activation energy also indicated the influence of temperature on reaction rate. Compared to 2,5-xylenol, 2,4-xylenol had a higher activation energy (39.36 kJ/mol vs 32.24 kJ/mol), suggesting that the reaction of 2,4-xylenol was more "sensitive" to temperature changes than that of 2,5-xylenol [38, 39]. It was in line with the experimental observation; the increase in temperature was more favorable for the alkylation of 2,4-xylenol, though both reaction rates increased with rising temperature.

As also seen from reaction rate Eqs. (9) and (10), the higher the reaction order, the greater the influence of concentration on the reaction rate [42]. Therefore, the influence of xylenol concentration and isobutylene partial pressure on the alkylation rate of 2,4-xylenol was greater than that of 2,5-xylenol (1.1 vs 1.0 for xylenol concentration, and 1.0 vs 0.8 for isobutylene partial pressure). As a result, the overall reaction rate and final yield of the 2,4-xylenol reaction was notably higher than that of 2,5-xylenol, though the effect of catalyst amount underwent an opposite way which, however, appeared to be insignificant.

For the alkylation of 2,5-xylenol, although the yield can be improved by optimizing the reactant ratio and reaction temperature, from the perspective of industrial production, the rate of chemical reaction can also be accelerated by optimizing the selection of catalyst, so as to improve the yield in a certain period of time.

# CONCLUSIONS

(a) For the alkylation a mixture of 2,4/2,5-xylenol (1 : 1 wt) with isobutylene catalyzed by *p*-toluenesulfonic acid, the yields of 6-tert-butyl-2,4-xylenol and 4-tert-butyl-2,5-xylenol were found to be 97.3 and 82.3%, respectively.

(b) Both of the total reaction orders of alkylation of 2,4-xylenol and 2,5-xylenol, catalyzed by *p*-toluene-sulfonic acid, were 2.5, and their activation energies were estimated to be 39.36 and 32.24 kJ/mol, respectively.

(c) The concentration of xylenol and isobutylene partial pressure had more significant influence on the alkylation rate of 2,4-xylenol, while catalyst has more influence on the alkylation rate of 2,5-xylenol.

(d) In view of industrial application, the yield of 2,5-xylenol can be potentially improved by designing and optimizing more effective catalysts. This aspect is currently under active investigation in our laboratories.

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# CONFLICTS OF INTEREST

There are no conflicts to declare.

#### SUPPLEMENTARY MATERIALS

Supplementary materials are available for this article at doi: 10.1134/S0965544120110031 and are accessible for authorized users.

# ADDITIONAL INFORMATION

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# REFERENCES

- C. M. Sparacino and D. J. Minick, Environ. Sci. Technol. 14, 880 (1980).
- 2. B. Lochab, S. Shukla, and I. K. Varma, RSC Adv. 4, 21712 (2014).
- L. S. Lee, C. W. Lin, and C. H. Kao, Ind. Eng. Chem. Res. 39, 2068 (2000).
- L. D. Shiau and C. C. Yen, J. Chem. Eng. Jpn. 44, 623 (2011).
- H.-G. Franck and J. W. Stadelhofer, *Industrial Aromat*ic Chemistry: Raw Materials, Processes, Products (Springer, Berlin, 2012).
- D. S. Fardhyanti, P. Mulyono, W. B. Sediawan, and M. Hidayat, in *Proceedings of the 2nd International Conference on Environment and Industrial Innovation* (*ICEII 2012*), June 2012, Hon Kong, China, vol. 6, p. 131.
- F. W. Lichtenthaler and S. Peters, C. R. Chim. 7, 65 (2004).
- 8. E. Kester, Ind. Eng. Chem. 24, 770 (1932).
- 9. D. R. Stevens, Ind. Eng. Chem. 35, 655 (1943).
- 10. F. E. Cislak and M. M. Otto, US Patent No. 2456582 (1948).
- 11. H. Grabowska, W. Kaczmarczyk, and J. Wrzyszcz, Appl. Catal. 47, 351 (1989).
- H. W. Prengle, Jr., X. van Tran, K. Moinzadeh, et al., Synthesis of Cresols and Xylenols from Phenol and Methanol (National Renewable Energy Lab., Golden, CO, 1992).
- K. Sreekumar and S. Sugunan, J. Mol. Catal., A 185, 259 (2002).

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- R. C. Wang, Q. X. Liu, Y. X. Ma, et al., J. China Coal Soc. 36, 664 (2011).
- 15. M. Sun, D. Zhang, Q. Yao, et al., Energy Fuels **32**, 7404 (2018).
- 16. BP Statistical Review of World Energy 2019—Coal. https://www.bp.com/en/global/corporate/energy- economics.html.
- 17. J. R. Kershaw and K. J. Black, Energy Fuels 7, 420 (1993).
- K. K. Tiwari, S. Banerjee, B. P. Das, et al., Fuel. Process. Technol. 86, 13 (2004).
- C. Karr, Jr., Analytical Methods for Coal and Coal Products (Academic, San Diego, CA, 2013), Vol. 2, p. 50).
- Q. Sun, X. Ma, C. Sun, and J. L. Xu, Appl. Chem. Ind., 42, 713 (2013).
- Y. Zhao, X. Mao, W. Li, et al., Int. J. Coal Sci. Technol. 4, 333 (2017).
- 22. H. Q. Sun, S. J. Qu, and L. B. Wang, Clean Coal Technol. **6**, 62 (2008).
- ZYHTYJY, 2019–2025 Market Trend and Analysis on Xylenols. http://www.zyhtyjy.com/report/269716.html
- 24. V. Gaikar and M. Sharma, Sadhana 10, 163 (1987).
- 25. B. Chaudhuri, A. A. Patwardhan, and M. Sharma, Ind. Eng. Chem. Res. **29**, 1025 (1990).
- 26. A. K. Mukhopadhyay, *Industrial Chemical Cresols and Downstream Derivatives* (CRC, Boca Raton, 2004).
- 27. L. D. Shiau, C. H. Huang, and K. F. Liu, Asia-Pac. J. Chem. Eng. 7, 26 (2012).
- 28. K. Y. Paranjpe, Int. J. Chem. Stud. 5, 300 (2017).

- 29. R. V. Kondapaneni, U. Virendra, and S. Vedantam, J. Environ. Chem. Eng. 5, 5280 (2017).
- 30. Y. Shinozaki and T. Kumagai, US6506815, 2003.
- S. Kawakami, M. Sogabe, T. Shibata, et al., US Patent No. 20180280315 (2018).
- 32. M. A. Harmer and Q. Sun, Appl. Catal., A **221**, 45 (2001).
- 33. E. Santacesaria, M. D. Serio, R. Tesser, and F. Cammarota, Ind. Eng. Chem. Res. 44, 9473 (2005).
- T. Patra, F. Parveen, and S. Upadhyayula, Mol. Catal. 433, 175 (2017).
- 35. V. G. Gaikar, A. Mahapatra, and M. M. Sharma, Ind. Eng. Chem. Res. 28, 199 (1989).
- M. Saha, M. Mosihuzzaman, and S. Saha, Indian. J. Chem. Technol. 3, 292 (1996).
- K. Ikimi, Y. Ikeda, A. Murakami, et al., US Patent No. 5600026 (1997).
- P. G. Smirniotis and E. Ruckenstein, Ind. Eng. Chem. Res. 34, 1517 (1995).
- G. D. Yadav and T. S. Thorat, Ind. Eng. Chem. Res. 35, 721 (1996).
- 40. G. Ganzer, H. Freund, Ind. Eng. Chem. Res. 58, 1857 (2019).
- J. F. Lorenc, G. Lambeth, and W. Scheffer, in *Kirk–Othmer Encyclopedia of Chemical Technology* (Wiley–VCH, Weinheim, 2003), Vol. 2, p. 170.
- 42. S. Al-Zahrani, M. Al-Kinany, K. Al-Humaizi, and S. Al-Khowaiter, Int. J. Chem. Kinet. **35**, 555 (2003).