

# Reflux–Recycle–Reactor for High Yield and Selectivity in TAME and TAEE Production

Nezahat Boz and Timur Dogu

Chemical Engineering Department, Middle East Technical University, Ankara, 06531 Turkey

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*The batch reflux–recycle–reactor (RRR) proposed here was shown to give high product yields and selectivities in the production of tert-ethers. Because the vapor pressures of product ethers are lower than those of the reactants, vapor-phase reactor inlet stream is always rich in reactants in this batch RRR. A first-order reversible reaction rate model was shown to give good prediction of experimental results. The apparent activation energy of the rate constant was evaluated as  $24.8 \text{ kJ mol}^{-1}$ . This low value of activation energy for vapor-phase synthesis of tert-amyl methyl ether (TAME) was concluded to be primarily attributed to the significance of transport resistances in the macropores of Amberlyst-15 and also through the thin liquid film covering catalyst particles. In the case of TAME production fractional conversion values reaching 0.91 were obtained at  $82^\circ\text{C}$  with almost 100% selectivity. Comparison of the results obtained for TAME and tert-amyl ethyl ether (TAEE) synthesis showed that reactivity of methanol was much higher than that of ethanol in the etherification reaction of isoamylene, over Amberlyst-15. © 2005 American Institute of Chemical Engineers *AIChE J.* 51: 631–640, 2005*

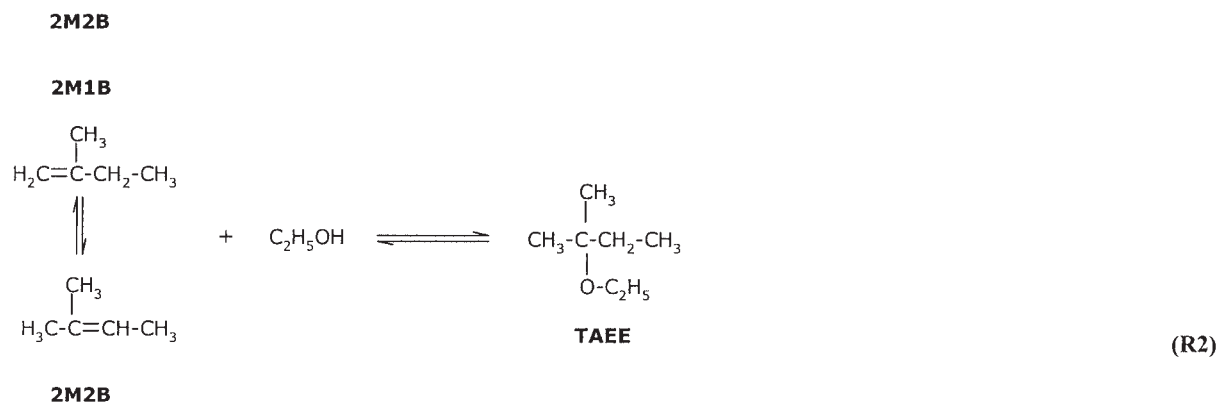
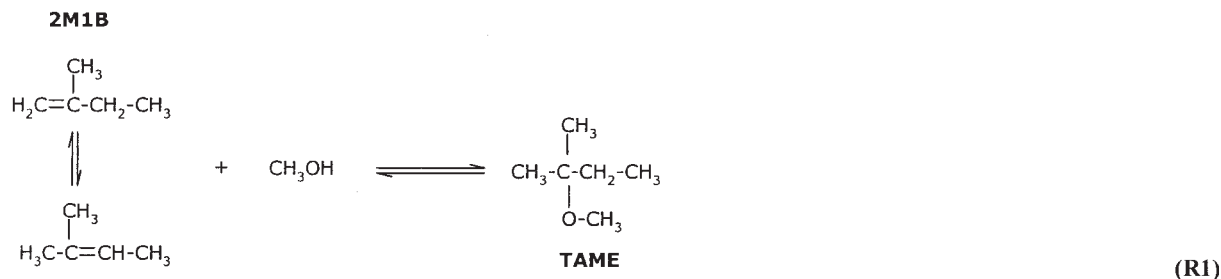
**Keywords:** oxygenates, 2M2B, 2M1B, TAEE, TAME, reflux–recycle–reactor, Amberlyst-15, diffusion resistance

## Introduction

Methyl-*tert*-butyl ether (MTBE) has become the major gasoline additive used in the last decade, to improve the octane number of gasoline as well as to reduce the exhaust emissions of CO and unburned hydrocarbons.<sup>1</sup> Because of water pollution problems

created by the extensive use of MTBE as a gasoline blending oxygenate and also because of insufficient supply of isobutene, which is the limiting reactant in MTBE production, extensive research has focused on alternative octane-enhancing oxygenates as gasoline additives. This attracted the attention of researchers to heavier ethers such as TAME (*tert*-amyl methyl ether) and TAEE (*tert*-amyl ethyl ether), which have vapor pressures lower than that of MTBE.<sup>2</sup> These ethers are produced by the reaction of isoamylenes [2-methyl-2-butene (2M2B) and 2-methyl-1-butene (2M1B)], with methanol or ethanol, respectively.

Correspondence concerning this article should be addressed to T. Dogu at [tdogu@metu.edu.tr](mailto:tdogu@metu.edu.tr).



The presence of isoamylenes (IAs) in significant quantities in fluid catalytic cracking (FCC) light gasoline brought up the possibility of direct etherification of gasoline with methanol or ethanol to produce oxygenated gasoline. Studies carried out for the possible environmental impacts of TAME<sup>3</sup> indicated that it had low toxicity to aquatic organisms. Also it is not expected to bioaccumulate. Use of ethanol-based higher ethers (TAE), using the ethanol produced from biomass, may also bring additional environmental advantages.

Etherification reactions of IAs are limited by chemical equilibrium. Reactive distillation processes are generally recommended to achieve high yields in such equilibrium-limited reactions.<sup>4-7</sup> Production of side products by the dimerization and oligomerization of isoamylenes or formation of dimethyl ether by methanol condensation may cause a decrease in the selectivities of TAME and TAE production, especially at excessive contact times of reactants with the catalyst.<sup>8,9</sup> Another possible side reaction is the formation of *tert*-amyl alcohol by the reaction of IA with water present as a feed impurity. In this study, a batch reflux-recycle-reactor (RRR) was proposed to achieve high yields and also high selectivities of desired products in such reactions.

Kinetic studies reported in the literature<sup>10-15</sup> and our recent DRIFT [diffuse reflectance FTIR (spectroscopy)] studies<sup>16</sup> showed that a Langmuir-Hinshelwood-type reaction mechanism, involving adsorbed alcohols and *tert*-olefins, gave good agreement with the kinetic data. However, Rideal-Eley-type reaction mechanisms, involving fluid-phase isoolefins and adsorbed alcohols in the rate-determining step of the reaction, were also considered in a number of other studies.<sup>17-19</sup> At low concentrations of olefins, the apparent reaction order is close to

unity with respect to the *tert*-olefin.<sup>14,20,21</sup> Also, adsorption equilibrium constants of alcohols were reported to be much higher than those of adsorption equilibrium constants of *tert*-olefins on acidic macroreticular resin catalysts.<sup>12,15,22</sup>

## Experimental

The batch RRR proposed in this work is composed of three parts: a reboiler, vertical catalytic reactor section, and a condenser used for the liquefaction of the reactor effluent stream.<sup>23</sup> A diagram of the experimental system is shown in Figure 1. The reactant mixture, which was fed to the reboiler, was vaporized into the reactor section and the reactor outlet stream was condensed and recycled back to the reboiler. In this work, the system was operated batchwise, although it might also be modified for continuous operation. Because the vapor pressures of tertiary ethers (TAME or TAE) are lower than those of both C<sub>5</sub> reactive olefins and alcohols (methanol or ethanol), the vapor-phase inlet stream composition of the reactor section was always rich in reactants. Because of short contact times of the reactants with the catalyst, very high selectivities were achieved. In the present study, 7 L of reactant mixture was fed to the reboiler. The reactor section (5 cm in diameter and 36 cm in length) contained 60 g of catalyst. Amberlyst-15 acidic resin catalyst particles were packed into small baskets, each containing about 1 g of catalyst. These baskets were uniformly distributed along the column by placing them over eight equally spaced perforated plates. Experiments were carried out with both methanol-isoamylenes and ethanol-isoamylenes mixtures. These experiments were repeated with different feed compositions between 4.6 and 25 mol % isoamylenes in alcohol and

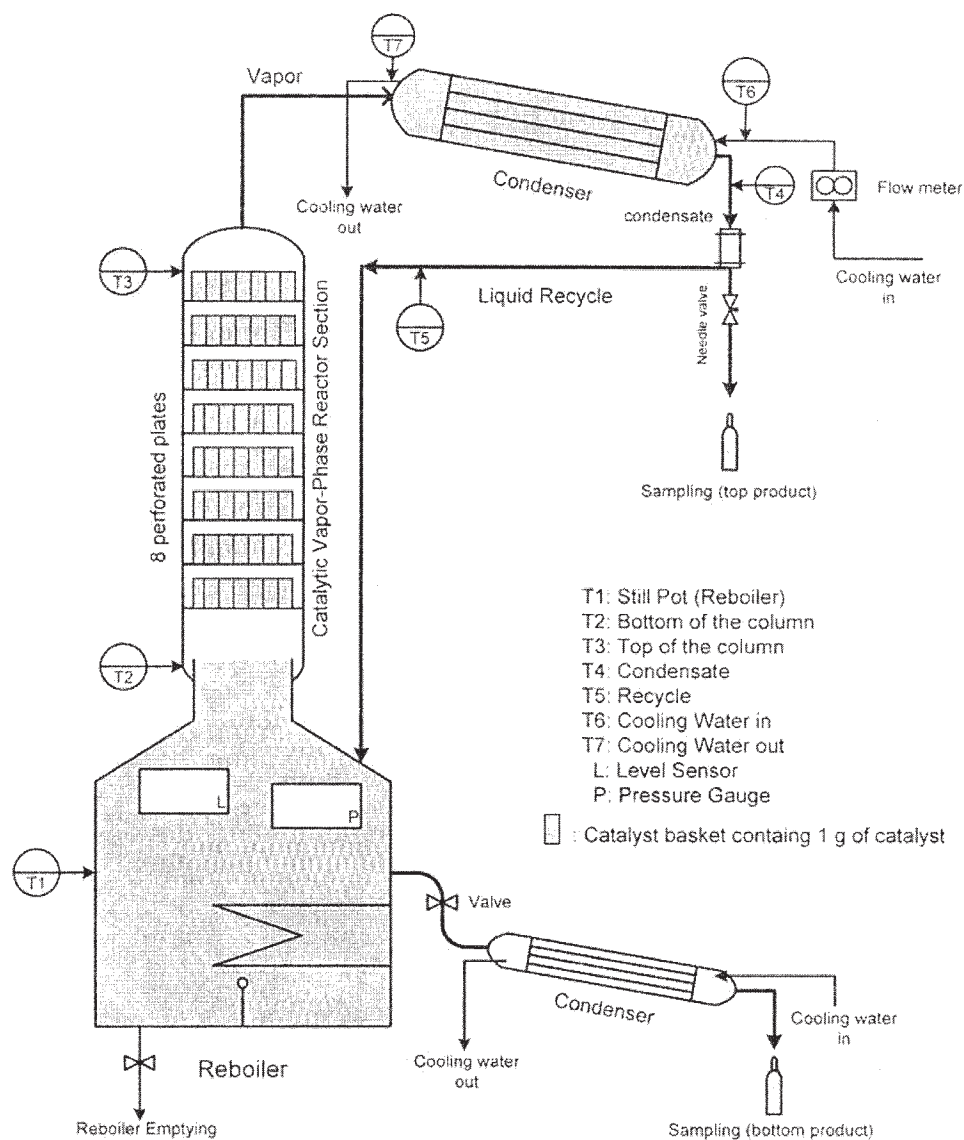


Figure 1. Experimental setup of the batch reflux-recycle-reactor.

also at different reboiler temperatures ranging between 72 and 104°C. The reactor section was well insulated. Experiments indicated that temperature variation along the reactor was negligibly small ( $<1^{\circ}\text{C}$ ) after the initial heat up period. The reboiler temperature was about  $1^{\circ}\text{C}$  higher than the reactor inlet temperature. In all these experiments, the mean residence time of reactants in the reactor section was of the order of magnitude of 5 s, with some variation from experiment to experiment. Physical and chemical properties of the catalyst used in this work (Amberlyst-15) were reported in our previous publications.<sup>15,22</sup> The catalyst used in this work is a strongly acidic macroporous resin catalyst with a macroporosity of 0.32 and a surface area of  $59.2\text{ m}^2/\text{g}$ .

In the experiments, analytical-grade methanol and ethanol (purity 99.8 vol %) and isoamylene (Merck, Darmstadt, Germany) were used as the reactants. Isoamylene used in our work contained 95% 2M2B, the remainder of which was primarily 2M1B, which is also reactive to produce ethers. 2M2B is the

major isomer of reactive isoamylenes and the isomerization reaction between 2M2B and 2M1B was usually assumed to be in equilibrium over acidic resin catalysts. Although isoamylene could be represented by the mixture of 2M2B and 2M1B, these two isomers could be lumped together as isoamylene (IA) with the properties of the major isomer.<sup>24</sup>

Operation of the batch RRR proposed in this work involves two distinct time periods. In the first heat-up period, the feed mixture charged to the reboiler was heated to the desired temperature and then heating was continued until condensation of the vapor stream was observed in the condenser at the exit of the reactor section. It took about 15 min (with some variation from experiment to experiment, depending on the composition of the feed mixture) to reach the desired temperature in the reboiler. However, formation of condensate in the condenser was observed about 40 min after the start-up of the heating period. During this initial heat-up period, the vapor stream was expected to heat up the reactor section and con-

dense. The condensed stream within the reactor was refluxed back to the reboiler. Of course, some conversion of the reactants to the product was also observed within the reactor section during this heat-up period.

The second period of the operation of the batch RRR proposed in this work started after condensation was observed in the condenser at the exit of the reactor section. In this second time period, the temperature was almost constant along the reactor. In this period, the desired reboiler temperature was kept constant by regulating the heat input to the reboiler and also by adjusting the flow rate of cooling water used in the condenser. After steady isothermal temperature was reached, heat input to the reboiler was primarily used up for the latent heat of vaporization of the mixture. Our calculations, based on the heat input to the reboiler, the heat taken by the cooling water in the condenser, and also the compositions of the condensate and reboiler mixtures, showed that the vapor stream composition in the reactor was close to the dew point along the reactor. Also, vapor stream flow rates at the inlet and outlet of the reactor section were very close to each other in this second period of the operation. In this period, very little condensation is expected in the reactor section, especially at later times. Some condensation of the product, which has much less volatility than that of the reactants, is possible within the reactor section at the initial times of the second period. Consequently, in the second period the reactor section may be assumed as a vapor-phase reactor.

Variations of chemical compositions of the mixture in the reboiler and also in the condensed stream, which was recycled to the reboiler, were determined by the chemical analysis of samples taken from the reboiler and from the recycle stream, at different times. For this purpose, a gas chromatograph (Varian Associates, Palo Alto, CA) equipped with an FID detector, and with a column packed with 15% FFAB on Chromosorb AW was used. Closed sample tubes were refrigerated before gas chromatographic analysis so as not to have any change in the composition arising from evaporation.

Although the isoamylene mole fraction of the mixture charged to the reboiler was quite low (<25 mol %), the mole fraction of isoamylene in the vapor-phase reactor inlet stream was much higher. This is attributed to the higher volatility of IA compared to that of alcohols (methanol and ethanol) and product ethers. The initial values of vapor-phase IA concentrations (in methanol) and the bubble point pressures, corresponding to each liquid-phase concentration used in experiments conducted at 94°C reboiler temperature, are summarized in Table 1. As seen in Table 1, a liquid-phase IA mole fraction of 0.25 corresponds to a vapor-phase IA mole fraction of about 0.55 at 94 °C. Similarly, vapor-phase reactor inlet IA mole fractions and the bubble point pressures, corresponding to different reboiler temperatures for a liquid-phase containing 6 mol % IA (in methanol), are given in Table 2. Vapor-phase

**Table 1. Initial Values of Liquid and Reactor Inlet Vapor Compositions in IA–Methanol Reaction at 94°C**

Liquid mole fraction of 2M2B in the reboiler	0.046	0.060	0.100	0.250
Reactor inlet vapor mole fraction of 2M2B	0.27	0.31	0.41	0.55
Bubble point pressure, bar	3.7	3.9	4.5	5.5

**Table 2. Initial Values of Reactor Vapor Compositions in IA–Methanol Reaction at a Liquid Feed Composition of 6 mol % IA in Methanol**

Reboiler temperature, °C	72	82	94	104
Reactor inlet vapor mole fraction of 2M2B	0.38	0.35	0.31	0.29
Bubble point pressure, bar	2.1	2.8	3.9	5.2

compositions were calculated using the experimental liquid mole fractions. In these calculations, the program WSMMAIN was used.<sup>25,26</sup> This program calculated multicomponent VLE using the PRSV EOS and the Wong–Sandler mixing rule. Also, the NRTL excess free-energy model was used with this mixing rule.

## Results and Discussion

Chemical analysis of the samples taken from the reboiler at different times showed that the only product observed in the reaction of isoamylene with methanol or ethanol is TAME or TAEE, respectively. No side products were observed in gas chromatographic analysis. Such very high selectivity values, approaching unity, were considered to be a result of the very short contact times (per pass) of reactants with the catalyst bed in the proposed batch RRR. Instantaneous values of fractional conversion of isoamylene to the respective ether were evaluated from the reboiler compositions. At any instant, conversion of isoamylene ( $\xi_{IA}$ ) in the reboiler was evaluated from

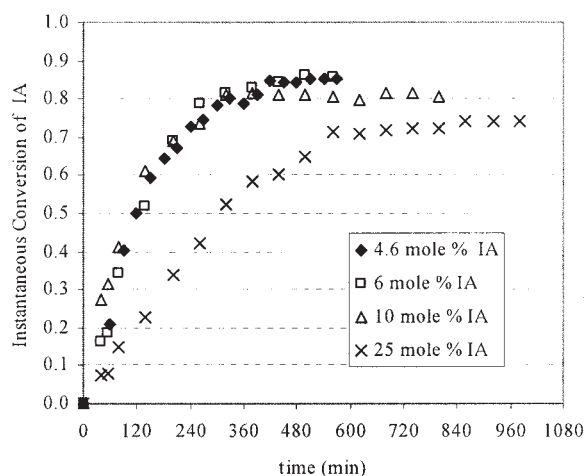
$$\xi_{IA} = \frac{x_E}{x_E + x_{IA}} \quad (1)$$

Here,  $x_E$  and  $x_{IA}$  are the mole fractions of ether (TAME or TAEE) and isoamylene in the reboiler, respectively.

### Batch RRR results for TAME production and model predictions

Time dependency of experimental conversion values of 2M2B to TAME, obtained at 94°C with different feed compositions, is shown in Figure 2. To predict the variation of the composition of the species and the instantaneous conversion of IA in the reboiler, conservation equations were written for both the reactor and the reboiler sections in the second isothermal period of operation of the batch RRR. Major assumptions of the model include plug flow in the reactor section, perfect mixing in the reboiler, and vapor–liquid equilibrium (VLE) between the liquid in the reboiler and reactor inlet stream. Considering very short residence times of molecules in the reactor section (couple of seconds per pass), compared to the timescale of concentration variations measured in the reboiler (couple of hours), a pseudo-steady-state assumption was made for the reactor section, after the preheating period. Also, the vapor stream flow rate  $Q$  was assumed as constant along the reactor (in this second period of operation), which was justified by calculations based on energy and material balances around the reboiler, condenser, and reactor.

$$QC_{IA,0}^V \frac{d\xi_{IA}^V}{dW} + R_{IA} = 0 \quad (\text{Reactor section}) \quad (2)$$



**Figure 2. Time dependency of instantaneous conversion of IA to TAME (evaluated at the reboiler) at different feed compositions ( $T = 94^{\circ}\text{C}$ ).**

$$QC_{\text{IA},0}^V(1 - \xi_{\text{IA},f}^V) - QC_{\text{IA},0}^V = V \frac{dC_{\text{IA}}^L}{dt} \quad (\text{Reboiler}) \quad (3)$$

There are a number of mechanisms, including Langmuir–Hinshelwood and Rideal–Eley-type rate models, proposed in the literature for such etherification reactions.<sup>9,10,13,17–19</sup> From the DRIFT studies conducted in our previous work<sup>16</sup> it was shown that adsorbed alcohols and adsorbed isoolefin molecules both participate in the reaction mechanism in vapor-phase etherification reactions. However, the adsorption equilibrium constants of alcohols are much higher than the adsorption equilibrium constants of isoolefins. In fact, the adsorption equilibrium constants of ethanol and methanol on Amberlyst-15 were reported to be at least two orders of magnitude greater than the adsorption equilibrium constants of isoamylenes.<sup>22</sup> As a result of this difference, most of the surface was expected to be covered by alcohol molecules and zero-order dependency of the rate on alcohol concentration was expected at sufficiently high alcohol concentrations. This zero-order dependency of the rate on alcohol concentration was also reported by Tejero et al.<sup>20</sup> for MTBE synthesis for alcohol/isoolefin mole ratios  $> 0.59$ . A similar conclusion was reached by Piccoli and Lovisi<sup>21</sup> for synthesis of TAME. For all of the experiments conducted in this work, alcohol concentration in the vapor-phase reactor section may be assumed to be in excess. With these considerations and based on the proposals reported in the literature, a simple reversible rate expression with apparent forward reaction rate orders of one and zero for isoamylenes and alcohol, respectively, was assumed to obtain model predictions

$$-R_{\text{IA}} = k_1[C_{\text{IA}}^V - C_{\text{E}}^V/(K^{(V)}C_{\text{M}}^V)] \quad (4)$$

Our earlier studies on TAAE synthesis over Amberlyst-15 had also shown an apparent first-order dependency of reaction rate on isoamylenes concentration in systems where alcohol concentration was in excess.<sup>14</sup> Our experimental results also indicated a small variation of alcohol concentration along the reactor. Consequently, the assumption of constant alcohol con-

centration in the reactor section is not expected to introduce major error in the analysis.

With these considerations, a first-order reversible reaction rate model was assumed and the following expression was obtained for conversion per pass at the reactor outlet

$$\xi_{\text{IA},f}^V = \xi_{\text{IA},e}^V \left\{ 1 - \exp \left[ - \frac{(M+1) k_1 W}{(M + \xi_{\text{IA},e}^V) Q} \right] \right\} \quad (5)$$

Here,  $\xi_{\text{IA},e}^V$  is the vapor-phase equilibrium conversion that could be achieved at the outlet of the reactor section and  $M$  is the ratio of concentrations of the product ether and isoamylenes at the reactor inlet, defined as  $M = C_{\text{E},0}^V/C_{\text{IA},0}^V$ .

By combining Eqs. 3 and 5, the following expression may be written for the rate of change of concentration of IA in the reboiler as a function of time:

$$\frac{dC_{\text{IA}}^L}{dt} = - \frac{QK_{\text{IA}}}{V} \xi_{\text{IA},e}^V \left\{ 1 - \exp \left[ - \frac{(M+1) k_1 W}{(M + \xi_{\text{IA},e}^V) Q} \right] \right\} C_{\text{IA}}^L \quad (6)$$

Here  $K_{\text{IA}}$  is the VLE constant of isoamylenes, evaluated at the reboiler composition, temperature, and pressure

$$C_{\text{IA},0}^V = K_{\text{IA}} C_{\text{IA}}^L \quad (7)$$

The system under consideration is highly nonideal. Because of variations in the composition of the mixture in the reboiler,  $K_{\text{IA}}$ ,  $\xi_{\text{IA},e}^V$ , and  $M$  are expected to change as a function of time. Consequently, instead of using the analytically integrated form of Eq. 6 in verifying the experimental data, differential analysis was preferred.

Experimental values of  $-(dC_{\text{IA}}^L/dt)$  were evaluated by differential analysis of the concentration data obtained for isoamylenes ( $C_{\text{IA}}^L$ ) in the reboiler. At each data point corresponding to different times,  $dC_{\text{IA}}^L/dt$ ,  $M$ ,  $Q$ ,  $K_{\text{IA}}$ , and  $\xi_{\text{IA},e}^V$  values were evaluated and substituted into Eq. 6 to calculate the forward apparent rate constant  $k_1$ . The values of  $M$  were determined from the experimental values of ether and isoamylenes mole fractions in the reboiler using the VLE calculations. The vapor flow rate ( $Q$ ) values in the reactor were estimated from the heat input rate to the reboiler by making adiabatic reboiler assumption. In this estimation procedure heat input from the electrical heater was equated to the summation of heat of vaporization of the reboiler mixture and sensible energy required to increase the temperature of the condensed recycled stream to the reboiler temperature.

In most of the experiments, reported in Figure 2, the average value of vapor flow rate within the reactor was kept in the range of 200–265 cm<sup>3</sup>/s. However, at high olefin concentrations, some decrease in heat input to the reboiler was necessary because of experimental difficulties of controlling the system pressure and temperature at the desired values in these experiments. This was especially fitting in experiments conducted with 25% isoamylenes. For this case, the average value of vapor flow rate within the reactor was about 62 cm<sup>3</sup>/min. This is the major reason for obtaining lower instantaneous conversions (as evaluated from the reboiler compositions) in the set of experiments conducted with that composition (Figure 2).

Vapor–liquid equilibrium constant values ( $K_{\text{IA}}$ ) were esti-



**Table 3. Estimated Vapor-Phase Chemical Reaction Equilibrium Constants**

Temperature (K)	$K^{(V)}$ for TAME Reaction (R1)	$K^{(V)}$ for TAE Reaction (R2)
345	0.471	0.165
355	0.313	0.110
367	0.200	0.071
377	0.141	0.046

mated using the WSMMAIN program.<sup>25,26</sup> In this estimation procedure, experimental reboiler compositions, temperature, and pressure values were used at each data point.

The vapor-phase equilibrium conversion value of isoamylene ( $\xi_{IA,e}^V$ ) at the exit of the reactor section was estimated from the corresponding equilibrium constants. Equilibrium constants for liquid-phase reactions R1 and R2 are reported by Rihko and Krause<sup>27</sup> and Kitchaiya and Datta<sup>8</sup> as follows.

*For TAME Synthesis*

$$\ln K_1^{(L)} = -8.2473 + \frac{3225.3}{T} \quad (8)$$

*For TAE Synthesis*

$$\ln K_2^{(L)} = 26.779 + \frac{2078.6}{T} - 6.5925 \times \ln T + 0.0231 \times T - 1.126 \times 10^{-5} \times T^2 - 1.414 \times 10^{-8} \times T^3 \quad (9)$$

For the same reactions, vapor-phase chemical equilibrium constants were estimated from the liquid-phase equilibrium constants, following the procedure reported by Jensen and Datta.<sup>28</sup> In this procedure, the free energy of reaction values for the vapor-phase reaction was estimated from the free energy of reaction in the liquid phase. Vapor-phase equilibrium constants for these two reactions, evaluated at different temperatures, are given in Table 3. Using the equilibrium constants reported in Table 3, equilibrium conversions of isoamylene were evaluated at each data point using the following expression

$$K^{(V)} = \frac{1}{P} \frac{(M + \xi_{IA,e}^V)(1 - y_{IA,0}\xi_{IA,e}^V)}{(1 - \xi_{IA,e}^V)(y_{M,0} - y_{IA,0}\xi_{IA,e}^V)} \quad (10)$$

Results obtained at 94°C with an initial reboiler composition of 10% isoamylene in methanol are reported in Table 4. As seen in this table, variation of the  $K_{IA}$  value with respect to time was quite small. However,  $M$  values and the corresponding  $C_E^L/C_{IA}^L$  values in the reboiler increased significantly (as ex-

**Table 5. Calculated Apparent Rate Constants for IA–Methanol Reaction Carried Out at Different Initial Feed Compositions at 94°C**

Initial Feed Composition of IA	$k_1$ , Average (cm <sup>3</sup> g <sup>-1</sup> s <sup>-1</sup> )
4.6	0.22
6	0.23
10	0.23
25	0.22

pected) with an increase in conversion. Equilibrium conversion of IA ( $\xi_{IA,e}^V$ ), as evaluated from Eq. 10, showed a significant decrease with increasing time. At very long times, reactor inlet composition may approach the chemical reaction equilibrium in the vapor phase at the corresponding temperature and the  $\xi_{IA,e}^V$  value is expected to reach zero. The value of rate constant  $k_1$ , obtained at different data points from differential analysis, is almost constant (Table 4). Similar results are obtained with different initial feed compositions at 94°C. As seen in Table 5,  $k_1$  values also scarcely changed by changing feed composition. These results showed that the pseudo-first-order rate assumption used in the derivation of Eq. 5 was quite acceptable.

An important conclusion reached from this analysis is related to the very high experimental conversion values obtained in this work. As seen in Table 4, even the initial value of vapor-phase equilibrium conversion that could be reached at the exit of the reactor section was <0.36. However, the experimental instantaneous conversion values obtained from the reboiler compositions reached values close to 0.90 at 94°C (Figure 2). These results showed one of the advantages of the proposed batch RRR over a single-pass vapor-phase fixed-bed catalytic reactor.

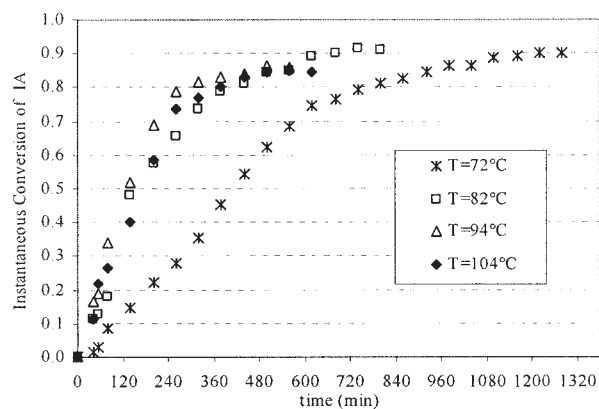
As mentioned earlier, in the experiments conducted with 25% isoamylene in methanol, the vapor flow rate in the reactor ( $Q$ ) was much lower than that in the other experiments. This is the major reason for obtaining lower instantaneous conversion values at that composition (Figure 2). However, the rate constant  $k_1$ , obtained at that composition, was about the same as the corresponding values obtained at other compositions (Table 5). This result justified that, even at that composition, pseudo-first-order dependency of the reaction rate on isoamylene concentration and pseudo-zero-order dependency on alcohol concentration did not introduce significant error to the analysis procedure.

### Temperature dependency of rate constant for TAME production

Figure 3 illustrates the time dependency of 2M2B conversion values obtained at different temperatures at a liquid stream

**Table 4. Parameters Evaluated at Some Data Points Corresponding to an Initial IA–Methanol Mixture of 10 mol % IA at 94°C**

Time (min)	$\xi_{IA,e}^V$	$K_{IA}$	$M = C_{E,0}^V/C_{IA,0}^V$ (Reactor inlet)	$C_E^L/C_{IA}^L$ (Reboiler)	$k_1$ (cm <sup>3</sup> g <sup>-1</sup> s <sup>-1</sup> )
40	0.358	0.0314	0.024	0.38	0.21
80	0.332	0.0295	0.047	0.70	0.21
320	0.205	0.0336	0.295	4.25	0.24
500	0.183	0.0316	0.307	4.26	0.23
680	0.185	0.0321	0.308	4.31	0.24



**Figure 3.** Time dependency of instantaneous conversion of IA to TAME (evaluated at the reboiler) at different temperatures (feed compositions: 6 mol % mixture of IA in methanol).

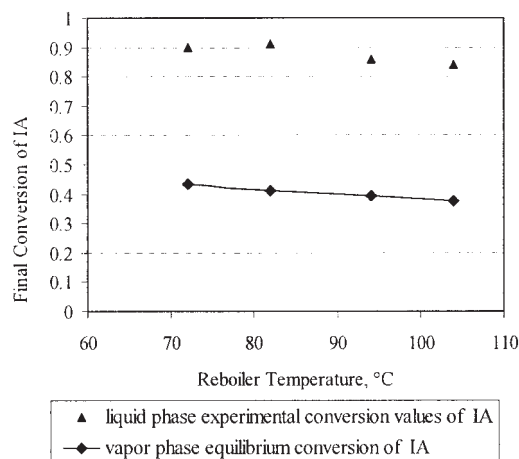
composition of 6 mol % 2M2B in methanol. Initial vapor-phase mole fractions of IA, as estimated from the corresponding liquid-phase compositions, are given in Table 2. Changes in reaction temperature are expected to change the equilibrium conversion at the reactor outlet ( $\xi_{IA,e}^V$ ) and  $K_{IA}$  values as well as the apparent rate constant  $k_1$ . A decrease in  $\xi_{IA,e}^V$  values is expected with an increase in temperature. Vapor-liquid equilibrium constants of isoamylene ( $K_{IA}$ ), evaluated using the WSMMAIN program, showed a nearly 45% increase with an increase in temperature from 72 to 104°C. The value of vapor flow rate in the reaction section ( $Q$ ) was around 240 cm<sup>3</sup>/s at 94 and 104°C. Because of experimental difficulties in controlling the system pressure, somewhat lower initial  $Q$  values were used at lower temperatures, and especially at 72°C. The reaction rate constant  $k_1$  was then evaluated at each data point following the differential analysis procedure. Results showed that fluctuations of  $k_1$  values, evaluated from different data points of experiments obtained at the same temperature, were quite small. Average values of the apparent rate constant evaluated at each temperature are reported in Table 6.

At lower temperatures, the reaction rate is rather low and, consequently, much longer times are necessary to reach conversion values > 0.90 (Figure 3). Experimental values of maximum conversions, obtained at longer times, are plotted as a function of temperature in Figure 4. In the same figure, vapor-phase equilibrium conversions that could be reached at the same temperature and with feed compositions corresponding to the initial compositions of the reboiler mixture are also shown. As clearly seen in this figure, conversions obtained in

**Table 6.** Apparent Rate Constants and Vapor-Phase Equilibrium Conversion Ranges in Each Set of IA–Methanol Reactions at Different Temperatures\*

$T$ (°C)	$k_1$ Average (cm <sup>3</sup> g <sup>-1</sup> s <sup>-1</sup> )
72	0.16
82	0.19
94	0.23
104	0.34

\*Initial composition: 6 mol % IA in methanol.

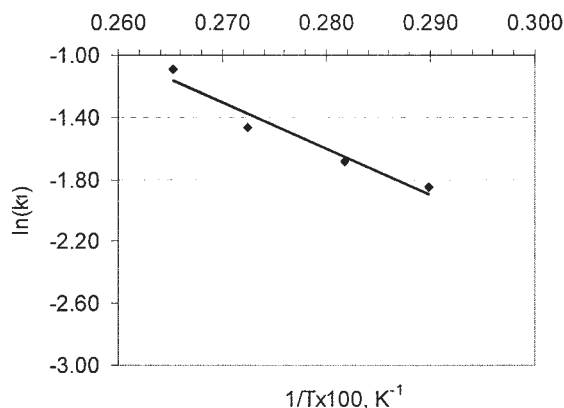


**Figure 4.** Comparison of maximum conversions of IA (at the reboiler) obtained in TAME synthesis at different temperatures with the corresponding vapor-phase equilibrium conversions (corresponding to the initial reboiler compositions).

this work are more than twice the corresponding equilibrium conversion values calculated with these assumptions.

The temperature dependency of reaction rate constants  $k_1$  is shown in Figure 5. The apparent activation energy of  $k_1$  was evaluated as 24.8 kJ mol<sup>-1</sup>. To our knowledge there is no activation energy value reported in the literature for vapor-phase synthesis of TAME. However, the liquid-phase activation energy values reported in the literature for etherification reactions of 2M1B and 2M2B with methanol are in the range of 72–94 kJ mol<sup>-1</sup>.<sup>10,21,29–32</sup> This low value of activation energy obtained in this work for vapor-phase synthesis of TAME is expected to be primarily attributable to significance of transport resistances in our system.

As discussed earlier, a thin liquid film is expected to form over the catalyst particles in the batch RRR as a result of condensation of the product, especially during the heat-up period and also at the initial times of the isothermal operation period of the reactor. Macropores of the Amberlyst-15 were also expected to be filled with liquid, which was expected to be



**Figure 5.** Temperature dependency of the apparent rate constants of IA etherification reaction with methanol.

primarily composed of product ether, and reactant alcohol. In fact, the catalyst particles removed from the reactor at the end of the experiments were found to be wet and swelled. It is well known that Amberlyst-15 particles swell in the presence of polar molecules, such as alcohols. In this system three transport resistances may affect the observed rate: (1) transport resistance of IA from the vapor phase to the catalyst surface through the thin liquid film covering the external catalyst surface; (2) diffusion resistance in the macropores; and (3) diffusion resistance in the gel-like micrograins of Amberlyst-15. Effects of diffusion resistances in the macropores and also in the gel-like micrograins of Amberlyst-15 may be tested using the criterion proposed in the literature<sup>33,34</sup>

$$\left( \frac{(R_{IA}\rho_p)R_0^2}{C_{IA,0}D_a} \right) (1 + G) \leq \frac{3}{4} \quad (11)$$

Here,  $G$  corresponds to the ratio of diffusion times in the micrograins and macropores, as follows

$$G = \left( \frac{r_0}{R_0} \right)^2 \frac{D_a}{D_i(1 - \varepsilon_a)} \quad (12)$$

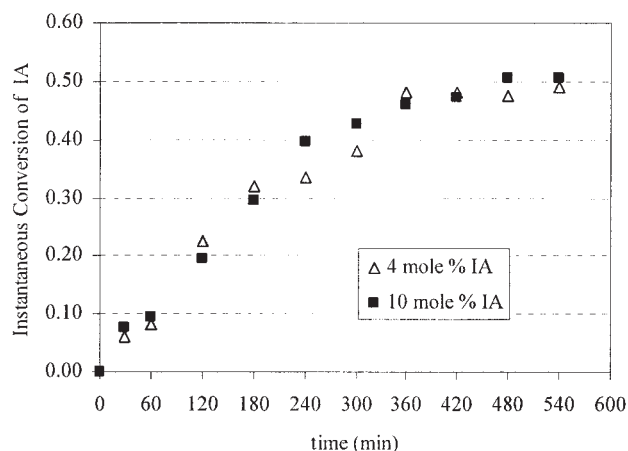
The value of effective diffusion coefficient of 2M2B in the macropores of Amberlyst-15 catalyst was estimated as  $1.8 \times 10^{-5} \text{ cm}^2/\text{s}$  at 370 K from the data reported in our recent publication.<sup>15</sup> Particle and gel-like micrograin radii of Amberlyst-15 are  $R_0 = 3.7 \times 10^{-4} \text{ m}$  and  $r_0 = 1.14 \times 10^{-8} \text{ m}$ , respectively.<sup>15</sup> There are no published data for diffusion coefficient ( $D_i$ ) of 2M2B in the gel-like micrograins. However, the  $D_i$  value of isobutylene was reported as  $2.6 \times 10^{-12} \text{ cm}^2/\text{s}$  at 358 K.<sup>22</sup> A somewhat smaller  $D_i$  value was expected for 2M2B. By taking the order of magnitude of  $D_i$  as  $1 \times 10^{-12} \text{ cm}^2/\text{s}$ , the value of parameter  $G$  in Eq. 11 was estimated as  $2 \times 10^{-2}$ . This is a clear indication that diffusion resistance in the gel-like micrograins is substantially smaller than the macropore diffusion resistance in our system and can be neglected. Knowing the observed reaction rate constants (Tables 5 and 6), observed rates were estimated and the order of magnitude of the dimensionless group, appearing on left-hand side of the criterion given in Eq. 11, was estimated to be  $>15$ . This is a clear indication of significance of macropore diffusion resistance on the observed rate. In this system, diffusion resistance through the liquid film covering the catalyst particles is also expected to have some effect on the observed rate. Because of such contributions of transport resistances, lower observed activation energies are expected in our system.

### Results obtained for TAAE synthesis

Similar experiments were also carried out with ethanol-IA mixtures to produce TAAE. Initial values of reactor inlet vapor

**Table 7. Initial Values of Reactor Inlet Vapor Compositions in IA-Methanol Reaction at 94°C**

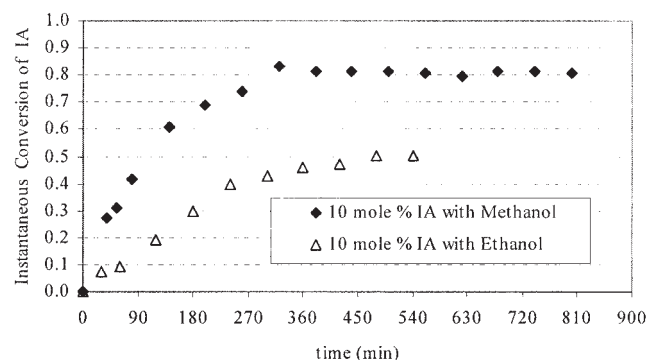
Liquid mole fraction of 2M2B in the reboiler	0.04	0.10
Reactor inlet vapor mole fraction of 2M2B	0.19	0.35
Bubble point pressure, bar	2.2	2.7



**Figure 6. Time dependency of instantaneous conversion of IA to TAAE (evaluated at the reboiler) at different feed compositions ( $T = 94^\circ\text{C}$ ).**

compositions of experiments conducted at  $94^\circ\text{C}$  using IA-ethanol mixtures are reported in Table 7.

As can be seen in Figures 6 and 7, lower conversion values of IA to TAAE were observed compared to conversion values obtained in TAME synthesis. This is primarily explained by less reactivity of ethanol compared to that of methanol. A similar differential analysis was applied to calculate the forward apparent rate constant  $k_1$ , by substituting  $dC_{IA}^L/dt$ ,  $M$ ,  $Q$ ,  $K_{IA}$ , and  $\xi_{IA,e}^V$  values in Eq. 6. To illustrate the results of these calculations, results obtained at some data points obtained with an initial reboiler composition of 10 mol % IA in ethanol are reported in Table 8 (at  $94^\circ\text{C}$ ). As can be observed in Table 8, the value of rate constant  $k_1$ , obtained at different data points from differential analysis, is almost constant. Similar results were obtained with 4 mol % IA in ethanol at an initial feed composition of  $94^\circ\text{C}$ . As seen in Table 9,  $k_1$  values also scarcely changed by changing the feed composition. For the IA-ethanol system, much longer times were needed to achieve high conversions, compared to those of the IA-methanol system. As illustrated in Figure 7, conversion values obtained with ethanol (using 10 mol % IA in the liquid feed) were much lower than the corresponding values obtained with methanol. This result agreed well with the literature, indicating that



**Figure 7. Comparison of conversions of IA in reactions with methanol and ethanol ( $T = 94^\circ\text{C}$ ).**



**Table 8. Parameters Evaluated at Some Data Points Corresponding to an Initial IA–Ethanol Mixture of 10 mol % IA at 94°C**

Time (min)	$\xi_{IA,e}^V$	$K_{IA}$	$M = C_{E,0}^V/C_{IA,0}^V$ (Reactor Inlet)	$C_E^L/C_{IA}^L$ (Reboiler)	$k_1$ ( $\text{m}^3 \text{g}^{-1} \text{s}^{-1}$ )
60	0.122	0.0449	0.005	0.11	0.062
120	0.117	0.0454	0.012	0.25	0.061
240	0.109	0.0494	0.032	0.65	0.056
420	0.091	0.0461	0.045	0.90	0.059
540	0.084	0.0454	0.051	1.03	0.059

methanol was more reactive than ethanol in etherification reactions using Amberlyst-15.

## Conclusions

The batch reflux–recycle–reactor (RRR) proposed here was shown to give high yields and selectivities and is recommended for equilibrium-limited reactions in which relative volatilities of reactants are much higher than those of products. Conversion values  $> 0.91$  were achieved in TAME synthesis with no formation of side products. The apparent activation energy of  $k_1$  was evaluated as  $24.8 \text{ kJ mol}^{-1}$  in TAME synthesis. This low value of activation energy for TAME synthesis is concluded to be primarily attributable to significance of transport resistances in the batch RRR. Pore diffusion resistance in the gel-like micrograins is significantly smaller than macropore diffusion resistance in our system and can be neglected. However, significant transport resistances are expected in the macropores and also through the thin liquid film covering the catalyst particles. It was also concluded that the reactivity of methanol was higher than that of ethanol in the etherification reaction of isoamylenes, over Amberlyst-15.

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## Notation

$C_{IA}^L$  = concentration of IA in liquid phase in reboiler,  $\text{mol/cm}^3$   
 $C_{IA,0}^V$  = initial concentration of IA in the vapor phase,  $\text{mol/cm}^3$   
 $C_M^V$  = concentration of alcohol in the vapor phase,  $\text{mol/cm}^3$   
 $D_a$  = macropore effective diffusivity,  $\text{cm}^2/\text{s}$   
 $D_i$  = effective diffusivity within gel-like micrograins,  $\text{cm}^2/\text{s}$   
 $G$  = the ratio of diffusion times in the micrograins and macropores  
 $K^{(V)}$  = vapor-phase chemical equilibrium constant  
 $k_I$  = apparent rate constant,  $\text{cm}^3 \text{g}^{-1} \text{s}^{-1}$   
 $K_I^{(L)}$  = liquid-phase chemical equilibrium constant for TAME synthesis (as defined by Eq. 8)  
 $K_2^{(L)}$  = liquid-phase chemical equilibrium constant for TAME synthesis (as defined by Eq. 9)  
 $K_{IA}$  = vapor–liquid equilibrium constant of IA evaluated at the reboiler composition (as defined by Eq. 7)

**Table 9. Calculated Apparent Rate Constants for IA–Ethanol Reaction Carried Out at Different Initial Feed Compositions at 94°C**

Initial Feed Composition of IA	$k_1$ Average ( $\text{cm}^3 \text{g}^{-1} \text{s}^{-1}$ )
4	0.060
10	0.059

$M$  = ratio of initial concentration of ether to isoamylenes;  $C_{E,0}^V/C_{IA,0}^V$

$Q$  = vapor stream flow rate,  $\text{cm}^3/\text{s}$

$R_{IA}$  = observed reaction rate,  $\text{mol g}^{-1} \text{s}^{-1}$

$R$  = catalyst particle radius,  $\text{cm}$

$r$  = gel-like micrograin radius,  $\text{cm}$

$V$  = reactor volume,  $\text{cm}^3$

$W$  = catalyst weight,  $\text{g}$

$X_{E, XIA}$  = mole fractions of ether (TAME or TAAE) and isoamylenes in the reboiler, respectively

$y_{IA}$  = inlet mole fraction of IA in the vapor phase

$y_M$  = inlet mole fraction of alcohol in the vapor phase

## Greek letters

$\varepsilon_a$  = macroporosity

$\rho_p$  = apparent density of catalyst,  $\text{g/mL}$

$\xi_{IA}^V$  = conversion of IA in the vapor phase

$\xi_{IA,e}^V$  = vapor-phase equilibrium conversion

$\xi_{IA,f}^V$  = conversion of IA in the vapor phase at the reactor outlet

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