

Comparison of the Various Kinetic Models of TAME Formation by Simulation and Parameter Estimation

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Various kinetic models proposed for the synthesis of TAME (*tert*-amyl methyl ether, 2-methoxy-2-methylbutane) were tested against experimental batch reactor data. The experiments were carried out with methanol/isoamylenes molar ratios varying from 0.2 to 2.0 at temperatures between 333 and 353 K. The range of validity of the various models was evaluated by simulating the experimental conditions and by comparing the adequacy of the models to predict the experimental changes of composition as a function of the catalyst contact time and composition at reaction equilibrium. Activity-based models were found to predict the experimental results better within a wider range of conditions than the concentration-based models. The activity-based models were additionally compared by estimating the values for the model parameters from the experimental data.

1 Introduction

The new reformulated gasoline requirements already legislated in the USA and many of the changes being currently considered in Europe for gasoline and diesel fuel present particularly challenging problems for refiners. The production of tertiary ethers will play a major role in meeting the new gasoline specifications, such as lower aromatics, olefins and RVP [1]. MTBE (methyl-*tert*-butyl ether, 2-methoxy-2-methylpropane) has been added to gasoline almost for two decades' time, but the limited supply of isobutene (2-methyl-1-propene) has turned the interest towards heavier ethers.

TAME (*tert*-amyl methyl ether, 2-methoxy-2-methylbutane) is synthesized in an acid-catalyzed equilibrium reaction of isoamylenes (2-methyl-1-butene, 2M1B, and 2-methyl-2-butene, 2M2B) with methanol (MeOH). The networks and nomenclature for the reactions are presented in Fig. 1. The reaction pairs (r_1 and r_2), (r_3 and r_4) and (r_5 and r_6) shown in Fig. 1 establish the reaction equilibrium. As the reaction system is a mixture of polar and unpolar compo-

nents, it is highly nonideal – a fact that will be shown also in this paper. The etherification reaction is highly selective, when acidic ion-exchange resins are used as catalyst and low temperatures (< 343 K) are applied. The reaction is carried out under pressure in order to ensure a liquid-phase operation.

The system is complex from the kinetic modeling point of view, as the rate parameters tend to be heavily correlated because the six simultaneous reactions are not linearly independent of each other. However, a proper kinetic model with a correctly predicted reaction equilibrium is essential in designing a reactor for etherification. Moreover, the model should cover a wide range of conditions because in the novel processes of etherification, the etherification conversions can be maximized by side-reactor configuration or by reactive distillation. Under these conditions, the methanol/isoamylyene ratio can differ greatly from the stoichiometric value [2,3]. Earlier, we have published a kinetic model for the synthesis of TAME [4–6]. Our approach was to measure the reaction rates from various directions of the triangle system, first with TAME as a feed [4], then with methanol and an equilibrium mixture of the two isoamylenes or a pure isoamylyene (2M1B) as a feed [5]. The values of the equilibrium constants were obtained experimentally [6]. Recently, we have also expanded the model to cover the dehydration of methanol as a relevant side reaction in the system [7]. The purpose of this study was to see how other authors have dealt with the complexity of the system, and to test the various kinetic models presented in the open literature against the same experimental batch reactor data [5], from which the values of our model parameters were partially obtained. The other complete kinetic models proposed for the synthesis of TAME are limited to a few publications. Hwang and Wu [8] and Piccoli and Lovisi [9] presented concentration-based kinetic equations for the reactions of TAME applying a pseudohomogeneous approach. The activity-based model presented by Oost and Hoffmann [10–12] was derived by applying a heterogeneous approach. The kinetic models as well as the values of the model parameters are presented in Tab. 1. There are also some other publications concerning

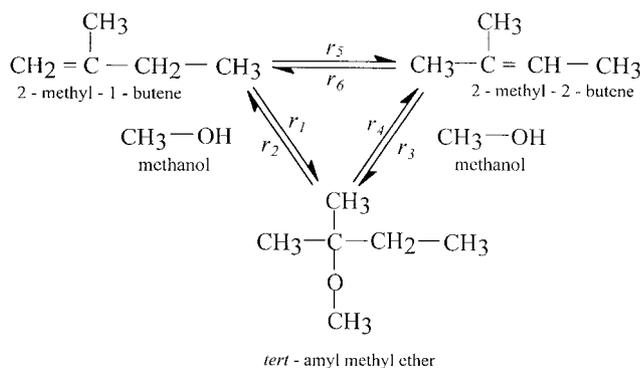


Figure 1. The reaction network in the formation and splitting of TAME.

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Table 1. The Various Kinetic Models Proposed for the Synthesis of TAME.

Ref.	Rate Expression for TAME	Values of the Model Parameters
	Rate of Isomerisation to 2M2B	
[4-7]	$r_f = \frac{k_1 a_M a_{IA} (1 - \frac{a_T}{K_1 a_M a_{IA}})}{(K_2 a_T + a_{IA})} + \frac{k_3 a_M a_{2B} (1 - \frac{a_T}{K_3 a_M a_{2B}})}{(K_3 a_T + a_{IA})}$	$k_1 = 3.2 \times 10^{10} \exp(-76800 / RT) \text{ mol kg}_{\text{cat}}^{-1} \text{ s}^{-1}$ $k_3 = 4.0 \times 10^{13} \exp(-99700 / RT) \text{ mol kg}_{\text{cat}}^{-1} \text{ s}^{-1}$ $k_2 = 7.5 \times 10^{10} \exp(-81700 / RT) \text{ mol kg}_{\text{cat}}^{-1} \text{ s}^{-1}$ $K_1 = \exp(-9.48 + 4382.3 / T)$ $K_2 = \exp(-9.17 + 3520.3 / T)$ $K_3 = K_1 / K_2$ $K_1 / K_3 = \exp(-10.13 + 2912.0 / T)$
	$r_{2B, \text{isom}} = k_2 (a_{IB} - \frac{a_{2B}}{K_2})$	(UNIFAC-method)
[8]	$r_f = k_{12} (C_{IA} C_M - C_T / K_{12})$	$k_{12} = 1.9 \times 10^{12} \exp(-94000 / RT) \text{ l}^2 \text{ mol}^{-1} \text{ kg}_{\text{cat}}^{-1} \text{ s}^{-1}$ $K_{12} = \exp(-7.84 + 2454 / T) \text{ l mol}^{-1}$ (K ₁₂ : UNIFAC-method)
[9]	$r_f = k_{13} (C_{IA} C_M - C_T / (K_{13} * x_M^2))$	$k_{13} = 3.7 \times 10^{11} \exp(-84400 / RT) \text{ mol kg}_{\text{cat}}^{-1} \text{ s}^{-1}$ $k_{2B} = 6.3 \times 10^{14} \exp(-92400 / RT) \text{ mol kg}_{\text{cat}}^{-1} \text{ s}^{-1}$ $K_{13} = \exp(-8.64 + 4330 / T)$ $K_{2B} = \exp(-8.10 + 3360 / T)$ (K ₁₃ : UNIFAC-method)
[10-12]	$r_f = k_3 (\frac{a_{IB}}{a_M} - \frac{a_T}{K_1 a_{IA}})$	$k_{13} = (1 - K_3) \times 1.4 \times 10^{12} \exp(-89500 / RT) \text{ mol kg}_{\text{cat}}^{-1} \text{ s}^{-1}$ $k_4 = 7.7 \times 10^{14} \exp(-90300 / RT) \text{ mol kg}_{\text{cat}}^{-1} \text{ s}^{-1}$ $K_1 = \exp(-10.95 + 4201.8 / T)$ $K_2 = \exp(-10.997 + 3426.9 / T)$ $K_3 = K_1 / K_2$
	$r_{2B, \text{isom}} = k_2 (a_{IB} - \frac{a_{2B}}{K_2})$	(UNIFAC-method)

the kinetics of TAME [13,14,15], but these studies are either not complete enough because only activation energies have been given or a very different kind of catalyst has been used (see the summary in Tab. 2).

Table 2. Summary of the Kinetic Studies of TAME.

Ref.	Feed	Catalyst	Reactor	Temperature °C	Pressure MPa	Kinetic analysis
[4]	TAME:	A16	CSTR	51-81	0.8	stationary reaction rates
	activity 0.1-0.9					
[5]	MeOH/IA: 0.2-2.0	A16	Batch	60-80	0.8	integral analysis
	MeOH/2M1B: 1.0					+initial rates
[8]	MeOH/IA > 1	A15	Batch	40-80	0.9	differential analysis
	C5-cut		PB			
[9]	MeOH/2M1B: 1-3	A15	Batch	50-80	1.0	integral analysis
	MeOH/2M2B: 1-3					
[10]	MeOH/IA: 0.5-7.9	Lewatit SPC 118	CFRR	50-70	1.6	low conversions:
	solvent: n-pentane	Lewatit SPC 108				initial rates
[13]	MeOH/2M1B>1	VIONIT-CS-34	Batch	60-90	?	?
	MeOH/2M2B>1					
[14]	MeOH/2M2B: 1.3	Dowex 50W;	Batch	55-90	2.0	?
	TAME	M31				
		Lewatit SPC 118				
		A15, Naffon 117				
[15]	MeOH/2M1B: 1-4	KIF-2	Batch	50-90	0.5-1.0	?
	MeOH/2M2B: 1-4					

2 Experimental

Experiments

The composition changes in the synthesis of TAME were measured in a batch reactor (80 cm³) with methanol/isoamylenene molar ratios varying from 0.2 to 2.0 at temperatures between 333 and 353 K. The rates of isomerization of 2M1B to 2M2B and the etherification of 2M1B to TAME were measured with an equimolar mixture of methanol and 2M1B. No solvent was used in the measurements. A commercial ion-exchange resin Amberlyst 16 was used as a catalyst. To ensure a liquid-phase operation at any temperature, the pressure was set at 0.7 MPa. The samples were taken manually via an ice-cooled sample valve at the top of the reactor as a function of contact time (i.e., amount of dried catalyst × time). The samples were analyzed with a HP gas chromatograph 5890 Series II, equipped with a glass capillary column DB-1 and a FID, using a HP 3396A integrator.

The apparatus, chemicals and catalyst have been described in detail in our previous paper [5]

Simulation Tool

The capability of the various kinetic models to predict the experimental composition changes and the reaction equilibrium compositions was tested by simulating the experimental conditions. The simulation program FLOWBAT of Neste Engineering [16] was used as the tool for the simulation studies. The program contains a module for a liquid-phase stirred batch reactor, where one or more reactions can occur and the tank volume is assumed to be totally mixed. Isothermal conditions were defined by input. The kinetic models were programed with Fortran 77 into a user-supplied subroutine describing the reaction rates. In the case of the activity-based models, the activity coefficients were calculated with the UNIFAC method [17]

3 Results and Discussion

The first model to be tested was the concentration-based model by Hwang and Wu [8] The authors lumped the isoamylenes together giving one rate parameter and one equilibrium constant describing both etherification reactions. Hwang and Wu actually intended to take into account the nonideality of the liquid phase by applying the UNIFAC method for the calculation of the component activities in equilibrium conditions and in this way they obtained the value of the activity-based equilibrium constant, but surprisingly the activities are no longer present in the rate equation (see Tab. 1). Some of the simulation results with their kinetic model are presented in Figs. 2a-c. The solid lines represent the component molar fractions predicted by the model and the marked points represent the experimentally measured

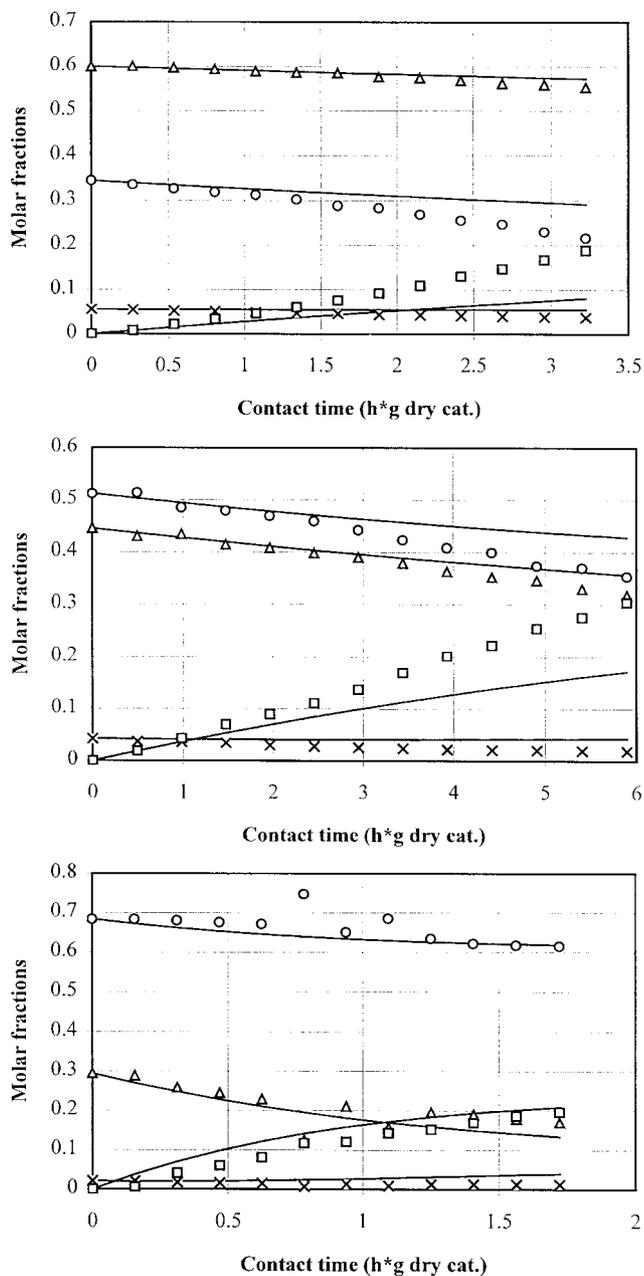


Figure 2. The simulated (–) vs. experimental molar fractions of MeOH (○), 2M1B (×), 2M2B (△), and TAME (□). Model by Hwang and Wu [8] (a) $R_{1A} = 0.5$ and $T = 333$ K; (b) $R_{1A} = 1.0$ and $T = 333$ K; (c) $R_{1A} = 2.0$ and $T = 353$ K.

molar fractions in conditions, where the reagents' (MeOH/IA) initial molar ratio R_{1A} was varied from 0.5 to 2.0. The figures show that the concentration-based model of Hwang and Wu can predict the experimental results *only* in conditions where methanol is present initially in excess.

The model by Piccoli and Lovisi [9] is also a concentration-based model, and the authors pointed out that their model is valid only in conditions where the methanol/isoamylenes molar ratio is greater than 1. They studied the two isoamylenes separately giving two rate constants and two equilibrium constants. However, they gave no results or con-

clusions about the isomerization reaction. They calculated the activities of components at equilibrium with the UNI-FAC method and further modified the equilibrium constants to depend on the molar fraction of the methanol, which is seen in the form of the rate equation (see Tab. 1). As the validity of the model was restricted, there were only a limited number of experiments that could be simulated. The results in Fig. 3 show that the model predicts the experimental results well in conditions where methanol is in excess.

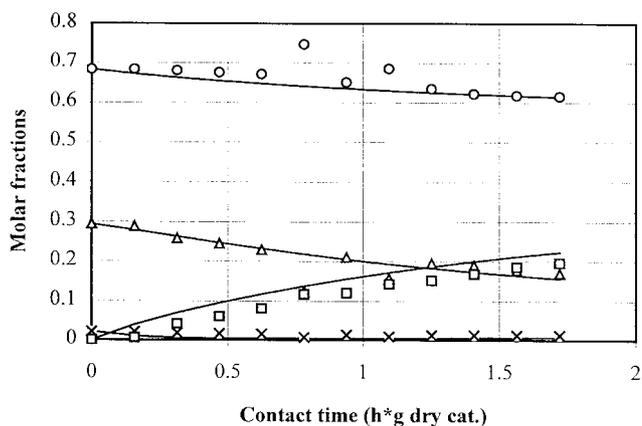


Figure 3. The simulated (–) vs. experimental molar fractions of MeOH (○), 2M1B (×), 2M2B (△), and TAME (□). Model by Piccoli and Lovisi [9] $R_{1A} = 2.0$ and $T = 353$ K.

Oost and Hoffmann [10] derived their model from the classical Langmuir-Hinshelwood approach assuming that methanol is the only one that is adsorbed and that there are no vacant sites present since the reaction proceeds in a liquid phase. Their kinetic equations are expressed in terms of component activities. They lumped the isoamylenes together, as they concluded that the isomerization reaction is very fast compared to the etherification reaction. They gave one lumped rate parameter determining the etherification rate and values of the equilibrium constants which were obtained from calculations with thermodynamic data (see Tab. 1). Fig. 4 shows that the experimental composition changes are

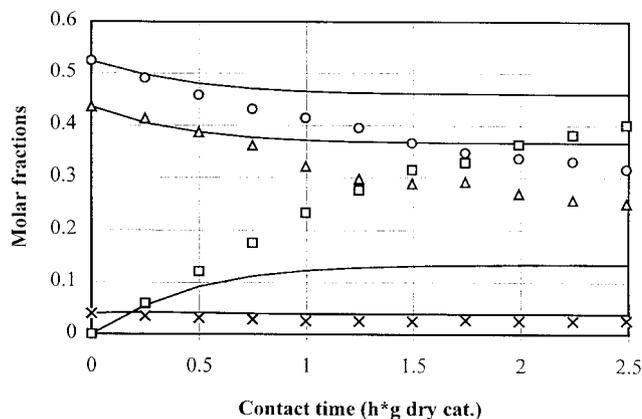


Figure 4. The simulated (–) vs. experimental molar fractions of MeOH (○), 2M1B (×), 2M2B (△), and TAME (□). Model by Oost and Hoffmann [10] $R_{1A} = 1.0$ and $T = 353$ K.

predicted well at the beginning of the experiment, but the calculated thermodynamic equilibrium constants and thus the driving force terms turn the compositions predicted by the model towards the equilibrium too soon because of the too low values of the equilibrium constants.

Recently, Thiel and Hoffmann [18] proposed that the value -114.65 kJ/mol for $\Delta_r G$ of TAME should be used instead of the value -109.55 kJ/mol, and thus the values of the equilibrium constants calculated from the thermodynamic data approach the values determined experimentally by us [6]. Considering this, we simulated the experimental conditions with the kinetic model of Oost and Hoffmann, but applied our experimentally determined values for the equilibrium constants as proposed also by Thiel et al. [19]. Figures 5a–c show that the conditions of excess olefins are now predicted very well (5a), but neither the conditions of excess alcohol (5b) nor the simultaneous isomerization and etherification (5c) are predicted satisfactorily.

On the basis of Fig. 5c we disagree with the value of the isomerization rate parameter k_5 and with the conclusion that the isomerization reaction is much faster than etherification reactions. The reason for the obvious discrepancy must be that the parameter k_5 was determined from experiments carried out without methanol [12]. We have recently carried out some additional experiments measuring the rates of the simultaneous etherification and isomerization reactions with methanol and 2M1B, covering a wide range of conditions ($R_{1b} = 0.2 - 4$, $T = 333$ K) [20]. According to these results, when the initial molar fraction of methanol is greater than 0.2, the initial etherification rate of 2M1B to TAME is about twice to three times as fast as the isomerization rate of 2M1B to 2M2B. These results were calculated with the method of initial rates (i.e., from experimental points where the fractional conversion of 2M1B to TAME was less than 10% and the fractional conversion of 2M1B to 2M2B less than 5%) and they are consistent with our previous observations [5]. Therefore, we estimated new ratios for the rate parameters of the model by Oost and Hoffmann from our data. Applying the basic model by Oost and Hoffmann [10] (see Fig. 1 for notation),

$$r_1 = k_1 \left(\frac{a_{1B}}{a_M} - \frac{1}{K_1} \frac{a_T}{a_M^2} \right) \quad (1)$$

$$r_3 = k_3 \left(\frac{a_{2B}}{a_M} - \frac{1}{K_2} \frac{a_T}{a_M^2} \right) \quad (2)$$

$$r_5 = k_5 \left(\frac{a_{1B}}{a_M} - \frac{1}{K_3} \frac{a_{2B}}{a_M} \right) \quad (3)$$

we got as an approximation that $k_1/k_3 \approx 2$ and $k_3/k_5 \approx 1.3$ when a value $k_3 = k_{1,3}/(1 + K_3)$ from Tab. 1 was applied. We simulated our experiments with these new dependencies and

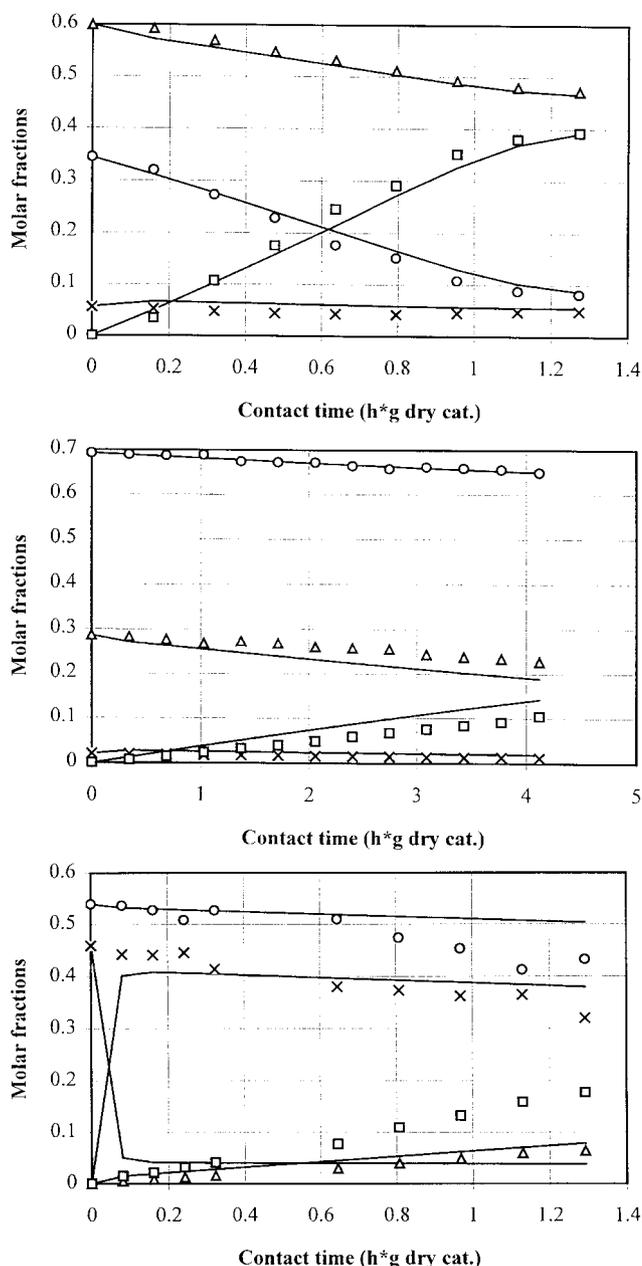


Figure 5. The simulated (–) vs. experimental molar fractions of MeOH (○), 2M1B (×), 2M2B (△), and TAME (□). Model by Thiel et al. [19] (a) $R_{1A} = 0.5$ and $T = 353$ K; (b) $R_{1A} = 2.0$ and $T = 333$ K; (c) $R_{1b} = 1.0$ and $T = 333$ K.

found out that now the simultaneous isomerization and etherification were predicted very well (see Fig. 6). Also, in conditions of excess olefins and stoichiometric conditions the experimental composition changes were predicted as well as before.

4 Summary

The range of validity of the various models are summarized in Tab. 3. Models based on component activities describe the etherification kinetics and reaction equilibrium

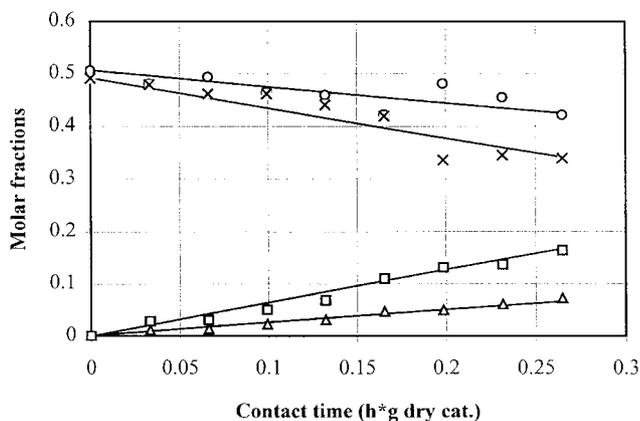


Figure 6. The simulated (–) vs. experimental molar fractions of MeOH (○), 2M1B (×), 2M2B (△), and TAME (□). Modified model by Thiel et al. [19] $R_{1b} = 1.0$ and $T = 353$ K.

Table 3. Range of Validity of the Various Kinetic Models for TAME.

Ref.	[5]	[8]	[9]	[10]	[19]
<u>Excess methanol ($1.0 < R < 2.0$)</u>					
-etherification kinetics	x	x	x		
-equilibrium	x	x	x		x
<u>Stoichiometric cond. ($R = 1.0$)</u>					
-etherification kinetics	x			x	x
-isomerisation kinetics	x				
-equilibrium	x				x
<u>Excess olefins ($0.2 < R < 1.0$)</u>					
-etherification kinetics	x			x	x
-equilibrium	x				x

better within a wider range of conditions than models based on component concentrations. Both concentration-based homogeneous models describe the kinetics and equilibrium only in conditions where methanol is initially in excess. One reason might be that the parameters of the two concentration-based models were obtained from experiments, where methanol was initially in excess. The activity-based model by Oost and Hoffmann predicts the experimental changes in a wide range of conditions after some revisions to the originally presented values of the parameters have been made. Our activity-based model predicts both the reaction kinetics and equilibrium very well [5], but this is natural as the values of our model parameters have been partially obtained from these data.

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Symbols used

a_i	[–]	activity of a component $i = \gamma_i x_i$
c	[mol/dm ³]	concentration of a component i
$\Delta_f G$	[kJ/mol]	component standard free energy of formation
k_j	[dm ⁶ /(mol kg s)] or [mol/(kg s)]	rate constant of a reaction $j, j = 1-6$
K_i	[–]	adsorption equilibrium constant for a component i
K_j	[–]	reaction equilibrium constant for a reaction $j, j = 1-3$
r_i	[–]	rate of a component i
r_j	[–]	rate of a reaction $j, j = 1-6$
R_{1A}	[–]	molar ratio of the reagents, methanol/isoamylene mixture
R_{1b}	[–]	molar ratio of the reagents, methanol/2-methyl-1-butene
T	[K]	temperature
x_i	[–]	molar fraction of component i

Subscripts

1B	2M1B
2B	2M2B
IA	isoamylenes (2M1B and 2M2B)
isom	isomerization
M	methanol
T	TAME

Abbreviations

2M1B	2-methyl-1-butene
2M2B	2-methyl-2-butene
CFRR	continuous flow recycle reactor
FID	flame ionization detector
MeOH	methanol
MTBE	methyl <i>tert</i> -butyl ether, 2-methoxy-2-methylpropane
PB	packed bed (reactor)
RVP	Reid vapor pressure
TAME	<i>tert</i> -amyl methyl ether, 2-methoxy-2-methylbutane

References

- [1] Simpson, S. G.; Hibbs, F. M., *Oil Gas J.* 94 (1995) Jan 1, pp. 30–38.
- [2] Ignatius, J.; Järvelin, H.; Lindquist, P., *Hydrocarbon Process.* 74 (1995) No. 2, pp. 51–53.
- [3] Patton, G. R.; Dunn, R. O.; Eldridge, B., *HTI Quarterly* (1995) Autumn, pp. 21–27.
- [4] Rihko, L. K.; Krause, A. O. I., *Ind. Eng. Chem. Res.* 34 (1995) pp. 1172–1180.

- [5] Rihko, L. K.; Kiviranta-Pääkkönen, P. K.; Krause, A. O. I., *Ind. Eng. Chem. Res.* **36** (1997) pp. 614–621.
- [6] Rihko, L. K.; Linnekoski, J. A.; Krause, A. O. I., *J. Chem. Eng. Data* **39** (1994) pp. 700–704.
- [7] Kiviranta-Pääkkönen, P. K.; Struckmann, L. K.; Linnekoski, J. A.; Krause, A. O. I., *Ind. Eng. Chem. Res.*, accepted for publication.
- [8] Hwang, W-S.; Wu, J-C., *J. Chin. Chem. Soc.* **41** (1994) pp. 181–186.
- [9] Piccoli, R. L.; Lovisi, H. R., *Ind. Eng. Chem. Res.* **34** (1995) pp. 510–515.
- [10] Oost, C.; Hoffmann, U., *Chem. Eng. Sci.* **51** (1996) pp. 329–340.
- [11] Oost, C.; Hoffmann, U., *Chem. Eng. Technol.* **18** (1995) pp. 110–117.
- [12] Oost, C., *Ph. D. Thesis*, Technische Universität Clausthal 1995.
- [13] Muja, I.; Goidea, D.; Marculescu, N.; Andreescu, G.; Curca, C.; Antonescu, I., *Rev. Chim. (Bukarest)* **37** (1986) pp. 1047–1054.
- [14] Randriamahefa, S.; Gallo, R.; Raoult, G.; Mulard, P., *J. Mol. Catal.* **49** (1988) pp. 85–102.
- [15] Pavlova, I. P.; Caplic, D. N.; Isuk, I. V.; Basner, M. E., *CNIE – Neftechim*, Moscow 1986.
- [16] Keskinen, K. I.; Aittamaa, J., *FLOWBAT User's Instruction Manual*, Neste Oy, Porvoo 1996.
- [17] Fredenslund, A.; Gmehling, J.; Rasmussen, P., *Vapour-liquid Equilibria Using UNIFAC*, Elsevier, Amsterdam, The Netherlands, 1977.
- [18] Thiel, C.; Hoffmann, U., *Chem. Ing. Tech.* **68** (1996) No. 10, pp. 1317–1320.
- [19] Thiel, C.; Sundmacher, K.; Hoffmann, U., *Chem. Eng. Sci.* **52** (1997) No. 6, pp. 993–1005.
- [20] Linnekoski, J. A.; Kiviranta-Pääkkönen, P., unpublished work.
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