Dehydration of the Alcohol in the Etherification of Isoamylenes with Methanol and Ethanol

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The kinetics of the dehydration of methanol and ethanol, which is a side reaction in the synthesis of tertiary ethers (TAME, 2-methoxy-2-methylbutane; TAEE, 2-ethoxy-2-methylbutane), were investigated in a continuous stirred tank reactor, with a commercial ion-exchange resin (Amberlyst 16) used as the catalyst. The effect of the alcohol concentration on the formation rates of dimethyl ether (DME) and diethyl ether (DEE) was measured between 323 and 363 K. The formation of the dialkyl ethers was favored by high temperatures and high-alcohol concentrations. At higher temperatures DME formed at a faster rate than DEE. The experimental results were best described with a model where one alcohol molecule is adsorbed and the other reacts from the liquid phase. Kinetic models for the synthesis of TAME and TAEE, expanded with the dehydration reactions and written in terms of component activities, are presented. The UNIFAC method was applied for the calculation of activity coefficients. The activation energy was determined to be 102.6 kJ/mol for methanol dehydration to yield DME and 90.5 kJ/mol for ethanol dehydration to yield DEE.

Introduction

The new reformulated gasoline requirements already legislated in the United States, and many of the changes currently being 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 (Simpson and Hibbs, 1995). The processing of FCC light gasoline with alcohol is one of the most economical methods for producing oxygenates to compensate for the octane deficits. In 1995, production capacities for the methanol-based tertiary ethers MTBE (methyl tert-butyl ether, 2-methoxy-2-methylpropane) and TAME ( tert-amyI methyl ether, 2-methoxy-2-methylbutane) were 27.5 Mm³/a (473 250 b/d) and 2.5 Mm³/a (42 700 b/d), respectively (IHI, 1995). A major reason for growing interest in the ethanol-based tertiary ethers ETBE (ethyl tert-butyl ether, 2-ethoxy-2-methylpropane) and TAEE ( tert-amyI ethyl ether, 2-ethoxy-2-methylbutane) is that ethanol can be produced by fermentation from renewable resources.

TAME and TAEE are synthesized in acid-catalyzed, equilibrium reactions of isoamylenes (2-methyl-1-butene, 2M1B, and 2-methyl-2-butene, 2M2B) with methanol and ethanol, respectively. The isomerization reaction between the two isoamylenes 2M1B and 2M2B establishes a third equilibrium. Typical side reactions are the dehydration of alcohol to yield dialkyl ether and water, hydration of isoamylenes to yield tertiary alcohol, and dimerization of isoamylenes.

So far, the majority of kinetic models published deal only with the main reactions. However, it is also important to investigate the formation of byproducts in the synthesis of the fuel oxygenates because of the specifications that are defined within an oil refinery both for the gasoline product and for the intermediates. The etherification reactions are exothermic, and possible hot spots resulting from uneven cooling may lead to unwanted side reactions. The dehydration of the alcohol, both methanol (MeOH) and ethanol (EtOH), is a relevant side reaction because in the novel processes for producing tertiary ethers the alcohol/olefin ratio may be greater than the stoichiometric value, as the conversions to tertiary ethers are maximized by side reactor configuration or by catalytic distillation (Ignatiu et al., 1995; Patton et al., 1995). Moreover, in a typical refinery the feed to the alkylation unit should be free of any oxygenates. Vila et al. (1994) studied the effect of temperature and the initial molar methanol/isobutene ratio on byproduct formation in MTBE synthesis in a batch reactor. The dimethyl ether formation was favored by high temperatures and high MeOH/IB molar ratios. The amount of DME formed at 355 K was correlated with the initial methanol concentration and the initial MeOH/IB molar ratio. Pavlova et al. (1986) have presented for TAME synthesis a complete activity-based kinetic model, which also includes the rate expression for DME formation.

Kinetic models have been published by our group for the synthesis of TAME (Rihko et al., 1997) and TAEE (Linnekoski et al., 1997). The modeling took into account the nonideality of the liquid phase by expressing both the reaction equilibria and the kinetic equations as functions of component activities. In this study, we present expanded kinetic models for the synthesis of TAME and TAEE, where the dehydration of MeOH and EtOH are properly formulated as relevant side reactions.

Experimental Section

The effects of temperature and reagent concentration on the formation rates of TAME and DME as well as TAEE and DEE were measured with various residence times.
**Apparatus.** Reaction rates were measured in a continuous stirred tank reactor (CSTR, 55.6 cm³, stainless steel), where the reaction mixture was magnetically stirred. The stirrer speed was set to 950 rpm to eliminate the influence of external diffusion control on the reaction rates (Rihko and Krause, 1995). The catalyst (0.2–2.3 g) was placed in a metal gauze basket (60 mesh). The temperature (323–363 K) was controlled within ±0.2 K by immerging the reactor in a thermostated water bath. The pressure was kept constant at 0.7–1.2 MPa to ensure a liquid phase operation at all temperatures. The pulse-free flow rate (5–82 g/h) of the feed was controlled by a liquid mass flow controller. A Mettler PM 6000 balance was used to measure the actual flow at the outlet of the reactor system. The composition of the feed and the reactor effluent were analyzed on-line with a gas chromatograph using an automated liquid sampling valve.

**Analysis.** Products were analyzed with a Hewlett-Packard gas chromatograph 5890 Series II, equipped with a flame ionization detector using a HP-1 (length 60 m, thickness 0.1 µm, column diameter 0.254 mm; Hewlett-Packard). Response factors were determined with calibration solutions.

**Chemicals and Catalyst.** The following reagents were used in the experiments: a mixture of isomylalenes (2-M2B, 92 wt %, Fluka Chemika), methanol (>99.8 wt %, Riedel-de Haën), and ethanol (>99.5 wt %, Alko Oy). In some experiments, the reagents were diluted with isopentane (>99.0 wt %, Fluka Chemika). The ethers used for the GC calibration solutions were TAME (>98.5 wt %, Neste), TAEE (>97 wt %, Yarsintez), DME (>99.2 wt %, Fluka Chemika), and DEE (>95 wt %, Yarsintez). A commercial macroporous strongly cation-exchange resin in hydrogen form (Amberlyst 16, Rohm & Haas) was used as the catalyst. The cross-linking level of the resin was 12 wt %, and the exchange capacity 5.0 mmol/g of dry catalyst measured by the method described in standard ASTM D 2187 (1991). Unsieved catalyst particles that varied in size from 0.3 to 1.0 mm, the main fraction (71.3 wt %) being 0.5–0.8 mm, were used in the experiments according to our earlier studies where the influence of pore diffusion control has been checked (Rihko and Krause, 1995). Before the experiments, the catalyst was treated with the respective alcohol at room temperature to remove the water from the catalyst pores.

**Dehydration Experiments.** Set I. The basic DME and DEE experiments were carried out both with undiluted methanol and ethanol and with methanol and ethanol diluted with isopentane so that the molar fraction of the alcohol was 0.2 in the mixture. The residence time (i.e., amount of catalyst/mass flow rate) was varied from 0.06 to 0.31 h and the temperature range was 323–363 K.

Set II. To study the alcohol dehydration as a side reaction in the formation of tertiary ethers, we carried out runs where the amount of isomylalenes was kept constant (molar fraction of 0.1) while the alcohol/isomylalenes molar ratio was increased from 5 to 20. Isopentane was used as a solvent. The temperature range was 333–353 K and the residence time was varied from 0.06 to 0.31 h.

Set III. The effect of alcohol concentration on the reaction selectivity within a kinetic regime was studied for TAME. Runs were carried out at 353 K, where shorter residence times 0.004–0.014 h were applied. In these experiments the methanol/isomylalenes molar ratio was varied between 1 and 9. Solvent was added in different amounts to obtain molar fractions of methanol between 0.2 and 0.8.

During the experiments the effects of the molar ratio of the reagents and the concentration of alcohol were studied in a random sequence, and in each set of different mixtures the temperature was varied randomly. The catalyst was changed after each set of mixtures. The stability of the catalyst was checked in each set of mixtures by repeating the experiment at first temperature after the experiments at the other temperatures had been carried out. The catalyst showed no deactivation even with the longest experiment (120 h). Depending on the residence time, it took about 4–5 h (set III) or 12–14 h (sets I and II) to attain a steady state in a CSTR.

The reaction rates $r_i$ (mol kg<sub>cat</sub>⁻¹ s⁻¹) of the products TAME, DME, TAEE, DEE, and TAA were calculated according to eq 1:

$$r_i = \frac{(F_{i,out} - F_{i,in})}{W_{cat}} = \frac{(w_{i,out} - w_{i,in})m_{cat}}{M_iW_{cat}}$$

(1)

**Results and Discussion**

The following main reactions (2–4 and 5–7) were observed in the synthesis of tertiary ethers (set II and set III, respectively):

1. **2M1B + MeOH** →<sub>fM2</sub> TAME
2. **2M2B + MeOH** →<sub>fM4</sub> TAME
3. **2M1B** →<sub>fM6</sub> 2M2B
4. **2M1B + EtOH** →<sub>fE2</sub> TAEE
5. **2M2B + EtOH** →<sub>fE4</sub> TAEE
6. **2M1B** →<sub>fE6</sub> 2M2B
7. **Formation of dialkyl ethers** was observed in lower quantities:

- **2MeOH** →<sub>fM7</sub> DME + H₂O
- **2EtOH** →<sub>fE7</sub> DEE + H₂O

The water produced in the dehydration reactions (8 and 9) reacted with isomylalenes to yield tert-amyl alcohol (TAA, 2-methyl-2-butanol) (10) and (11):

10. **2M1B + H₂O** →<sub>fM9,E9</sub> TAA
11. **2M2B + H₂O** →<sub>fM11,E11</sub> TAA

The amount of possible residual water could not be
mole specific volumes and consequent concentration directly compared from Figure 1, because of the different values of the thermodynamic equilibrium constants from Daubert and Danner (1992).

The thermodynamic pure component data were obtained (Keskinen and Aittamaa, 1996) by applying the Gibbs flowsheet program FLOWBAT were calculated with the flowsheet program FLOWBAT (Keskinen and Aittamaa, 1996) by applying the Gibbs energy minimization for equilibrium calculations. The thermodynamic pure component data were obtained from Daubert and Danner (1992).

The dehydration rates of the alcohols cannot be measured by GC analysis. However, our calculations based on the stoichiometry of the reaction scheme above indicate that almost all water reacted further in the hydration reactions (10) and (11), producing the tertiary alcohol. No dimerization products were detected in the experiments.

The rates of formation of the dehydration products from pure alcohols (set I) as a function of temperature are presented in Figure 1. The results show the formation of DME and DEE to be favored by higher temperatures. Moreover, the reactions are not thermodynamically controlled within the investigated range. Separate thermodynamical calculations presented in Table 1 (DME) and Table 2 (DEE) also show that the rate of the reverse reaction (splitting of the dialkyl ether) must be negligible since the values of the calculated equilibrium conversions are large relative to the measured conversions of DME and DEE.

The values of the thermodynamic equilibrium constants were calculated with the flow sheet program FLOWBAT (Keskinen and Aittamaa, 1996) by applying the Gibbs free energy minimization for equilibrium calculations. The thermodynamic pure component data were obtained from Daubert and Danner (1992).

The dehydration rates of the alcohols cannot be directly compared from Figure 1, because of the different mole specific volumes and consequent concentration difference. The liquid densities of the product streams were calculated with FLOWBAT by applying the model of Aalto et al. (1996). Although the model was originally developed for hydrocarbon mixtures, the authors tested it against liquid density data of alcohol–hydrocarbon mixtures. The average absolute deviation was found to be less than 5%, a level of accuracy adequate for our purposes since the concentrations are used only for qualitative conclusions. The results for experiments where the concentration was varied (set II for MeOH and EtOH; set III for MeOH) at a temperature of 353 K are presented in Figure 2. The figure shows that the dehydration rates of both methanol and ethanol increase with increasing alcohol concentration. A clear difference can be seen between the dehydration rates of methanol and ethanol, with the rate of methanol dehydration being faster. The same difference was observed at 343 K, but at 333 K the dehydration rates were so small that they are undistinguishable.

The results of the selectivity studies on TAME (set III) are presented in Table 3. Selectivity was studied by comparing the formation rate of TAME with the formation rate of DME. As the results show, when the reaction is maintained in a kinetic regime, the reaction is highly selective for tert-etherification. Although no similar experiments were carried for TAEE, the reaction for tert-etherification (TAEE formation) must be highly selective as the dehydration rate of ethanol was even smaller than the dehydration rate of methanol.

### Table 1. Calculated Thermodynamic Equilibrium Constants and Conversions, and the Obtained Experimental Conversions (Set I) between 323 and 363 K for the Formation of DME from MeOH

<table>
<thead>
<tr>
<th>T (K)</th>
<th>ΔG (kJ/mol)</th>
<th>K (thermodyn.)</th>
<th>eq. conv. of MeOH (%)</th>
<th>exp. conv. of MeOH (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>323.15</td>
<td>-12.1</td>
<td>88.56</td>
<td>94.78</td>
<td>0.04</td>
</tr>
<tr>
<td>333.15</td>
<td>-12.0</td>
<td>77.14</td>
<td>93.35</td>
<td>0.07</td>
</tr>
<tr>
<td>343.15</td>
<td>-12.0</td>
<td>67.82</td>
<td>93.92</td>
<td>0.21</td>
</tr>
<tr>
<td>353.15</td>
<td>-12.0</td>
<td>60.15</td>
<td>93.50</td>
<td>0.62</td>
</tr>
<tr>
<td>363.15</td>
<td>-12.0</td>
<td>53.77</td>
<td>93.07</td>
<td>1.49</td>
</tr>
</tbody>
</table>

### Table 2. Calculated Thermodynamic Equilibrium Constants and Conversions, and the Obtained Experimental Conversions (Set I) between 323 and 363 K for the Formation of DEE from EtOH

<table>
<thead>
<tr>
<th>T (K)</th>
<th>ΔG (kJ/mol)</th>
<th>K (thermodyn.)</th>
<th>eq. conv. of EtOH (%)</th>
<th>exp. conv. of EtOH (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>323.15</td>
<td>-12.2</td>
<td>94.05</td>
<td>91.17</td>
<td>0.01</td>
</tr>
<tr>
<td>333.15</td>
<td>-12.2</td>
<td>82.35</td>
<td>90.71</td>
<td>0.02</td>
</tr>
<tr>
<td>343.15</td>
<td>-12.2</td>
<td>72.61</td>
<td>90.25</td>
<td>0.03</td>
</tr>
<tr>
<td>353.15</td>
<td>-12.2</td>
<td>64.37</td>
<td>89.79</td>
<td>0.14</td>
</tr>
<tr>
<td>363.15</td>
<td>-12.2</td>
<td>57.33</td>
<td>89.33</td>
<td>0.40</td>
</tr>
</tbody>
</table>
The formation rate of DME according to model 1 is

\[ r_{\text{DME}} = \frac{k_M a_M^2}{1 + K_M a_M + K_T a_T} \]  

and according to model 2 is

\[ r_{\text{DME}} = \frac{k_M K_M a_M^2}{(1 + K_M a_M + K_T a_T)^2} \]  

For the TAEE kinetics (Linnekoski et al., 1997), the fraction of the vacant sites obtains the following form \((\theta_{\text{DEE}} \sim 0)\):

\[ \theta_{\text{Sa}} = \frac{1}{1 + K_E a_E + K_T a_T + \Sigma(K_{IA} a_{IA})} \]  

The formation rate of DEE according to model 1 is

\[ r_{\text{DEE}} = \frac{k_E E^2}{1 + K_E a_E + K_T a_T + \Sigma(K_{IA} a_{IA})} \]  

and according to model 2 is

\[ r_{\text{DEE}} = \frac{k_E K_E^2 a_E^2}{(1 + K_E a_E + K_T a_T + \Sigma(K_{IA} a_{IA}))^2} \]  

**Results of Parameter Estimation.** The rate equations for DME and DEE formation were further modified for parameter estimation. Since the practical objective of our study was to expand the previously presented kinetic models to cover the dehydration of the alcohol as a side reaction, we made the same assumptions as in our previous papers (Rihko et al., 1997; Linnekoski et al., 1997). Thus, by dividing eq 18 by \(K_M\), and assuming that the term \(1/K_M\) is small relative to the other terms in the denominator, we obtain according to model 1 a formation rate for DME in the form

\[ r_{\text{DME}} = \frac{k_M a_M^2}{a_M + \frac{K_T}{K_M} a_T} \]  

Similarly, dividing eq 19 by \(K_M^2\), we obtain according to model 2 a formation rate for DME in the form

\[ r_{\text{DME}} = \frac{k_M K_M a_M^2}{(a_M + \frac{K_T}{K_M} a_T)^2} \]  

In a similar manner, the kinetic equations for the formation rate of DEE are simplified by assuming that the adsorption of the strongly polar component (alcohol) is much stronger than the adsorption of the less polar components (isoamylenes and ether). In other words, the terms \(\Sigma(K_{IA} a_{IA})\) and \(K_T a_T\) are considered to be much smaller than the term \(1 + K_E a_E\) in the denominator. The formation rate of DEE according to model 1 then reduces to the form

\[ r_{\text{DEE}} = \frac{k_E E^2}{K_E a_E + 1} \]  

and according to model 2 to the form

\[ r_{\text{DEE}} = \frac{k_E K_E^2 a_E^2}{(K_E a_E + 1)^2} \]  

After these simplifications, it was possible to apply the parameter values \(K_T/K_M\) and \(K_E\) obtained earlier.
The parameter gave us Arrhenius-type temperature dependency for dependencies of the parameter from the data sets II and III because the correlations were estimated from the correlations $\ln[r_{1977}]$ method for estimation of the activity coefficients. Calculated by applying the UNIFAC (Fredenslund et al., 1977) method. However, expansion of the model required a more generalized approach, and all earlier data for TAME, including the equilibrium, splitting, and synthesis experimental data, were accordingly recalculated by applying the UNIFAC (Fredenslund et al., 1977) method for estimation of the activity coefficients.

The parameter values for DME formation were estimated by linear regression from the correlations $\ln[r_{DME} (1/\alpha_M + [K(1/K_M)(\alpha_M/2)])] vs 1/T$ (model 1) and $\ln[r_{DME} (1 + [K(1/K_M)(\alpha_M/2)])] vs 1/T$ (model 2). This method gave us an Arrhenius-type temperature dependency for the parameter $k_M$. Parameter values were estimated from the data sets II and III because the correlations include the ratio of the adsorption equilibrium constants for TAME and MeOH. Similarly, the temperature dependencies of the parameter $k_E$ for DEE formation were estimated from the correlations $\ln[r_{DEE} (1/\alpha_E + 1/[K_E(\alpha_E^2)])] vs 1/T$ (model 1) and $\ln[r_{DEE} (1 + 1/[K_E(\alpha_E^2)])] vs 1/T$ (model 2) from the data set I. The obtained values and some statistical data are presented in Table 4. The statistical results show that for DME formation the correlation ($R^2$) is better with model 1 than with model 2. The standard error (SE) is also smaller with model 1. For DEE formation the correlation is better with model 1 than with model 2, and the standard error is again smaller with model 1. Figures 5 and 6 present the plots of the experimental and calculated rates of dehydration. As seen from the figures, there is some experimental fluctuation, but still the deviation is much more severe with model 2. Moreover, according to Laidler (1987) a Langmuir–Rideal-type mechanism (model 1) is expected if the plot of rate vs concentration reaches an asymptotic maximum value similar to that presented in Figure 2.

From these results we can assume that, within the experimental range of our study, the alcohol dehydration is better described with a model where one alcohol molecule is adsorbed and the other reacts from the liquid phase. The difference between the dehydration rates of methanol and ethanol can be explained in terms of their differences in polarity. Methanol is a more polar medium than ethanol—the dielectric constant of methanol being 32.6 and that of ethanol 24.3 (CRC, 1992)—so that methanol has a greater tendency than ethanol to form a hydrogen bond with the sulfonic group. If the reaction were to occur between two adsorbed molecules of alcohol, an alkyl group would need to invert in order to form an alkyl cation and simultaneous proton-donating and -accepting properties would be required of the sulfonic groups (Tejero et al., 1996). Moreover, our experimental results would then be in contradiction with the stability order of carbocations, since the methyl cation $(\text{CH}_3^+)$ is less stable than the ethyl cation $(\text{CH}_2\text{CH}_3^+)$(Fessenden and Fessenden, 1990).

The expanded kinetic equations for the synthesis of TAME are presented in Table 5, and the UNIFAC-based parameters for the TAME model are presented in Table 6. Values of the earlier UNIQUAC-based parameters
for TAME are included in Table 6 in parentheses. The differences between the numerical values of the UNIFAC- and UNIQUAC-based parameters are appreciable. It must be pointed out again how important it is to apply these parameter values in their correct context, i.e., to use the proper method for estimating the activity coefficients when applying the model for reactor modeling. The expanded kinetic model for TAEE as well as the values for the UNIFAC-based parameters are presented in Tables 7 and 8.

In designing a reactor for etherifications, low temperatures are preferred to achieve both high conversions and less formation of byproducts. The high concentration of feed alcohol drives the equilibrium-controlled main reactions to the right, but also increases the formation of the unwanted dialkyl ethers and water. Therefore, the optimum feed alcohol/olefin ratio is near to the stoichiometric ratio. The water produced in dehydration reacts with the olefins to yield tertiary alcohol, which can be blended into the gasoline pool. The right amount (or place) of catalyst in the various reactor schemes can be calculated from the reactor simulations by applying kinetic models of the type presented in this paper.

### Table 6. Values of UNIFAC-Based Parameters for the TAME Model (Earlier UNIQUAC-Based Parameters in Parentheses)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>UNIFAC</th>
<th>UNIQUAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>k_M1</td>
<td>0.065</td>
<td>0.079</td>
</tr>
<tr>
<td>k_M2</td>
<td>0.026</td>
<td>0.035</td>
</tr>
<tr>
<td>k_M3</td>
<td>0.027</td>
<td>0.030</td>
</tr>
<tr>
<td>k_M4</td>
<td>5.0 × 10^-5</td>
<td>102.6</td>
</tr>
</tbody>
</table>

The dehydration was best described with a model where one alcohol molecule is adsorbed and the ether reacts from the liquid phase. According to calculations the water formed in the dehydration reactions reacts with the isomyl ethers yielding tert-amyl alcohol (TAA), which can be blended into the gasoline pool. Expanded kinetic models for the synthesis of TAME and TAEE were presented and reactor design was briefly discussed.

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### Notation

- $a_i$: activity of component $i = \gamma_i x_i$
- $\Delta G$: reaction Gibbs free energy change, kJ mol$^{-1}$
- $\Delta H$: reaction enthalpy change, kJ mol$^{-1}$
- $\Delta S$: reaction entropy change, kJ mol$^{-1}$ K$^{-1}$
- $E_{act}$: activation energy, kJ mol$^{-1}$
- $F_i$: molar flow of component $i$, mol s$^{-1}$
- $m_{tot}$: total flow, g s$^{-1}$
- $k_{Aj}$: rate constant of reaction $Aj$, A = M, E and $j = 1$–7, mol kg$^{-1}$ s$^{-1}$
- $K_i$: adsorption equilibrium constant for component $i$
- $K$: thermodynamic equilibrium constant
- $K_{Aj}$: reaction equilibrium constant for a reaction $Aj$, A = M, E and $j = 1$–3
- $M_i$: molar mass of the component $i$, g mol$^{-1}$
- $r_i$: rate of reaction for component $i$, mol kg$^{-1}$ s$^{-1}$
- $r_{Aj}$: rate of reaction $Aj$, A = M, E and $j = 1$–11
- $r_{calc}$: rate of dehydration calculated by a model, mol kg$^{-1}$ s$^{-1}$
- $r_{exp}$: rate of dehydration measured experimentally, mol kg$^{-1}$ s$^{-1}$
- T: temperature, K
- w_i: weight fraction of the component $i$
- W_m: catalyst mass, kg
- $\chi_i$: molar fraction of component $i$

### Abbreviations

- 2M1B: 2-methyl-1-butene
- 2M2B: 2-methyl-2-butene
- cat: catalyst, kg
- DEE: diethyl ether
- DME: dimethyl ether
- ETBE: ethyl tert-butyl ether, 2-ethoxy-2-methylpropane
- EtOH: ethanol
- FCC: fluid catalytic cracking
- IB: isobutene, 2-methyl-1-propene
- MeOH: methanol
- MTBE: methyl tert-butyl ether, 2-methoxy-2-methylpropane
- R$^2$: regression = 1 - (|S(y_{exp} - y_{calc})|^2)/(|S(y_{exp} - \bar{y})|^2)
RVP = Reid vapor pressure
SE = standard error
TAA = tert-amyl alcohol, 2-methyl-2-butanol
TAEE = tert-amyl ethyl ether, 2-ethoxy-2-methylbutane
TAME = tert-amyl methyl ether, 2-methoxy-2-methylbutane

Subscripts and Superscripts
A = alcohol (MeOH or EtOH)
D = dialkyl ether (DME or DEE)
DEE = diethyl ether
DME = dimethyl ether
E = ethanol
IA = isoamylenes (2M1B and 2M2B)
M = methanol
Sa = vacant adsorption site
T = tertiary ether (TAME or TAEE)
TAEE = tert-amyl ethyl ether
TAME = tert-amyl methyl ether

Greek Letters
γ = activity coefficient of component i
θ = fraction of the surface covered by component i

Literature Cited


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