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# Equilibrium of the simultaneous etherification of isobutene and isoamylenes with ethanol in liquid-phase

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## ABSTRACT

The simultaneous etherification of isobutene and isoamylenes with ethanol has been studied using macroreticular acid ion-exchange resins as catalyst. Most of the experiments were carried out over Amberlyst-35. In addition, Amberlyst-15 and Purolite CT-275 were also tested. Chemical equilibrium of four chemical reactions was studied: ethyl tert-butyl ether formation, tert-amyl ethyl ether formation from isoamylenes (2-methyl-1-butene and 2-methyl-2-butene) and isomerization reaction between both isoamylenes. Equilibrium data were obtained in a batchwise stirred tank reactor operated at 2.0 MPa and within the temperature range from 323 to 353 K. Experimental molar standard enthalpy and entropy changes of reaction were determined for each reaction. From these data, the molar enthalpy change of formation of ethyl tert-butyl ether and tert-amyl ethyl ether were estimated. Besides, the chemical equilibrium between both diisobutene dimers, 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene, was evaluated. A good agreement between thermodynamic results for the simultaneous etherification carried out in this work and those obtained for the isolated ethyl tert-butyl ether and tert-amyl ethyl ether systems was obtained.

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**Keywords:** Simultaneous etherification; Oxygenates; Ethyl tert-butyl ether; Tert-amyl ethyl ether; Chemical equilibrium; Diisobutenes isomerization

## 1. Introduction

In order to reduce hazardous and evaporative gasoline exhausts and from refueling emissions, as well as their environmental impact at the time that engines energetic efficiency is enhanced, new legislation and major efforts have been devoted to fuel reformulation. The European Directive 2009/28/EC promotes the usage of combustibles from renewable resources, such as bioethanol, and the directive 2009/30/EC establishes the main guidelines related to fuel reformulation.

As it is well known, olefins of the C<sub>5</sub> fraction from oil, mainly the reactive isoamylenes (IA) 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B), present some disadvantages as components of a gasoline, particularly in tropical zones. This is because these are the olefins with the highest

Reid vapor pressure (RVP), the highest atmospheric reactivity, the highest potential of tropospheric ozone formation (around 90%) and these are the largest amount of the olefins present in a gasoline (above 25 wt.% of the C<sub>5</sub> fraction from fluid catalytic cracking, FCC) (Rock et al., 1992). Thus, to diminish the impact of their use as fuel components on the environment, the reduction of the content of these compounds by means of either its etherification with primary alcohols or via oligomerization would result in a more suitable alternative than the reduction of the total olefin content of a gasoline.

Oxygenated compounds have been gradually gaining importance in the gasoline market since lead compounds were banned as octane enhancers. The two main types of oxygenates used as high octane additives are alcohols and ethers. Among alcohols, the most widely used is ethanol (EtOH), whereas the main tertiary ethers are methyl tert-butyl ether

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### Nomenclature

$a, b, c, d$	temperature dependence parameters of thermodynamic functions
$a_j, b_j, c_j, d_j$	temperature dependence coefficients of heat capacity expression for compound $j$
$a_j'$	activity of compound $j$
$C_{pj}^\circ$	molar heat capacity of compound $j$ in the liquid phase (J/(mol K))
$\Delta_f G_j^\circ$	liquid-phase standard molar enthalpy change of formation of compound $j$ (kJ/mol)
$\Delta_f H_j^\circ$	liquid-phase standard molar enthalpy change of formation of compound $j$ (kJ/mol)
$\Delta_r G_i^\circ$	standard Gibbs free energy change of reaction $i$ in the liquid phase (kJ/mol)
$\Delta_r H_i^\circ$	standard molar enthalpy change of reaction $i$ in the liquid phase (kJ/mol)
$\Delta_r S_i^\circ$	standard molar entropy change of reaction $i$ in the liquid phase (J K <sup>-1</sup> mol <sup>-1</sup> )
$I_H$	van't Hoff integration constant (dimensionless)
$I_K$	Kirchoff integration constant (J/mol)
$K_i$	thermodynamic equilibrium constant of reaction $i$ (dimensionless)
$K_{xi}$	equilibrium constant of reaction $i$ based on molar fractions (dimensionless)
$K_{yi}$	activity coefficients ratio of reaction $i$
$K_{ri}$	Poynting correction factor of reaction $i$ (dimensionless)
$n$	number of mole (mol)
$P$	pressure (bar)
$R$	gas constant, 8.31447 J/(mol K)
$R_{A/O}$	initial molar ratio alcohol to olefins
$R_{C4/C5}$	initial molar ratio between C <sub>4</sub> and C <sub>5</sub> isoolefins
$S_g$	specific surface area (m <sup>2</sup> g <sup>-1</sup> )
$S_j^\circ$	absolute entropy of compound $j$ (J K <sup>-1</sup> mol <sup>-1</sup> )
$T$	temperature (K)
$t$	time (min)
$T_{max}$	maximum working temperature (K)
$V_j$	molar volume of compound $j$ (L mol <sup>-1</sup> )
$W_{cat}$	mass of dry catalyst (g)
$X_j$	relative conversion of reactant $j$
$x_j$	molar fraction of compound $j$
<b>Subscript</b>	
0	initial
<b>Greek letters</b>	
$\gamma_j$	activity coefficient of compound $j$
$\nu_{ji}$	stoichiometric coefficient of compound $j$ in reaction $i$

(MTBE), ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME) and tert-amyl ethyl ether (TAEE). These ethers can be obtained by means of the addition of primary alcohols to tertiary olefins over acid catalysts (Dogu and Varisli, 2007). MTBE and TAME are produced from the reaction of methanol (MeOH) with isobutene (IB) and IA (2M1B and 2M2B), respectively. Analogous reactions of these olefins with EtOH lead to ETBE and TAEE production.

Generally, ethers are preferred rather than alcohols due to their blending characteristics, since they are more like conventional constituents hydrocarbons of a gasoline (Kitchaiya and

Datta, 1995). Due to azeotropes formation, alcohols blending normally confer a higher RVP, what implies more evaporative and exhaust emissions, and also a possible phase separation due to the water presence within the system (Arteconi et al., 2011). Despite the choice of some countries like the US and Brazil of a direct blending of EtOH or bioethanol, mainly for economic advantages, it has some drawbacks such as: high vapor pressure, high latent heat of vaporization, possibility to introduce water in the system, less energetic content and less enthalpy of combustion compared to ethers. As a result, specific fuel consumption induced by direct blending of EtOH is around 40% higher than that induced by tertiary ethers blending (mainly ETBE and TAEE) (Cataluña et al., 2008). Likewise, its high oxygen content can promote nitrogen oxides (NO<sub>x</sub>) formation or limit the amount of blended additive in order to fulfill the maximum legislated oxygen content (Kiatkittipong et al., 2008).

It is worth noting that, despite being currently the tertiary ether most widely produced, MTBE usage was banned in some states of the US such as California, due to its toxicity, its water solubility and consequently, its potential danger to pollution of freatic waters (Ahmed, 2001). On the other hand, ETBE production has experienced fast global growth in the last two decades, especially in Europe, due to the ease of revamping of MTBE existent plants. ETBE is synthesized industrially through the reaction between IB and ETOH in liquid phase, usually catalyzed by macroporous sulfonic acid resins at a temperature below 353 K under pressurized conditions (Yee et al., 2013). Nowadays, TAEE is not produced industrially at large scale, but it could become an interesting alternative since both ETBE and TAEE can be obtained from bioethanol, a renewable resource.

Several authors have studied the etherification of C<sub>5</sub>–C<sub>8</sub> alkenes with C<sub>1</sub>–C<sub>4</sub> alcohols (Karinen et al., 2001a; Kiatkittipong et al., 2011; Oktar et al., 1999a). Thermodynamic and kinetic parameters of MTBE (Gómez et al., 1997; Iborra et al., 2002; Izquierdo et al., 1994) and TAME (Krause and Hammarström, 1987; Mao et al., 2008; Muja et al., 2005; Rihko and Krause, 1995; Rihko et al., 1997; Serdá et al., 1995; Solà et al., 1997; Syed et al., 2000) production reactions are available in literature, and also the influence of mass transfer effects (Pääkkönen and Krause, 2003). Similarly, kinetics of ETBE (Fitó et al., 1994; François and Thyron, 1991; Iborra et al., 2002; Izquierdo et al., 1994; González, 2011; Solà et al., 1995; Vila et al., 1993) and TAEE (Aiouache and Goto, 2003; Boonthamtirawuti et al., 2009; Boz et al., 2005; Boz and Dogu, 2005; Bozga et al., 2008; Cruz et al., 2007; Linnekoski et al., 1997; Oktar et al., 1999b; Zhang et al., 1997) formation reactions have been widely studied for the isolated systems in previous works. Activation energies and kinetic constants values have been published, concluding that a Rideal–Eley mechanism fits better for the liquid phase ETBE synthesis from IB and EtOH and that a Langmuir–Hinshelwood model describes better the liquid phase reaction between IA and EtOH to produce TAEE. Thermodynamics of these reactions for the isolated systems has also been studied and equilibrium constants, enthalpies and entropies of formation and reaction have been determined (Fitó and Linnekoski, 2008; Gómez et al., 1997; Izquierdo et al., 1994; Jensen and Datta, 1995; Kitchaiya and Datta, 1995; Linnekoski et al., 1998, 1999; Muja et al., 2005; Rihko and Krause, 1993; Rihko et al., 1994; Sharonov et al., 1995).

The use of bioethanol as reactant entails a potential source of water into the system, hence it is worthy to study the effect

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