

Investigations of the etherification process under model mixture

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Abstract: Tertiary ethers are formed in a reaction between alcohols and alkenes. They are used in gasoline to enhance its burning and to reduce harmful exhaust emissions. They also have high octane rating, which is beneficial for gasoline blending. Regulations in regard to fuel composition and exhaust emissions are tightening and new, cleaner burning high octane gasoline components are of wide interest.

This work concerns the etherification of C_8 -alkenes. Several C_8 -alkenes were screened for their reactivity. Study of the properties of the resulting ethers showed that some of them are potential for gasoline blending.

Key words: etherification, alkenes, high octane components, gasoline blend

INTRODUCTION

Our consciousness of the environment has been awakened in a dramatic way during the last few decades. In the case of road traffic, this has led to a focus on exhaust emissions and, in particular, on reducing them. The industrialised world has established regulations for the composition of fuel and harmful exhaust emissions as a means of ensuring reduced load to the environment.

The composition of fuel has changed tremendously, and also engine technology has played an important role in improvements related to combustion. At the same time the number of motor vehicles has increased rapidly world-wide and the cut-backs on harmful emissions have become of utmost importance. One of the major changes in gasoline composition has been the development of reformulated gasoline and the introduction of high-octane oxygen-containing compounds, known as oxygenates, into the gasoline pool. Oxygenates reduce the emissions of carbon monoxide and hydrocarbons by improving the combustion of the fuel. The first oxygenate, *tert*-butyl alcohol (TBA), was incorporated in gasoline in 1969, and the blending of the first tertiary ether, methyl *tert*-butyl ether (MTBE) was first commercialised in the United States in 1979. Oxygenates have been key components of reformulated gasoline, with MTBE and ethanol the two most widely used. The next step in the regulation of gasoline composition will be the reduction of the total aromatic and olefin (i.e. alkene) content to improve the gasoline quality and to further reduce harmful emissions.

Tertiary ethers are typically produced in liquid phase reaction under mild conditions with acid catalysts, mainly with strong cation exchange resins. The double bond in the alkene must be attached to a tertiary carbon atom. Elevated pressure is used to ensure that the reactants remain in the liquid phase at typical reaction temperatures, i.e. below 100°C. Tertiary ethers currently finding commercial use as gasoline components are MTBE produced from isobutene and methanol, TAME (*tert*-amyl methyl ether) produced from isoamylenes and methanol, and ETBE (ethyl *tert*-butyl ether) produced from isobutene and ethanol. One of the most useful properties of oxygenates is their high octane rating. Oxygenates are one of the few high octane alternatives to aromatics in gasoline.

The aim of this work is to study the ethers with the view to their use as fuel components, but these components have also been proposed for use as low volatility solvents in paints, inks and lacquer.

MATERIALS AND METHODS

The experiments were carried out in an 80-cm³ stainless steel batch reactor equipped with a magnetic stirrer and a mixing baffle. The reactor was placed in a water or oil bath to adjust the temperature of the reactor to 50–65°C. Reaction pressure was maintained at 0.8 MPa with nitrogen to ensure that the reaction mixture remained in the liquid phase. Liquid samples were taken manually via a cooled sample valve.

Samples were analysed with a Hewlett-Packard 5890 Series III gas chromatograph equipped with a capillary column DB-1 (J&W Scientific, length 60 m, film thickness 1.00 μm , diameter 0.250 mm) and a flame ionisation detector. The products were quantified by the internal standard method.

The alkenes used in this work were a mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene (diisobutylene, Fluka Chemica AG, 95%, molar ratio of isomers was approximately 3.5), a mixture of 2-methyl-1-heptene and 2-methyl-1-heptene (Fluka Chemica AG, 96.0%) and a mixture of 2-methyl-1-butene and 2-methyl-1-butene (Aldrich, 90.5 %).

Isooctane (2,2,4-trimethyl pentane, Merck, >99.5%) was used to dilute the reaction mixtures. In addition, toluene (Riedel-de Haën, >99.7%) was used in the experiments as a solvent.

In the etherification experiments the alcohol was methanol (Riedel-de Haën, >99.8%). The properties of used alcohol are given in Table 1.

Etherification experiments were carried out between alkene and alcohol. All the model mixture was tested with Amberlyst 120 IR ion exchange resin catalyst. The properties of catalyst Amberlyst 120 IR are presented in Table 2.

Table 1. Properties of used methanol

| № | Parameters | Value |
|----|---|--------|
| 1. | Molecular mass, $\text{g}\cdot\text{mol}^{-1}$ | 32.04 |
| 2. | Critical temperature, $^{\circ}\text{C}$ | 239 |
| 3. | Relative density at 20 $^{\circ}\text{C}$ | 0.7915 |
| 4. | Boiling point, $^{\circ}\text{C}$ | 64.6 |
| 5. | Freezing point, $^{\circ}\text{C}$ | -97.6 |
| 6. | Reid vapour pressure, kPa | 32 |
| 7. | Flash point with closed crumble, $^{\circ}\text{C}$ | 12 |

Table 2. Properties of used catalyst Amberlyst 120 IR

| № | Parameters | Value |
|----|------------------|--------------------------------|
| 1. | Shape | beads |
| 2. | Matrix | styrene-divinyl benzene |
| 3. | Size | diameter 700-950 μm |
| 4. | Capacity, mmol/g | 5.2 |
| 5. | Active group | sulfonic acid |

Conventionally, the etherification of alkenes has been catalysed by strong cationic ion exchange resin. Structurally this commercial resin is sulfonated copolymers of styrene and divinyl benzene [2]. The catalyst particles are spherical beads and the active sulfonic acid group is distributed throughout the catalyst. Cross linking makes the structure of the particles stiff but limits the mobility of the molecules inside the catalyst particles.

RESULT AND DISCUSSION

Initial rates are interpolated from the curves of molar amount of ether or alkenes formed as a function of contact time. Activation energies are calculated from the initial rates according to the Arrhenius' equation.

Table 3 presents the initial rates and activation energy of etherification of the individual alkenes in experiments carried out with stoichiometric feed of alkene and

methanol. Apparent activation energies, which describe the temperature dependency of the etherification reaction, were determined for the formation of the methyl ethers. Activation energy can also be used as a measure of the internal diffusion resistances: the apparent activation energy is lower when diffusion is limiting the reaction than it is in a diffusion-free situation.

Table 3. Initial rates and activation energy of etherification experiments at 55 °C

| | Alkene | Initial rates, mmol/ (s kg _{cat}) | Activation energy, kJ/mol |
|----|---------------------------|---|---------------------------|
| 1. | 2,4,4-trimethyl-1-pentene | 0.23 | 60 |
| 2. | 2,4,4-trimethyl-2-pentene | 0.75 | 65 |
| 3. | 2-methyl-1-heptene | 0.80 | 81 |
| 4. | 2-methyl-2-heptene | 0.45 | 83 |
| 5. | 2-methyl-1-butene | 0.35 | 75 |
| 6. | 2-methyl-2-butene | 0.68 | 80 |

As can be seen from Table 3 the total reaction rate was highest and faster for 2-methyl-1-heptene. Typically in reactions of this kind of alkene the α -form is more reactive. The obtained higher reactivity of the β -form of 2,4,4-trimethyl pentenes can be attributed to the highly branched and sterically hindered structure.

The values obtained for the etherification of 2,4,4-trimethyl pentenes are clearly lower, than values obtained for the etherification of other tertiary ethers, indicating the existence of diffusional limitations. Indeed, a comparison of the structures of the alkenes shows that 2,4,4-trimethyl pentenes are the most highly branched alkenes of the study and, owing to their structure, one would expect them to encounter mass transfer limitations.

CONCLUSION

The investigated mixture was screened for their reactivity in etherification. The several alkenes were etherified with methanol and with Amberlyst 120 IR as catalyst. It were calculated the initial rates and activation energy of separated processes, which may conclude that the etherification of C₈ – alkenes is thermodynamically possible. All alkenes reacted to the respective methyl ether and it's base for perspective work in the future.

REFERENCE

- [1]. Dobrev, D., Stratiev, D., Kirilov, K., Ivanov, A., " Effect of bio-ethanol quality on gasoline / bio-ethanol mixture properties, Oxidation Communications, 2007, 35,3, p.342.
- [2]. Dobrev, D., Stratiev, D., Kirilov, K., Petkov, P.," Effect of gasoline hydrocarbon composition on the properties of the blend gasoline/bioethanol", Proc. International Petroleum Conference, Bratislava, September 25th – 26th, 2007.
- [3]. Martinez, R.B., Macris, A., Hunter M.G., Gentry, A.R.,"Meet Gasoline Pool Sulfur and Octane Targets with the ISAL Process", 2000 NPRA Annual Meeting, San Antonio, Texas, March 2000.
- [4]. Cataluna, R., De Menezes, E.W., Samios, D., Piatnicki, D., "Trends in future automobile fuels", Fuel, 2005, 84, p. 951.
- [5]. De Menezes, E.W., Cataluna, R., Samios, D., Da Silva, R., "Gasolines perspectives and trends", Fuel, 2006, 17, p. 2567.
- [6]. Karinnen R., PhD thesis, 2002.

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This paper has been reviewed