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INVESTIGATION OF THE ETHERIFICATION PROCESS UNDER MODEL MIXTURE

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Abstract. 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.

Keywords: etherification, gasoline, model mixture, additive

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 (Da Silva et al., 2005).

The composition of fuel has changed tremendously, and also engine technology has played an important role in improvements related to combustion (Dobrev et al., 2007).

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 (Dobrev, 2011).

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 50–110°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 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).

Isooctane (2, 2, 4-trimethyl pentane, Merck, >99.5%) was used to dilute the reaction mixtures.

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

Table 1. Properties of the methanol used

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

In addition, toluene (Riedel-de Haën, >99.7%) was used in the experiments as a solvent.

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. It was used ratio methanol:alkene = 10:1; 12:1 and 15:1.

Table 2. Properties of the 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. 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

Table 3. Alkene conversion in experiments at 60 °C

alkene	Ratio alkene:	s kg$_{cat}$	
Mmxture of alkenes	methanol	etherification	isomerisation
	1:10	0.26	0.06
	2:10	1.24	0.32
	1:12	0.34	0.03
	2:12	0.42	0.26
	1:15	1.38	0.12
	2:15	0.74	0.30

Table 4. Alkene conversion in experiments at 80 °C

alkene	Ratio alkene: methanol	Initial rate mmol/(s kg_{cat}	
		etherification	isomerisation
Mmxture of alkenes	1:10	0.38	0.10
	2:10	1.56	0.34
	1:12	0.47	0.33
	2:12	0.89	0.46
	1:15	1.58	0.22
	2:15	0.77	0.08

Tables 3 and 4 present the alkene conversion of etherification and isomerisation of the individual alkene in experiments carried out with methanol. The two main reactions observed in the experiments were the etherification and isomerisation of alkene. Double bond isomerisation was detected with alkene, but isomerisation could not be detected in the experiments with the thermodynamic mixtures of 2,4,4-trimethyl pentenes. Some isomerisation, which reestablished the ratio of the alkene, can nevertheless be presumed to have occurred for the etherification probably did not consume the isomers in the same proportion and the equilibrium ratio of the alkene was restablished through isomerisation. Hydration of alkene to tertiary alcohol and dehydration of methanol to dimethyl ether were detected as side reactions.

Etherification and isomerisation are competing parallel reactions and in most case etherification was the main reaction.

Conclusion

The investigated mixture was screened for their reactivity in etherification. 2,4,4-trimethyl pentenes were etherified with methanol and with Amberlyst 120 IR as catalyst. All alkenes reacted to the respective methyl ether and, at the same time, double bond isomerisation of alkenes occurred. Determination of selected properties of the ethers indicated their potential as gasoline components.

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