

Production of Clean Transportation Fuel Dimethylether by Dehydration of Methanol Over Nafion Catalyst

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ABSTRACT

Dimethylether (DME) which is a very attractive synthetic transportation fuel alternate is synthesized by the dehydration reaction of methanol over nafion as the catalyst. The objective is to test the activity of this catalyst in methanol dehydration reaction. Experiments carried out in a vapor phase flow reactor in a temperature range of 120-220°C and with a space time of 1.35 s.g/cm³ showed quite high activity of Nafion to produce DME, giving conversion values of about 0.4 at 220°C. An increase in temperature caused an increase in DME selectivity (reaching to one over 200 °C) and a decrease in formaldehyde selectivity.

Keywords: Dimethylether, Nafion, Dehydration

1. INTRODUCTION

Research on the synthesis of clean alternative fuels have been significantly increased in recent decades. Fast depletion of fossil fuel reserves, environmental and economical considerations diverted the researchers and fuel producers to the synthesis of alternative synthetic transportation fuels. The largest fraction of petroleum is consumed for transportation and as indicated in many of the published work, the oil reserves are being depleted at an increasing rate [1,2]. Due to fast increase in the population of the world with increasing necessities, alternative sources for fuel requirement have been searched. Global warming is another important problem that affects human life, animals and plants. Emissions during the combustion of fossil fuels, such as carbondioxide, NO_x, SO_x etc. are reported to contribute to this problem greatly [3]. Considering this fact, the proposed alternative fuels should emit less pollutants than the conventional ones. Nowadays, alcohols and ethers, are considered as attractive alternative fuels due to their good burning properties and less carbon emissions. Dimethylether (DME) is one of the most promising alternates of such synthetic fuels.

DME, having a chemical formula of CH₃OCH₃, is produced by either direct synthesis from syngas, i.e. hydrogen and carbonmonoxide; or by methanol dehydration reaction. It has a boiling point of -25°C and

can be easily liquified. The physical and chemical properties of this oxygenate are very close to LPG which makes the storage of DME easier by using current LPG technology. Due to its high cetane number DME is also considered as an alternate for diesel fuel. The toxicity of DME is very low [4]. When it is burned, neither SO_x emission nor particulate matter formation take place. Also, less NO_x formation occurs compared to conventional fuels. Explosion limit of DME is larger than that of butane or propane, which makes DME safer than LPG [1]. Therefore, using DME as a fuel brings great advantages regarding human health and environment. Some of the physical properties of diesel fuel, DME, methanol, methane and propane are summarized in Table 1. Among these properties, cetane number is an important criterion for a fuel to be suitable for diesel engines. DME has a cetane number in the range of 55-60 which is higher than that of conventional diesel fuel (40-55) [1]. This property makes DME appropriate for diesel engines. It has a heating value of 28 000 kJ/kg, which is somewhat lower than that of LPG or diesel fuel. When net calorific values are considered, approximately 1.25 m³ of DME is equivalent to either 1m³ of LPG or 1 m³ of diesel fuel [7]. Besides being used as a transportation fuel, DME can also be converted to light olefins such as ethylene and other hydrocarbons.

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Table 1. Some Properties of Different Fuels (Adapted from [1])

Properties	Diesel Fuel	MetOH	CH ₄	C ₃ H ₈	DME
Cetane Number	40-55	5	3	5	55-60
Heating Value kJ/kg	42000	20000	48500	46000	28000
Autoignition Temperature °C	320	460	532	470	350
Boiling Point, °C	180-350	64.8	-161.5	-42	-24.9

DME formation takes place by the following dehydration reaction,



Conventionally, this dehydration reaction was carried out by heating the alcohol with strongly acidic compounds such as H₂SO₄. However, recovery of the catalyst and the toxicity of the acids are some of the problems that should be solved in this process. Due to such environmental and economical reasons, researchers and fuel producers have diverted their attention to solid acid catalysts, such as γ -alumina, heteropolyacids etc., to be used in dehydration reactions.

In methanol dehydration reaction to produce DME, solid acid catalysts, such as γ -alumina and modified γ -Al₂O₃ [5], Na-modified H-ZSM-5 [6], Amberlyst 35 [7] heteropolyacids such as Tungstophosphoric acid, Silicotungstic acid [8] and mesoporous Aluminosilicate [8] were tested in the literature.

Nafion is a perfluorinated ion-exchange polymer and it is known as a superacidic catalyst having a terminal –CF₂CF₂SO₃H group. It is a copolymer of tetrafluoroethene and perfluoro-2-(fluorosulfonylethoxy)propyl vinyl ether. Due to its high acidity and chemical inertness of the fluorocarbon backbone, nafion is considered as an alternative catalyst to homogeneous acid catalysts [9]. Its acidity is given in the literature with Hammet acidity (-H₀≈12) which is similar to 100% H₂SO₄ [9, 10]. Nafion NR50 resin is well known type of nafion in the form of bead shape in millimeter sized. It has very low surface area, around 0.02 m²/g, in this form. For this reason, its catalytic activity is limited in many reactions [9]. To increase the surface area and catalytic activity of nafion, researchers have concentrated on the preparation of nanocomposite of nafion resins.

Previously in the thesis work, methanol dehydration had been investigated using mesoporous aluminosilicate and heteropolyacid catalysts [8]. In the present study, methanol dehydration reaction was studied using nafion as the catalyst in a fixed bed flow reactor. The effects of reaction temperature and the space time on the

methanol conversion and product distribution were investigated.

2. EXPERIMENTAL METHODS

The vapor phase methanol dehydration reaction was carried out in a tubular flow reactor. nafion was placed into the stainless steel tubular reactor, which has ¼ in diameter and 50 cm in height . Liquid methanol (having 99.9 % purity) was first sent to the evaporator by using a syringe pump. In the evaporator, vapor phase methanol was mixed with helium and went through the reactor. The effluent of the reactor was analysed with a Gas Chromatograph (Varian) equipped with a Porapak T column and connected on-line to the reactor outlet.

In all the experiments, total flow rate of methanol and helium mixture was set to 44.2 ml/min, measured at room conditions. The mole fraction of methanol in the feed stream was adjusted to 0.48. The flow lines between the evaporator and the reactor and between the reactor and the GC were heated to 150°C in order to prevent the condensation of alcohol and products. The reaction temperature was changed in the range of 120-220°C. Minimum three successive measurements were carried out for each data point. The amount of nafion charged to the reactor was changed in the range of 0.2-1.0 g.

3.RESULTS and DISCUSSIONS

In this study, methanol is converted to DME by dehydration reaction using nafion as the catalyst. Beside DME, formaldehyde is also produced as a by-product. In this study, the conversion of methanol and the product selectivities were calculated using the data obtained from gas chromatography.

Experimental results showed that methanol conversion was increased by increasing reaction temperature from 120°C to 220°C. Also, increasing the amount of nafion charged to the reactor resulted in higher conversion values of methanol (Figure 1). When 1 g of nafion is used, 40 % of methanol is converted to the products at 220°C. Although this conversion value does not seem to be very high, it should be noted that the space time in

the reactor was only 1.35 s.g/cm³ (measured at room temperature) and the surface area of the catalyst was around 0.02 m²/g. Besides, no catalyst activity loss and coke formation was observed during the reaction. Each

set was completed in 8 hours and it was not observed any decrease in catalytic activity of catalyst during this period. There was not observed any coke formation on the surface of the used catalyst during 8 hr period.

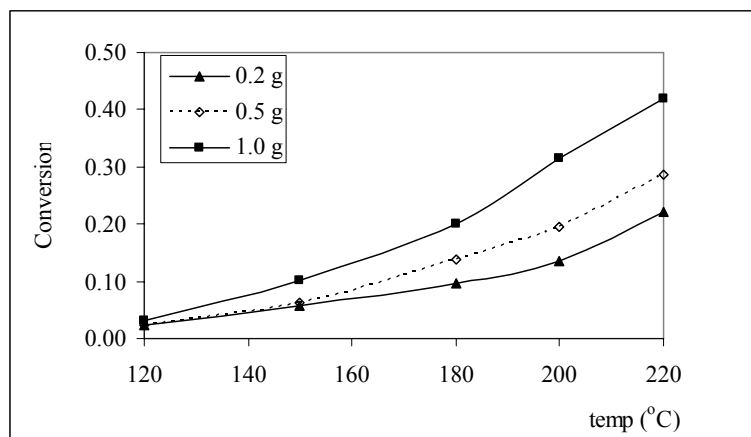
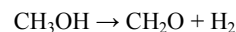


Figure1. Conversion of methanol by using nafion catalyst at different amounts, (Methanol mole fraction : 0.48)

Since nafion is in the form of millimeter sized beads, negligible pressure drop was observed when the amount of catalyst charged to the reactor was increased. Therefore, its usage in fixed bed reactors is highly promising considering the operating conditions.

Heteropolyacid catalysts show high activity in alcohol dehydration reactions [8]. Major disadvantage of the heteropolyacid catalysts is their high solubility in polar solvents and their fast deactivation. However, nafion is insoluble in alcohol so it can also be used easily in liquid phase reactions. It is also highly stable. According to these results, further increase in methanol conversion could be achieved by increasing the space time in the reactor.

According to the experimental results, methanol was converted mainly to DME. The second product which was produced as a result of dehydrogenation of methanol is formaldehyde.



The selectivity of DME was increased with an increase in temperature (Figure 2), whereas the selectivity of formaldehyde was decreased with an increase in temperature (Figure 3). Results showed that high purity DME were be obtained at temperatures higher than 160°C.

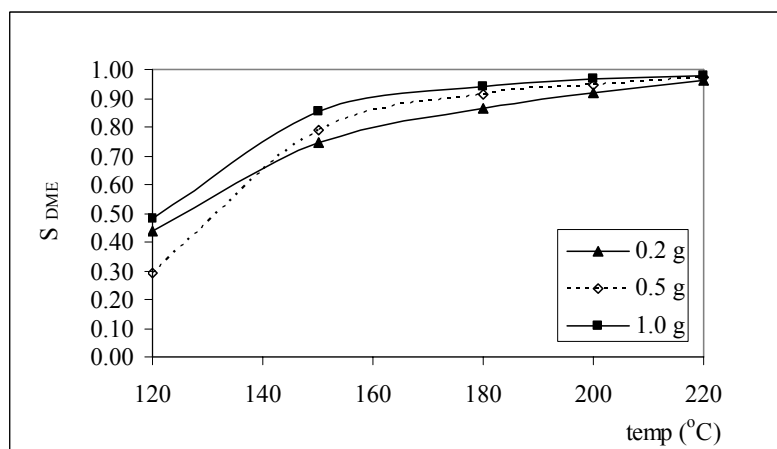


Figure 2. Variation in DME selectivity using different amounts of nafion, (Methanol mole fraction : 0.48)

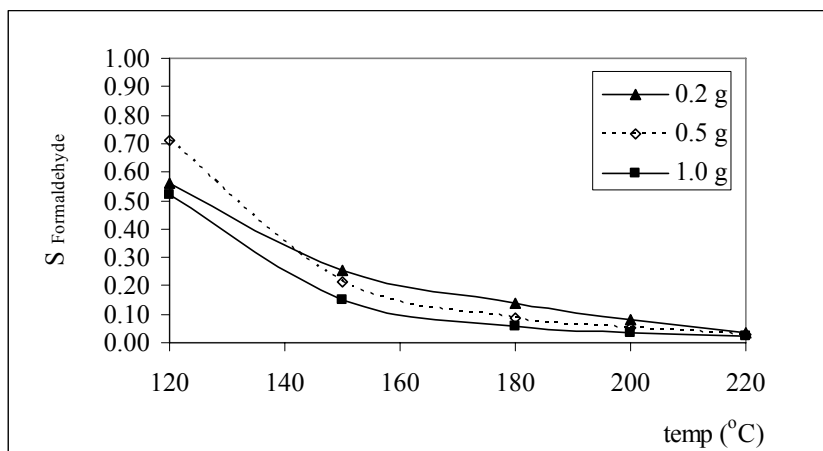


Figure 3. Variation in Formaldehyde selectivity using different amounts of nafion, (Methanol mole fraction : 0.48)

Increasing the amount of catalyst have little effect on the product selectivities. However, space time greatly effects the yield of DME, especially at high temperatures (Figure 4). The yield values presented in this paper were calculated by multiplying the conversion of methanol with selectivity of each product.

For example at 220°C, DME yield increased from 0.20 to 0.40 by increasing the amount of nafion charged to the reactor from 0.2 g to 1.0 g.

These results show that nafion can be an alternative catalyst in the production of DME from methanol.

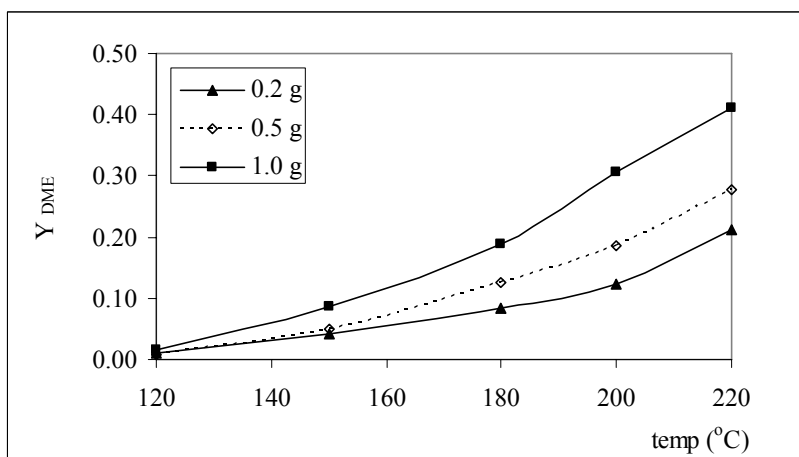


Figure 4. Variation in DME yield over different amounts of nafion, (Methanol mole fraction : 0.48)

4. CONCLUSIONS

Dimethylether is an attractive transportation fuel alternate. In spite of its very low surface area, nafion showed remarkable activity in vapor phase methanol dehydration reaction to produce dimethylether. Besides DME, formaldehyde formation was also observed. An increase in temperature caused an increase in DME selectivity, reaching to about one at temperatures over 200 °C. Results of this work proved that nafion was a highly attractive catalyst for the synthesis of DME from methanol.

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