

# **Conversion of Synthesis Gas to Higher Ethers and Other Oxygenates**

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## **Synthesis of Higher Ethers from Syngas using a Single-Step Liquid Phase Process**

The objective of this research is to develop improved transportation fuels by producing higher ethers and oxygenates for use as additives and blending agents in reformulated gasolines and ultra clean diesel fuels. The addition of oxygenates to gasoline and diesel fuels raises combustion temperatures, improves engine efficiencies, and causes the fuel to burn more cleanly, resulting in lower levels of carbon monoxide and unburned hydrocarbons in the exhaust stream. Ethers are the favored oxygen-containing additives for reformulated gasoline since they have high octane numbers and burn cleanly. Using higher ethers as fuel additives would help achieve the goal of adding oxygenates with lower vapor pressures and lower water solubilities to the fuels while simultaneously increasing the energy density of the added oxygenate.

### **Single-Step Liquid Phase Process**

The focus of this research is to develop a single-step, liquid phase process to produce higher ethers from synthesis gas. The conventional method of producing ethers is first to produce methanol from synthesis gas and then to convert the methanol to an ether. For example, this process is typically used to produce dimethyl ether (DME) from methanol by either a gas or a liquid phase reaction (Snamprogetti; Peng et al., 1998; Sofianos and Scurrall, 1991; Espino and Pletzke, 1973). The conversion of syngas to methanol can be increased by removing, either chemically or physically, the alcohol as it is formed, because this removal lowers the thermodynamic constraints and promotes syngas conversion (Wender, 1996). A single-step, liquid phase DME synthesis reaction has been developed that converts DME directly from synthesis gas using a bifunctional catalyst that promotes methanol synthesis and methanol dehydration for forming DME (Lewnard et al., 1990). Performing this single-step reaction in a liquid phase environment offers the advantage of heat dissipation, thereby allowing a lower reaction temperature to be maintained. The liquid phase reaction results in less catalyst deactivation and longer catalyst lifetime (Brown et al., 1991)

The objective of this research is to develop a catalytic reaction system to produce higher ethers from synthesis gas and olefins using a single-step liquid phase reaction. In this system, as methanol is produced from syngas, the methanol would react with olefins to produce higher ethers. Diethers could also be synthesized from diolefins. One study (Kazi et al., 1995) has been found that has etherified methanol in a single step reaction for the synthesis of higher ethers. A dual catalyst bed was used with Pd/SiO<sub>2</sub> as the methanol synthesis catalyst and a zeolite as an etherification catalyst. The yield of ether from this reaction, which was operated at 175 °C and 7 atm, was very low. This result was most likely caused by the choice of catalyst. Not only is Pd/SiO<sub>2</sub> a methanol synthesis catalyst but it also serves as an effective hydrogenation catalyst for the added olefin, in this case isobutylene. The work that is currently underway will use a CuO/ZnO on alumina methanol synthesis catalyst and dry Amberlyst 15 as the etherification catalyst at reaction temperatures ranging from 60 to 100 °C.

### **Current Work: Proof of Concept**

A comprehensive literature study has been performed to determine the current state of the literature for the single-step synthesis reactions of high ethers from the reaction of syngas and olefins. The patent literature concerning DME formation and the production of higher ethers and the article by Kazi et al. (1995) indicate the feasibility of developing the process. For the initial studies, the study was divided into two parts: the first part was an analysis of the ether production from the reaction of C<sub>6</sub> and C<sub>8</sub> olefins with alcohols which is described in this report; and the second part is single step process where both methanol and ether synthesis reactions are performed simultaneously. The work described herein evaluated the degree of reactivity of C<sub>6</sub> and C<sub>8</sub> olefins with methanol and the selectivity for production of higher ethers. The initial parametric conditions were selected on the basis of the conditions expected to be encountered from the methanol synthesis reaction.

### **Experimental**

A series of four reactions were performed to determine the efficacy of ether production from the reactions of olefins with methanol. Those reactions were thermal with olefin only; thermal with olefin and methanol; catalytic with olefin only; and catalytic with olefin and methanol. The first three sets of reactions were conducted to establish baseline reactivity of the

system without methanol. The reactions were performed using a 25-cm<sup>3</sup> stainless steel tubular reactor, which was immersed and agitated at 100 cpm in a temperature controlled sand bath. The reactions were performed at temperatures of 60 to 150 °C and reaction times from 15 min to 24 hr using a pressure of 200 psig H<sub>2</sub>. One experiment was performed at an elevated pressure of 800 psig H<sub>2</sub>.

**Materials.** The olefins used in this study were straight-chain  $\alpha$ -olefins, 1-hexene, 1-heptene, and 1-octene, and the branched olefins, 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene, 2,4,4-trimethyl-1-pentene, and 2,4,4-trimethyl-2-pentene. The reactions with the  $\alpha$ -olefins were conducted at higher temperatures of 100 to 150 °C while the reactions with the branched olefins were conducted at temperatures ranging from 60 to 100 °C with most of the experiments being conducted at 70 °C. Reactions were initially performed at a 2:1 ratio of olefin to methanol and then the ratio was changed to a 1:8 ratio of olefin to methanol so that an excess of methanol would be present in the reactor. All of the olefins were obtained from Sigma Aldrich Chemical Co. Methanol was obtained from Fisher Scientific Co.

The catalyst used in the reactions was dry Amberlyst 15 and was charged to the reactor at 10 weight percent of the total charge. Catalyst studies were conducted in which the dry Amberlyst 15 catalyst was compared to wet Amberlyst and to crushed and extrudate HZSM-5. Only the dry Amberlyst showed any reactivity and, hence, was used for the rest of the experiments. Both dry and wet Amberlyst 15 were obtained from Sigma-Aldrich Chemical Co. and the HZSM-5 was obtained from United Catalysts, Inc. Additional reactions using 2,3-dimethyl-1-butene and 2,4,4-trimethyl-1-pentene were performed in which the amount of dry Amberlyst 15 was doubled to 20 weight percent and tripled to 30 weight percent of the total charge; the Amberlyst was also crushed and charged at 10 weight percent.

**Analysis.** Reaction products were analyzed by gas chromatography using a Varian model 3400 equipped with J&W Scientific DB-5 25m x 0.32mm I.D. with 0.52  $\mu$  thickness. The injector was maintained at 200 °C and flame ionization detector was maintained at 210 °C. The initial column temperature was 50 °C and was kept at that temperature. The internal standard used was isooctane. Response factors were obtained for all available reactants and products. Response factors for those products, which were not commercially available, were estimated by obtaining the response factors from structurally similar available compounds.

## **Results**

**Straight Chain Olefins.** For the produced ethers to be acceptable additives in diesel fuel, the ethers must have sufficient carbon chain length to boil in the range of diesel fuel in order to maintain an acceptable boiling point range. From an environmental perspective, the ethers should have low water solubility and low vapor pressure. The ethers selected to be produced were in the C<sub>7</sub> to C<sub>10</sub> range.

The initial experimental work focused on determining the reactivity and selectivity of straight-chain olefins when reacted with methanol using dry Amberlyst 15 catalyst. The reaction sets performed were thermal reaction conditions with olefin only, catalytic reaction with olefin only, and thermal and catalytic reactions with olefins and methanol. The reactions using 1-hexene, 1-heptene, and 1-octene, performed at 100 and 150 °C, showed no reactivity under thermal with or without methanol as shown in Table 1a and 1b. Rearrangement of the olefins was observed in the presence of a catalyst regardless of whether methanol was present. While in the presence of methanol, a small amount of higher boiling material was an observed product.

**Branched Olefins.** The next phase of the experimental work involved reactions of branched C<sub>6</sub> and C<sub>8</sub> olefins, 2,3-dimethyl-1-butene and 2,4,4-trimethyl-1-pentene, with methanol using 10 weight percent dry Amberlyst. Baseline reactions of the two branched olefins were performed at 80 °C to determine the amount of rearrangement that occurred under thermal and catalytic conditions with the 1- and 2-pentene isomers of 2,4,4-trimethylpentene and 1- and 2-butene isomers of 2,3-dimethylbutene. In the catalytic reaction, 1-pentene rearranged forming 22% 2-pentene while 2-pentene rearranged yielding 80% 1-pentene. After reacting for 2 hr, the product distributions from both isomers were similar. Similar results were obtained from the C<sub>6</sub> olefin. After 2 hr catalytic reaction regardless of the initial isomer, the reaction composition was similar yielding ~ 90% 2,3-dimethyl-2-butene. When the 2-pentene isomer was reacted in the presence of methanol, 3 mole percent of the ether, 2-methoxy-trimethylpentane was formed while the 1-pentene isomer yielded 7.3 mole percent. Similarly, the reaction with 2-butene yielded 11 mole percent 2-methoxy-2,3-dimethylbutane while the 1-butene isomer yielded 27 mole percent. In both cases the reaction of the 1-olefin isomer with methanol was favored.

Hence, once the 2-butene or 2-pentene isomer was formed, the reaction proceeded very slowly yielding much less ether than the 1-butene or 1-pentene in an equivalent amount of time.

The effect of reaction temperature and time on the production of ether from 2, 4, 4-trimethyl-1-pentene and 2,3-dimethyl-1-butene was evaluated. The production of ether, 2-methoxy-2, 4, 4-trimethylpentane, from 2, 4, 4-trimethyl-1-pentene in reactions performed at 70, 80, and 100 °C is shown in Table 3. The reactions performed at 70 °C from 1 to 24 hrs showed an increase in ether production from 2.5 to 9.0 mole percent. The reactions performed at 80 °C and 100 °C produced similar amounts of ether as the 70 °C reaction at shorter reaction times. The amount of rearrangement of the 1-pentene isomer to the 2-pentene isomer increased with both temperature and reaction time, which in effect reduced the amount of ether formed since the 2-pentene isomer is less reactive than the 1-pentene. Ether production from 2,3-dimethyl-1-butene after 2 hr reactions at 60, 70, 80, and 100 °C showed little effect of temperature between 70 and 100 °C, with all reactions yielding ~27 to 30 mole percent ether (Table 4). However a substantial increase in ether production from 16.5 to 27 mole percent was observed between 60 and 70 °C. The effect of longer reaction times of 4, 6, 8, and 24 hr was minimal on ether production, which ranged from 27 to 36.5 mole percent. In all of these reactions the amount of rearrangement to the 2,3-dimethyl-2-butene was substantial yielding nearly 60% of 2-butene isomer after 6 hr as presented in Table 5.

Since this experiment is the second part of single step reaction process, the reaction conditions were initially chosen to simulate as closely as possible the conditions expected to be present in the synthesis of methanol from synthesis gas. The reactions discussed heretofore used a 2:1 olefin to methanol ratio, which was selected because the methanol would most likely be reacted as soon as it is formed. The amount of ether produced was less than 30%. Several parametric factors may have affected the conversion of the olefin to ether. The parameters tested were the effect of olefin to methanol ratio, of reaction pressure, and of increased catalyst loading. Table 6 shows the effect of changing the olefin to methanol ratio from 2:1 to 1:8 for 2 hr reactions of 2,3-dimethyl-1-butene and 1 and 2 hr reactions of 2,4,4-trimethyl-1-pentene. In the 1-butene reaction at a 1:8 ratio an additional product was formed and is currently being analyzed. The amount of ether formed in the 1:8 was nearly double that obtained in the reaction with 2:1 ratio. In the 1-pentene reaction, the increased ratio had the effect of more than tripling the ether

formation, indicating that the reaction had been starved for the methanol reactant. Increasing the pressure from 200 to 800 psig in the reactor that contained a 1:8 ratio of olefin to methanol, which was reacted for 2 hr, did not affect the amount of ether that was produced as shown in Table 7.

The effect of the catalyst loading on the conversion of 2,3-dimethyl-1-butene and 2,4,4-trimethyl-1-pentene is given in Table 8. The crushed and single loading were both at 10 weight percent of total reactor charge while the double loading was 20 weight percent and the triple was 30 weight percent of total loading. The catalyst loading affected both olefins; however, the 1-butene was affected more than the 1-pentene. The crushed, double and triple loading of catalyst all increased ether production compared to the single loading. The ether production ranges from 48 weight percent for the single loading to 64 weight percent for triple loading. Both the double and triple loading of catalyst increased the ether production from 2,4,4-trimethyl-1-pentene. The increase was not as dramatic as for the C<sub>6</sub> olefin. Therefore, increased ether production was obtained by increasing the amount of methanol available for the reaction and by increasing the number of active catalyst sites available to the olefins for the reaction.

### **Conclusions and Future Work**

The feasibility of producing higher ethers from C<sub>6</sub> and C<sub>8</sub> olefins has been demonstrated at temperatures below 80 °C. Increasing the number of catalyst sites and the amount of methanol available for the reaction raised the ether production to reasonable levels. The branched olefins have a greater reactivity than the straight chain olefins and are better candidates for producing higher ethers as diesel fuel additives. The ethers can be produced at reaction conditions that are favored for the single step reaction of higher ethers from synthesis gas. The next step in the experimentation is to determine the effect of reacting mixtures of olefins and alcohols on the types and quantity of products produced. Reactions will be performed in the liquid phase using an inert solvent like decalin to dissipate the heat and promote mass transfer.

Liquid phase reaction in which methanol synthesized from synthesis gas is immediately reacted with branched olefins to form higher ethers will be performed in a continuous reactor. A continuous reactor will be built that is similar in design to the super critical continuous reactor described in the next section. Appropriate modifications will be made to outfit the reactor for the

reactant feeds, reaction conditions and separation requirements of the single step, liquid phase synthesis of higher ethers from synthesis gas.

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**Table 1a. Thermal and Catalytic Reactions of  $\alpha$ -Olefins and Methanol**

Reaction time = 2 hours

Pressure: 200 psig H<sub>2</sub>

Catalyst: 10 wt%

Reactant	Catalyst	Temperature	Products
Methanol	Amberlyst 15 dry	150 °C	no reaction
1-hexene	none	150 °C	no reaction
1-heptene	none	150 °C	no reaction
1-octene	none	150 °C	no reaction
1-hexene	Amberlyst 15 dry	100 °C	rearrangement
1-heptene	Amberlyst 15 dry	150 °C	rearrangement
1-octene	Amberlyst 15 dry	150 °C	rearrangement

**Table 1b. Thermal and Catalytic Reactions of  $\alpha$ -Olefins with Methanol**

Reaction time: 2 hours

Molar ratio of  $\alpha$ -olefin to methanol: 2:1Pressure: 200 psig H<sub>2</sub>

Catalyst: 10 wt%

Reactant	Catalyst	Temperature	Products
1-hexene : methanol	none	100 °C	no reaction
1-heptene : methanol	none	150 °C	no reaction
1-octene : methanol	none	150 °C	no reaction
1-hexene : methanol	Amberlyst 15 dry	100 °C	no reaction
1-heptene : methanol	Amberlyst 15 dry	100 °C	no reaction
1-heptene : methanol	Amberlyst 15 dry	150 °C	rearrangement and 7% of a higher boiling product
1-octene : methanol	Amberlyst 15 dry	150 °C	rearrangement and ~3% high boiling products

**Table 2. Thermal and Catalytic Reactions of Branched Olefins**

Reaction time: 2 hours

Pressure: 200 psig H<sub>2</sub>

Catalyst: 10wt% Amberlyst 15 dry

Temperature: 80 EC; \*\* 70 EC

Molar ratio of olefin to methanol: 2:1

Reactions of C <sub>8</sub> and C <sub>6</sub> Olefins	Mole Percent of Products (%)			
	Thermal without Methanol	Catalytic without Methanol	Thermal with Methanol	Catalytic with Methanol
<b>Starting Material: 2,4,4-trimethyl-1-pentene</b>				
2,4,4-trimethyl-1-pentene	98	78	98.4	85
2,4,4-trimethyl-2-pentene	2.0	22	0.01	8.0
2-methoxy-2,4,4-trimethylpentane				7.3
<b>Starting Material: 2,4,4-trimethyl-2-pentene</b>				
2,4,4-trimethyl-1-pentene	aborted	80	0.3	5.1**
2,4,4-trimethyl-2-pentene		20	99.2	92
2-methoxy-2,4,4-trimethylpentane				3.0
<b>Starting Material: 2,3-dimethyl-1-butene</b>				
2,3-dimethyl-1-butene	82	9.1	99.8	8.5
2,3-dimethyl-2-butene	17	89	0.06	63
2-hydroxy-2,3-dimethylbutane				1.5
2-methoxy-2,3-dimethylbutane				27
<b>Starting Material: 2,3-dimethyl-2-butene</b>				
2,3-dimethyl-1-butene	<1	6.0	0.01	3.1**
2,3-dimethyl-2-butene	98	92	97.8	84
2-hydroxy-2,3-dimethylbutane				2.6
2-methoxy-2,3-dimethylbutane				11

**Table 3. Effect of Reaction Time on Reactions of 2,4,4-Trimethyl-1-pentene with Methanol at 70, 80, and 100 °C**

Molar ratio of 2,4,4-trimethyl-1-pentene to methanol: 2:1

Pressure: 200 psig H<sub>2</sub>

Catalyst: 10 wt% Amberlyst 15 dry

Reaction at 70 °C	Mole Percent of Products at Different Reaction Times				
Reaction Time (hours)	1	2	4	8	24
2,4,4-trimethyl-1-pentene	96	92	87	82	70
2,4,4-trimethyl-2-pentene	2.2	3.4	5.4	9.2	20
2-methoxy-2,4,4-trimethylpentane	2.5	5.1	7.5	9.0	9.6

Reaction at 80 °C	Mole Percent of Products at Different Reaction Times				
Reaction Time (hours)	0.25	0.5	1	2	4
2,4,4-trimethyl-1-pentene	93	91	84	85	77
2,4,4-trimethyl-2-pentene	3.3	4.3	8.5	8.0	16
2-methoxy-2,4,4-trimethylpentane	3.8	5.0	7.8	7.3	7.6

Reaction at 100 °C	Mole Percent of Products at Different Reaction Times			
Reaction Time (hours)	0.25	0.5	1	2
2,4,4-trimethyl-1-pentene	80	76	76	75
2,4,4-trimethyl-2-pentene	14	18	18	15
2-methoxy-2,4,4-trimethylpentane	5.4	5.6	6.2	5.1

**Table 4. Effect of Temperature on the Reaction of 2,3-Dimethyl-1-butene with Methanol**

Molar ratio of 2,3-dimethyl-1-butene to methanol: 2:1

Pressure: 200 psig H<sub>2</sub>

Catalyst: 10 wt% Amberlyst 15 dry

Reaction time: 2 hours

Temperatures ( °C )	Mole Percent of Products for Reactions at Different Temperatures			
	60 °C	70 °C	80 °C	100 °C
2,3-dimethyl-1-butene	60.5	14.2	8.5	6.8
2,3-dimethyl-2-butene	18.5	53	63	61
2-hydroxy-2,3-dimethylbutane	4.3	1.2	<1	2.4
2-methoxy-2,3-dimethylbutane	16.5	32	27	30

**Table 5. Effect of Reaction Time on Reactions of 2,3-Dimethyl-1-butene with Methanol at 70 °C**

Molar ratio of 2,3-dimethyl-1-butene to methanol: 2:1

Pressure: 200 psig H<sub>2</sub>

Catalyst: 10 wt% Amberlyst 15 dry

Temperature: 70 °C

Reaction Time (hours)	Mole Percent (%) of Products for Reactions at Different Reaction Times				
	2	4	6	8	24
2,3-dimethyl-1-butene	14.2	6.4	6.3	4.9	6.8
2,3-dimethyl-2-butene	53	57.5	59.5	57.5	59
2-hydroxy-2,3-dimethylbutane	1.2	1.3	0.8	0.87	4.5
2-methoxy-2,3-dimethylbutane	32	34	33.5	36.5	29.5

**Table 6. Effect of Olefin to Methanol Ratio at 70 °C on Ether Production from 2,3-Dimethyl-1-butene and 2,4,4-Trimethyl-1-pentene**

Pressure: 200 psig H<sub>2</sub>

Catalyst: 10 wt % Amberlyst 15 dry

Reaction at 70 °C	Mole Percent of Products at Different Times and Ratios			
Reaction Time	1 hour		2 hour	
olefin to methanol molar ratio	2:1	1:8	2:1	1:8
<b>2,3-dimethyl-1-butene reaction</b>				
2,3-dimethyl-1-butene			14.2	5.2
2,3-dimethyl-2-butene			53	31.5
unknown				11
2-hydroxy-2,3-dimethylbutane			1.2	3.5
2-methoxy-2,3-dimethylbutane			32	48.5
<b>2,4,4-trimethyl-1-pentene reaction</b>				
2,4,4-trimethyl-1-pentene	96	82	92	73
2,4,4-trimethyl-2-pentene	2.2	5.3	3.4	9.2
2-methoxy-2,4,4-trimethylpentane	2.5	13	5.1	18

**Table 7. Effect of Pressure on Ether Production from 2,3-Dimethyl-1-butene**

Catalyst: 10 wt % Amberlyst 15 dry

Temperature: 70 °C

Reaction Time: 2 hour

Ratio: 1:8 ether to methanol ratio

Reaction at 70 °C	Mole Percent of Products at Different Pressures	
Pressure	200 psig	800 psig
2,3-dimethyl-1-butene	4.9	7.2
2,3-dimethyl-2-butene	59	59
2-hydroxy-2,3-dimethylbutane	0.4	1.2
2-methoxy-2,3-dimethylbutane	35	33

**Table 8. Effect of Catalyst Loading on Reactions of C<sub>6</sub> and C<sub>8</sub> Olefins with Methanol at 70 °C**

Molar ratio of olefin to methanol: 1:8

Pressure: 200 psig H<sub>2</sub>

Temperature: 70 °C

Reaction Time: 2 hours

Catalyst: Amberlyst 15 dry; 10wt% for crushed and single; 20 wt% for double; and 30wt% for triple

Products	Mole Percent of Products for Reactions with Different Catalyst Loading (%)			
	Crushed	Single	Double	Triple
<b>Reaction of C<sub>6</sub> Olefin with Methanol</b>				
2,3-dimethyl-1-butene	2.4	5.2	2.0	1.0
2,3-dimethyl-2-butene	24	31.5	26	26
unknown	22	11	11.5	2.9
2-hydroxy-2,3-dimethylbutane	2.5	3.5	2.3	5.6
2-methoxy-2,3-dimethylbutane	54	48.5	58.5	64
<b>Reaction of C<sub>8</sub> Olefin with Methanol</b>				
2,4,4-trimethyl-1-pentene	66	73	58	58
2,4,4-trimethyl-2-pentene	7.9	9.2	13	15
Unknown	10.2	0.6	7.6	6.2
2-methoxy-2,4,4-trimethylpentane	16	17	22	21