

Dehydration of C₅–C₁₂ Linear 1-Alcohols over η -Alumina to Fuel Ethers

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Naphtha from low temperature Fischer–Tropsch (LTFT) synthesis is rich in *n*-paraffins, but it also contains alcohols and olefins. These alcohols and olefins can be converted into linear fuel ethers and olefin dimers to improve the overall yield and quality of distillate from LTFT refining. The reaction network was studied for the conversion of 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol, and 1-dodecanol over an η -alumina catalyst in a fixed bed flow reactor at 250–350 °C, 0–4 MPa, and WHSV of 1–4 h^{−1}. The main products were the corresponding linear ethers and linear α -olefins. The highest ether yield (54%) was obtained at 300 °C, 1 MPa, and WHSV of 1 h^{−1} (unoptimized conditions). The main side-products were aldehydes and olefin dimers. Dehydration occurred predominantly on Lewis acid sites, with acid-catalyzed side-reactions taking place over Brønsted acid sites and dehydrogenation taking place over basic and/or redox sites. Dehydration to produce 2-olefins was *cis*-selective and occurred mainly over Lewis acid sites by dehydration–hydration–dehydration. GC-FID response factors for di-*n*-butyl ether and heavier linear ethers were determined experimentally. The GC-FID response factors were expressed in terms of the equivalent carbon number (ECN) concept as an ECN of -0.6 ± 0.1 for the linear ether oxygen atom, and this value could be mechanistically justified (literature ECN is -1.0).

Introduction

The refining of low temperature Fischer–Tropsch (LTFT) syncrude from gas-to-liquids (GTL) facilities is becoming increasingly important for the production of transportation fuels.¹ It is current commercial practice to hydroprocess the LTFT syncrude, mainly by hydrocracking, to produce paraffinic naphtha, kerosene, and distillate fractions.^{2,3} The naphtha is an excellent feed for steam cracking,⁴ the kerosene can be blended into jet fuel,⁵ and the distillate can be employed as a high cetane number (>70) diesel fuel blend component.⁶ The hydroprocessing-only approach has been challenged, by showing that a more complex refinery design that produces final products has a better return on investment.⁷ This is understandable, because the capital cost of the refinery portion of a GTL complex is only 10–20%,⁸ yet, it is the refinery design that determines the value of the final products. The quality and quantity of products from the refining operation are important in determining the overall economic benefit. To increase the efficiency of LTFT refining, it is therefore important to target volume and/or quality improvements, rather than focusing on refinery capital cost reduction.

The present study is concerned with the refining of oxygenates in LTFT syncrude. Alcohols (mainly 1-alcohols) constitute around 90% of the oxygenates present in LTFT naphtha and distillate, making it the dominate oxygenate class. The alcohol concentration depends on the operating conditions and the type of Fischer–Tropsch catalyst being used, with the naphtha and distillate from iron-based LTFT synthesis containing 6–7% oxygenates on a carbon atom basis.⁹ The efficiency of LTFT refining can be improved if some of the oxygen, which is presently being lost during hydroprocessing, can be retained in the final product. Ideally, this should be accomplished without a loss in product quality, or the need for complex and costly refining equipment.

It has been shown that C₃ and heavier alcohols can be recovered and purified from the Fischer–Tropsch aqueous product and blended directly into diesel fuel.¹⁰ Separation of the alcohols from the Fischer–Tropsch organic product is more difficult, because the matrix hydrocarbons are coboiling with the alcohols. This problem can be overcome by converting the alcohols into fuel ethers. The linear C₉ and heavier ethers, such as di-*n*-pentyl ether (DNPE) and methyl octyl ether (MOE), provide a good compromise between blending cetane number and blending cold flow properties.¹¹ It appears that the conversion of LTFT 1-alcohols into linear ethers can be used to overcome alcohol separation problems, as well as to improve refining efficiency by increasing the product quality.

Much of the previous work on linear fuel ether synthesis was conducted in the liquid phase over ion-exchange resin catalysts.^{12–19} Initial reaction rates were typically around 0.01–0.03 mol h^{−1} per gram catalyst at 150 °C, and with some reaction systems linear ether yields of better than 90% could be achieved. However, it is known that etherification on acidic resin catalysts is inhibited by water,¹⁷ as well as by some of the oxygenates typically found in Fischer–Tropsch syncrude.²⁰ Inhibition by water, which is a reaction product from the alcohol etherification reaction, can be reduced by continuous water removal during reaction.¹⁶ This approach is unfortunately not practical for removing the oxygenates that are also present in the LTFT syncrude (carbonyls and carboxylic acids)⁹ and that are coboiling with the alcohols in the reaction mixture. Removing only the water may not be sufficient to prevent inhibition of the etherification reaction over acidic resin catalysts in the presence of the range of LTFT oxygenates.

Our work has consequently focused on alumina (although we took note of the interesting recent work²¹ on zeolite catalysts). η -Alumina is a robust catalyst, and alcohol dehydration is not affected by the nonalcohol oxygenate species that are present in LTFT syncrude.^{22,23} It has also been pointed out

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that η -alumina is more active and stable than γ -alumina for the dehydration of alcohols to ethers.²⁴

Experimental Section

Materials. The linear 1-alcohols were all obtained from Aldrich and used without further purification: 1-pentanol (99%), 1-hexanol (98%), 1-heptanol (98%), 1-octanol (99%), 1-nonanol (98%), 1-decanol (99%), and 1-dodecanol (98%). Flame ionization detector response factors for the linear ethers were determined using di-*n*-propyl ether (99%, 1-propoxypropane), di-*n*-butyl ether (99.3%, 1-butoxybutane), di-*n*-pentyl ether (98.5%, 1-pentoxypentane), di-*n*-hexyl ether (97%, 1-hexoxyhexane), and di-*n*-octyl ether (99%, octoxyoctane). In these experiments, *n*-heptane (99%) was used as standard. The di-*n*-pentyl ether was obtained from Fluka, while the *n*-heptane and the other linear ethers were all obtained from Aldrich. The *n*-heptane and linear ethers were dried over sodium for 24 h before use.

Commercially available η -alumina (Syndol), in the form of 4.5×4.5 mm extrudates, was employed for all of the dehydration experiments. The alumina contained about 0.9% silica. Metal impurities (Na, Mg, K, Ca, Ni, and Mo) in the catalyst were less than 1 mg g⁻¹. The catalyst had a BET surface area of 192 m² g⁻¹ and a pore volume of 0.44 cm³ g⁻¹.

Equipment and Procedure. The alcohol dehydration experiments were performed in an automated fixed bed reactor system. The uncrushed η -alumina catalyst (10 g) was diluted with carborundum (20 g) with an average particle size of 0.7 mm to minimize hydrodynamic effects. This mixture was loaded into a 316 stainless steel reactor, 600 mm in length with an internal diameter of 15 mm and centrally placed 3 mm (1/8 in.) thermowell. The rest of the reactor was filled with carborundum in such a way that the catalyst bed, with a packed length of 120–130 mm, was in the middle of the reactor. The temperature in the reactor was controlled by four independent and equally spaced resistance heaters. Pressure was controlled by a control valve, although most of the experiments were conducted at near atmospheric pressure with the control valve in the full-open position.

Fresh η -alumina catalyst was loaded for each experiment with a different alcohol feed. As a safety precaution, the reactor was heated under constant nitrogen flow (10 L h⁻¹) to displace any oxygen (from air) that might have been present. Once the reactor reached a temperature of 250 °C, the nitrogen flow was stopped and replaced by the alcohol feed (0.26 mol h⁻¹). The reactor was kept at each reaction condition for a period of 24–48 h, during which time samples were collected for analysis. During the course of an experimental run with a specific feed, conversion and selectivity data at different conditions were obtained by a stepwise increase of the temperature. At the end of each run (typically after 100–120 h), the reactor was returned to the initial operating conditions to check for catalyst deactivation.

The product from the reaction was condensed to produce a two-phase liquid product. For mass balance closure, the total liquid product as well as the off-gas flow rate (that turned out to be negligible) were recorded. Mass balance closure was typically in the order of 95–105%, except for the experiments with 1-pentanol, where evaporative losses resulted in poorer mass balances. Only the organic phase of the liquid product was analyzed, because the partition coefficients of the unconverted alcohols were such that the alcohols preferred the organic phase. For example, a 45:1 partition coefficient between organic and aqueous phases has been reported for 2-methyl-2-butanol.²⁵

Table 1. Experimentally Determined GC-FID Response Factors of Linear Ethers

compound	response factor
di- <i>n</i> -propyl ether	0.695 ± 0.005
di- <i>n</i> -butyl ether	0.803 ± 0.003
di- <i>n</i> -pentyl ether	0.856 ± 0.010
di- <i>n</i> -hexyl ether	0.878 ± 0.007
di- <i>n</i> -octyl ether	0.906 ± 0.008

Table 2. Temperature-Dependent Conversion of Linear 1-Alcohols during Dehydration over η -Alumina in a Fixed Bed Flow Reactor, Near Atmospheric Pressure and at a Flow Rate of 0.026 mol h⁻¹ per gram Catalyst

compound	alcohol conversion (mol %)			deactivation rate (% conv. h ⁻¹)
	250 °C	300 °C	350 °C	
1-pentanol		69 ± 4		
1-hexanol	56 ± 4	75 ± 1	94 ± 2	0.03
1-heptanol	51 ± 1	79 ± 1	93 ± 1	0.05
1-octanol	50 ± 6	80 ± 2	97 ± 1	0.02
1-nonanol	44 ± 1	83 ± 1	93 ± 1	0.01
1-decanol	25 ± 2	46 ± 1	55 ± 1	0.08
1-dodecanol	58 ± 1 ^a	79 ± 3	87 ± 1	<0.01

^a Experiment conducted at 275 °C (not 250 °C) to avoid condensation.

Analyses. The organic products were analyzed using an Agilent 6890N gas chromatograph with flame ionization detector (GC-FID) equipped with a 50 m HP-Pona methyl siloxane column (Agilent 19091S-001). Hydrogen was used as carrier gas, and the temperature program that was employed started at 40 °C for 5 min, whereafter the temperature was increased from 40 to 120 °C at 4 °C min⁻¹ and then from 120 to 300 °C at 20 °C min⁻¹. A hold time of 10 min at 300 °C was included in the temperature program that was used for experiments conducted with C₈ and heavier alcohols. To quantify the alcohols and ethers in the reaction product by GC-FID analysis, appropriate GC-FID response factors were employed.

The response factors for the linear ethers were experimentally determined (Table 1) by preparing samples of each ether in *n*-heptane (in triplicate) and analyzing these calibration samples with a gas chromatograph equipped with a flame ionization detector. The response factors (RF) were calculated from the ratio of the *n*-heptane to ether peak areas in the chromatograms that were compared to the known quantities of each compound in the various calibration samples (eq 1).²⁶ The *n*-heptane (RF = 1.00) was used as the reference compound.

$$\text{RF}_{\text{ether}} = [(\text{area})_{\text{ether}}/(\text{area})_{\text{C}_7}] \times [(\text{mass})_{\text{C}_7}/(\text{mass})_{\text{ether}}] \quad (1)$$

Results

Alcohol Conversion. The conversion of the C₅–C₁₂ linear 1-alcohols was experimentally determined at three temperatures (Table 2). The operating conditions were selected to ensure that the feed was in the gas phase. At the end of each experimental run, the data point at the initial reaction conditions was repeated to check for catalyst deactivation.

Because of problems with evaporative losses during the 1-pentanol dehydration experiments, most of the conversion data had to be discarded.

The results obtained during 1-decanol dehydration were anomalous. The conversion was much lower than anticipated, and the highest rate of catalyst deactivation was found during this run. Despite the high purity (99%) of the starting material, the feed seemingly contained one or more compounds in low concentration that deactivated the alumina catalyst. Analysis of

Table 3. Product Selectivity during Alcohol Dehydration over η -Alumina in a Fixed Bed Flow Reactor at 250 °C, Near Atmospheric Pressure and at a Flow Rate of 0.026 mol h⁻¹ per gram Catalyst

compound	selectivity (mol %)			
	linear ether	olefins	aldehyde	other
1-hexanol	61 ± 3	37 ± 3	0.2	2
1-heptanol	71 ± 3	28 ± 2	0.3	1
1-octanol	65 ± 3	32 ± 3	0.4	2
1-nonanol	73 ± 1	26 ± 1	0.1	1
1-decanol	66 ± 3	29 ± 1	1.0	4
1-dodecanol ^a	50 ± 6	48 ± 6	0.2	2

^a Experiment conducted at 275 °C (not 250 °C) to avoid condensation.

Table 4. Product Selectivity during Alcohol Dehydration over η -Alumina in a Fixed Bed Flow Reactor at 300 °C, Near Atmospheric Pressure and at a Flow Rate of 0.026 mol h⁻¹ per gram Catalyst

compound	selectivity (mol %)			
	linear ether	olefins	aldehyde	other
1-pentanol	30 ± 6	69 ± 7	0.8	1
1-hexanol	11 ± 1	87 ± 1	0.6	1
1-heptanol	13 ± 2	86 ± 2	0.5	<1
1-octanol	11 ± 4	88 ± 4	0.4	1
1-nonanol	8 ± 1	91 ± 1	0.3	1
1-decanol	18 ± 2	78 ± 3	1.0	2
1-dodecanol	7 ± 2	92 ± 2	0.2	1

Table 5. Product Selectivity during Alcohol Dehydration over η -Alumina in a Fixed Bed Flow Reactor at 350 °C, Near Atmospheric Pressure and at a Flow Rate of 0.026 mol h⁻¹ per gram Catalyst

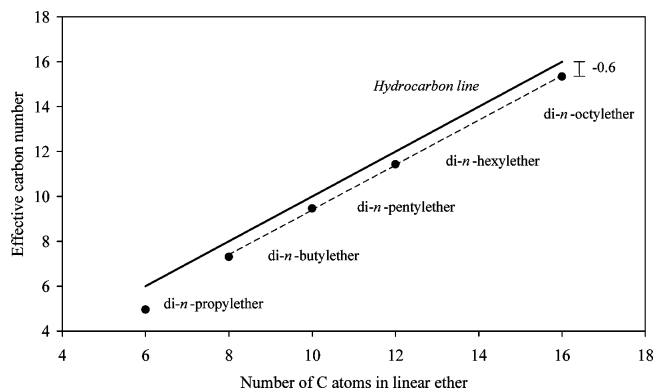
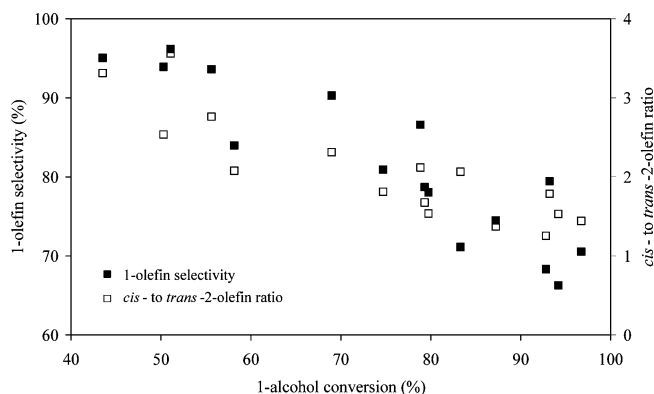
compound	selectivity (mol %)			
	linear ether	olefins	aldehyde	other
1-hexanol	1 ± 1	95 ± 0	2.2	2
1-heptanol	2 ± 1	97 ± 1	1.0	1
1-octanol	1 ± 0	97 ± 0	0.8	1
1-nonanol	2 ± 1	97 ± 1	0.6	1
1-decanol	8 ± 1	88 ± 1	2.0	2
1-dodecanol	4 ± 0	95 ± 0	0.4	1

the feed revealed some decanol isomers, as well as isomers of dodecanol and small quantities of C₁₄ and C₁₆ alcohols. It is speculated that the heavier alcohols may have condensed in the catalyst pores at the lowest operating temperature, causing the anomalous results.

Product Selectivity. The two main products from alcohol dehydration are ethers and olefins (Tables 3–5). Olefin dimers that were produced by subsequent dimerization of the olefins were included in the olefin selectivity. A breakdown of the olefin selectivity is provided separately. The ether selectivity decreased with increase in temperature, while the olefin selectivity increased with increase in temperature.

In all experiments, a small amount of aldehydes was found that was produced by alcohol dehydrogenation. The other side-products were not all individually identified and, among others, included aldol condensation products produced by secondary reactions of the aldehydes.

Olefin Selectivity. Although the aim of the study was to investigate fuel ether production, the results of the experimental work also provided olefin selectivity data (Tables S2–S4 in the Supporting Information). The selectivity to the α -olefin decreased with increasing alcohol conversion (Figure 2), while the selectivity to the other double bond and skeletal isomers increased. In general, little skeletal isomerization was found, and the dominant isomers were the linear 2-olefins. Double bond

**Figure 1.** Effective carbon number plot derived from the experimentally determined response factors of the linear ethers.**Figure 2.** Selectivity to linear α -olefins (■) and *cis*- to *trans*-2-olefin ratio (□) as functions of C₅–C₉ and C₁₂ linear 1-alcohol conversion over η -alumina at 250–350 °C and near atmospheric pressure. The α -olefins selectivity is expressed as the ratio of the α -olefin (1-C_n) to the sum of all of the C_n-olefin isomers.

isomerization to yield the 2-olefin was *cis*-selective at all temperatures studied, although the *cis*- to *trans*-2-olefin ratio decreased with increasing alcohol conversion (Figure 2). Olefin dimerization selectivity remained around 1–2% over the temperature range 250–350 °C and did not display any specific trend.

Effect of Flow Rate. The effect of flow rate on the conversion and selectivity was investigated at 250 °C (275 °C for 1-dodecanol) for some of the alcohols. Rather than operating at a constant molar flow rate of 0.026 mol h⁻¹ per gram catalyst, the flow rate was changed to a weight hourly space velocity (WHSV) of 4 g h⁻¹ per gram catalyst. As expected, the alcohol conversion decreased with an increase in flow rate. The ether selectivity depended on the alcohol conversion (Figure 3), which was in turn affected by the flow rate. However, the side-product selectivity seemed not to be affected by the change in flow rate, with the selectivity to aldehydes and to linear α -olefins on an olefin basis remaining constant (Table S5 in the Supporting Information).

Effect of Pressure. The effect of pressure was investigated as way to increase the ether selectivity during alcohol dehydration over η -alumina using 1-hexanol as feed material. By increasing the pressure, alcohol conversion was suppressed, and the flow rate had to be reduced to compensate for the lower conversion at higher pressure. At 250 °C, 2–4 MPa and a WHSV of 1 h⁻¹ (0.01 mol h⁻¹ per gram of catalyst) conversion of 1-hexanol was 9%, with an ether selectivity of 82%. At these conditions, the feed was in the liquid phase (see Figure S1 in the Supporting Information), and there was little difference in

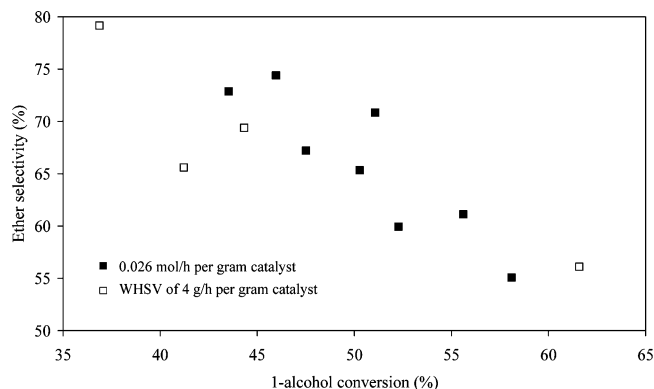


Figure 3. Ether selectivity during the dehydration of 1-alcohols (C_6 – C_8 and C_{12}) over η -alumina at 250–275 °C, near atmospheric pressure, and at 0.026 mol h^{-1} (■) and 4 g h^{-1} (□) per gram of catalyst.

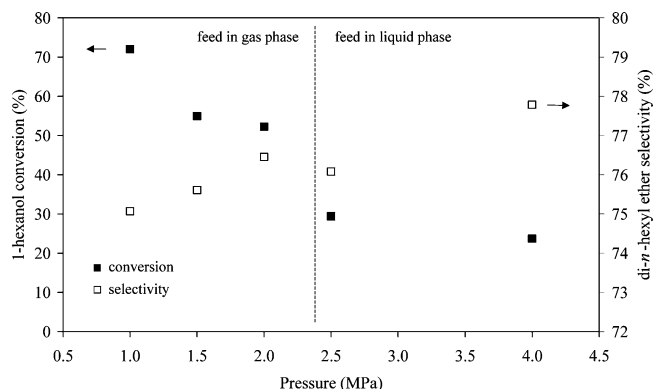


Figure 4. Influence of pressure on 1-hexanol conversion (■) and ether selectivity (□) over η -alumina in a fixed bed flow reactor at 300 °C and WHSV of 1 h^{-1} .

conversion and selectivity profile between reaction at 2 and 4 MPa. Although the increase in ether selectivity was directionally favorable, the alcohol conversion was low, and ether yield at 250 °C and 2–4 MPa (8%) was similar to the ether yield at 250 °C and near atmospheric pressure. It was consequently decided to conduct the rest of the investigation at 300 °C instead.

The alcohol conversion at 300 °C also decreased with an increase in pressure (Figure 4). There was little gain in ether selectivity on increasing the pressure from 1 to 4 MPa, but in comparison to reaction at near atmospheric pressure, there was a considerable gain. For example, near atmospheric pressure and 75% 1-hexanol conversion, the ether selectivity was around 11% (Table 4), but at similar conversion and 1 MPa pressure the ether selectivity was 75% (Figure 4). The ether yield at 300 °C, 1 MPa, and WHSV of 1 h^{-1} was 54% and decreased as the conversion decreased with increasing pressure.

The selectivity to different olefin species was also affected by pressure (Table S6 in the Supporting Information). The most significant influence of increasing pressure was on the selectivity to C_7 and heavier olefins, which increased at the expense of the linear α -olefins that decreased with increasing pressure (Figure 5).

Discussion

GC-FID Response Factors. Unlike aliphatic hydrocarbons, the relative response of aliphatic oxygenates in flame ionization detectors is not directly proportional to their mass.^{27–30} To accurately quantify the reaction products from the present study, which deal with the conversion of linear 1-alcohols to linear

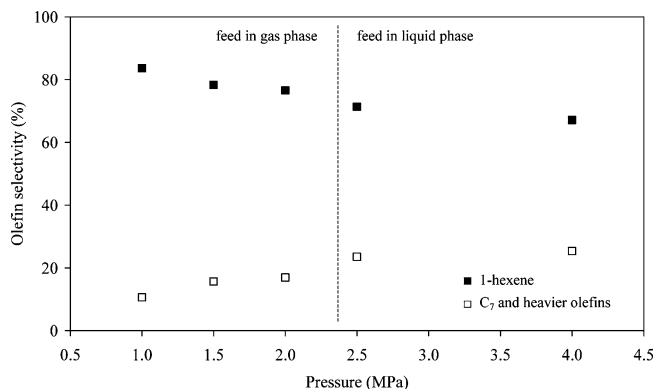


Figure 5. Influence of pressure on linear α -olefin (■) and C_7 and heavier olefin (□) selectivity during 1-hexanol dehydration over η -alumina in a fixed bed flow reactor at 300 °C and WHSV of 1 h^{-1} .

ethers, it was essential to make use of appropriate GC-FID response factors.

It has previously been recognized that within a specific class of oxygenates the relative GC-FID response can be approximated by a linear relationship, using the equivalent carbon number concept. According to this description, the response factor (RF) can be calculated from the molar mass (MM) and effective carbon number (ECN) of a compound relative to that of a known reference compound (eq 2).²⁶

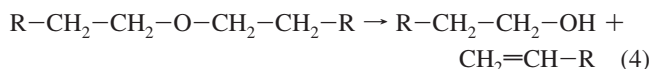
$$RF = [(MM)_{ref}/(MM)] \times [(ECN)/(ECN)_{ref}] \quad (2)$$

The ECN of a compound is a function of the number of non-hydrogen atoms of each type, n_i , and the effective carbon number contribution of each type of atom, ECN_i (eq 3).

$$ECN = \sum n_i \cdot ECN_i \quad (3)$$

Values for the ECN contributions of different types can be found in the literature, with the pertinent contributions being those of aliphatic C (1.0), olefinic C (0.95), primary alcohol O (−0.6), and ether O (−1.0).²⁷ For the primary alcohols, the experimental values in the literature (Table S1 in the Supporting Information) cover the range of alcohols of interest in the present study, and ECN values in the range of −0.4 to −0.6 have been suggested.^{26,27,29,31,32} The response factors for the primary alcohols were calculated using eq 2, with n -heptane as the reference compound and using −0.5 as ECN for the primary alcohol oxygen atom.

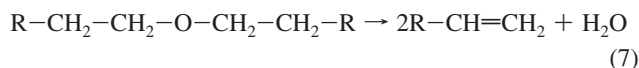
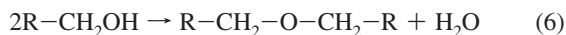
The ECN of ethers reported in literature is based on a limited number of compounds, with only diethyl ether (ethoxyethane) being representative of the linear ethers. It was considered prudent to determine the ECN of the ether oxygen atom for the heavier linear ethers that are of interest in the present study. It has been found that the experimentally determined response factors (Table 1) correlated well with the calculated values only for di- n -propyl ether. When the ECN of the ether oxygen atom is calculated for di- n -butyl ether and heavier linear ethers, a value of -0.6 ± 0.1 is found (Figure 1). This value is close to that reported for the oxygen atom of primary alcohols, and it seems likely that for heavier linear ethers flame ionization is preceded by disproportionation (eq 4), with the intermediate requiring an alkyl chain length of at least 4 carbon atoms.



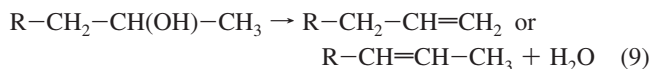
The apparent ECN of −0.6 for the longer linear ethers is then actually the sum of the contributions of the primary alcohol

oxygen (ECN = −0.5) and the two paraffinic carbons that were converted into olefinic carbons (ECN = $2 \times [0.95 - 1.0] = -0.1$). In this study, the response factors for the linear ethers were calculated using eq 2, with *n*-heptane as the reference compound and using −0.6 as ECN for the ether oxygen atom.

Reaction Network. The experimental results indicated that it is likely that there is more than one type of site present on the η -alumina catalysts. The dominant site type is a coordinatively unsaturated alumina site (Lewis acid),³³ which is normally associated with the catalytic dehydration of linear 1-alcohols to linear α -olefins (eq 5) and linear ethers (eq 6), as well as dehydration of linear ethers to linear α -olefins (eq 7).



The dominant alumina site is of course also active for catalyzing the reverse reactions of eqs 5 and 6, olefin hydration and ether hydrolysis. When olefin hydration takes place, the alcohol that is formed is no longer a primary alcohol (eq 8), and subsequent dehydration may yield an internal olefin (eq 9).



It is likely that a significant proportion of the 2-olefins in the product (Tables S2–S4 in the Supporting Information) was produced by dehydration–hydration–dehydration, rather than double bond isomerization. This would explain the high *cis*-2-olefin selectivity (Figure 2) in line with alcohol dehydration by the mechanism proposed by Shi and Davis.³³ Oxygenates will preferentially adsorb on the catalyst, and it is likely that olefin readsorption only becomes significant at high alcohol conversion. The commonly held view that 2-olefins are produced mainly by double bond isomerization^{19,34,35} may be true for catalysts with significant Brønsted acidity, but this view is questioned in the case of alumina. It has previously been demonstrated that alumina-catalyzed dehydration does not proceed via a carbocation intermediate, even for a tertiary alcohol, but takes place by a concerted mechanism that involves bond breaking as rate-determining step.³⁶ This also explains the apparent sluggishness with which conversion of 1-olefins to 2-olefins and *cis*-2-olefins to *trans*-2-olefins takes place, even when alcohol conversion is almost complete (Figure 2). Although some acid-catalyzed double bond isomerization cannot be ruled out, the results indicate that it is not the dominant mechanism whereby 2-olefins are formed.

Alcohol dehydration to produce olefins and ethers involves reactions in parallel (eqs 5 and 6) and in series (eqs 6 and 7). There are thermodynamic equilibrium constraints,¹⁸ with lower temperature and higher pressure favoring ether formation, but the reaction network is complex and not all reactions are reversible. Kinetic considerations are therefore important too, because secondary products such as *sec*-alcohols (eq 8) and internal olefins (eq 9) introduce different etherification equilibria.

The side-reactions that were observed (Tables 3–5 and Tables S2–S6 in the Supporting Information) indicated that there were other site types present apart from the dominant

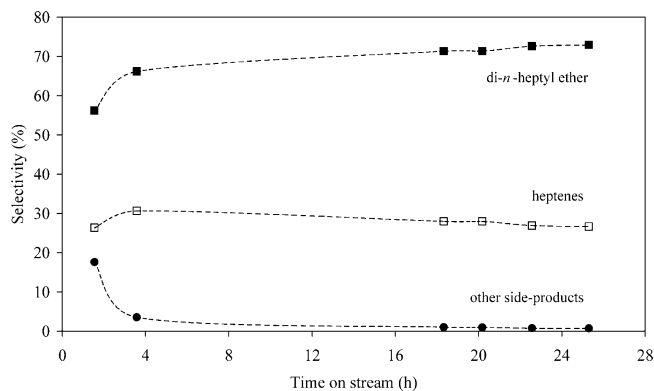


Figure 6. Initial selectivity changes observed when performing alcohol dehydration over a fresh η -alumina catalyst. Dehydration of 1-heptanol at 250 °C, near atmospheric pressure and constant conversion (50–53%), to show how the selectivity to the linear ether (■), olefin (□), and other side-products (●) levels out with time on stream.

Lewis acid alumina sites. The two main side-reactions were olefin dimerization (eq 10) and alcohol dehydrogenation (eq 11).



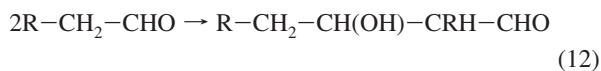
Olefin dimerization (eq 10) is a typical Brønsted acid-catalyzed side-reaction and indicated the presence of at least some H^+ -sites. The insensitivity of olefin dimerization selectivity to changes in flow rate indicated that it was a primary product. The olefin dimerization selectivity was increased by lower temperature (Tables S2–S4 in the Supporting Information) and higher pressure (Table S6 in the Supporting Information). This can be related to the probability of the carbocation intermediate desorbing as an olefin before it can interact with another olefin in the reaction mixture.

It is speculated that initially some of the strong Brønsted acid sites are present, but these sites are rapidly deactivated, resulting in significant changes with time on stream after fresh catalyst has been loaded (Figure 6). These sites are likely to be responsible for the high initial rate of side-product formation and could explain the high initial carbonyl and carboxylic acid conversion during alcohol dehydration over η -alumina that was reported previously.²²

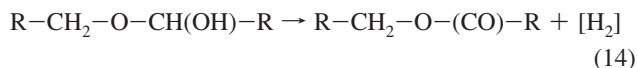
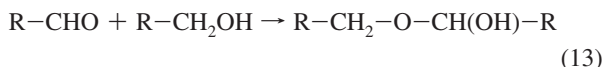
Alcohol dehydrogenation (eq 11) is normally associated with sites that have more basic and/or redox properties.^{37–41} Such sites may be deliberately introduced (not the case in our study) or be present as a consequence of impurities, such as MgO and CaO. In the commercial alumina catalyst that was employed, elemental analysis of the catalyst failed to indicate the presence of such impurities.

Dehydrogenation of alcohols may also take place as a consequence of catalyst pretreatment, with oxidative pretreatment resulting in a significant increase in alcohol dehydrogenation selectivity as compared to reductive pretreatment.⁴² Yet, irrespective of the pretreatment, some dehydrogenation was found. Various other properties have also been suggested to explain the origin of dehydrogenation over alumina,⁴³ and resolving the origin of dehydrogenation activity in the present work was beyond the scope of the investigation.

Alcohol dehydrogenation selectivity was not influenced by change in flow rate, and the linear aldehydes were primary products. The aldehydes led to further side-reactions, such as aldol condensation (eq 12).



Esterification was an important side-reaction only during the experiments conducted at higher pressure (Table S6 in the Supporting Information). It is likely that this reaction takes place via the hemiacetal (eq 13) that is dehydrogenated to the ester (eq 14).^{44,45}



It is speculated that esterification occurs on the same site that is responsible for aldehyde formation (eq 11), because it also requires a dehydrogenation step (eq 14). In support of this statement, it can be noted that pressure favors hemiacetal formation (Table S6 in the Supporting Information), which occurs by an Eley–Rideal mechanism.⁴⁴ With increasing pressure, the partial pressure of the alcohol is increased and thereby the probability that a hemiacetal can be formed before the aldehyde intermediate (eq 11) can desorb from the catalyst surface. However, if the hemiacetal did not form on the same type of site that is responsible for alcohol dehydrogenation, it would be difficult to explain hemiacetal dehydrogenation on a different site to yield the ester.

From the discussion of the reaction network, it can be concluded that the side-reactions over alumina are catalyzed mainly by Brønsted acid sites and basic oxidic sites, neither of which are necessary for alcohol dehydration. It should therefore in principle be possible to reduce side-reactions without affecting alcohol dehydration activity.

Acid site density²⁴ and acid strength⁴⁶ are also important variables. A higher acid site density is likely to favor bimolecular (etherification) over monomolecular reactions, and stronger acid sites are more likely to catalyze complete dehydration to the olefin. These variables have not been investigated in the present study.

Kinetics. The investigation used commercial size catalyst particles, and the results are not useful for a kinetic analysis. On the basis of comparison with the kinetic descriptions available in literature,^{34,47} it was clear that the reaction system was mass transfer limited. Although mass transfer limitations do not affect the reaction network, it should be noted that the conversion-selectivity profile may be affected by mass transfer effects. The impact of mass transfer on conversion is significant. However, considering the small selectivity change observed on changing from gas phase to liquid phase (Figure 4), the impact of mass transfer on selectivity is not expected to be significant.

Ether Addition to Diesel Fuel. The inclusion of oxygenates in diesel fuel to improve one or more diesel fuel property is frequently claimed in patent literature. Some important fuel properties to consider are as follows.

a. Cetane Number. The linear fuel ethers are good cetane improvers. It has been reported that the blending cetane number of the symmetrical linear ethers increases with increasing carbon number, leveling off at di-*n*-hexyl ether (Table 6).⁴⁸ Good blending cetane numbers have been reported for unsymmetrical linear ethers too (Table 6), albeit lower than that of the symmetrical ethers.

b. Cold Flow Properties. Despite their linearity, the linear ethers exhibit acceptable cold flow properties (Table 6)⁴⁸ for moderate climates and “summer grade” diesel fuels, but not necessarily for more stringent cold flow requirements. It is also

Table 6. Blending Cetane Number (BCN), Blending Cloud Point (BCP), Blending Cold Filter Plugging Point (BCFPP), Normal Boiling Point (T_b), and Density at 20 °C (ρ) Reported for Some Linear Ethers

compound	BCN	BCP (°C)	BCFPP (°C)	T_b (°C) ^a	ρ (kg m ⁻³) ^a
di- <i>n</i> -butyl ether	85	-20	-13	142	769
di- <i>n</i> -pentyl ether	109	-22	-20	184–190	784
di- <i>n</i> -hexyl ether	117	-7	-5	228–229	793
di- <i>n</i> -heptyl ether	117	-7	-5	259–263	801
di- <i>n</i> -octyl ether	118	-17	-15	286–287	806
<i>n</i> -hexyl butyl ether	94				
<i>n</i> -heptyl propyl ether	94			187–188	787
<i>n</i> -octyl ethyl ether	100				

^a Boiling point and density values are only indicative of values reported in the literature.

interesting to note that the cold flow properties of the ether deteriorate with the introduction of methyl branching.⁴⁸

c. Density. The linear ethers have a higher density (Table 6) than do linear paraffins of similar molecular mass. This is a beneficial attribute for LTFT diesel fuel, because it will improve the inherently low density (770–780 kg m⁻³) of LTFT diesel fuel.

d. Lubricity. The improvement of boundary layer lubrication by oxygenates follows the order: carboxylic acids > aldehydes > alcohols > methyl esters > ketones > ethers.⁴⁹ The linear ethers are therefore not expected to contribute much improvement in this regard. In a lubricity study⁵⁰ that included di-*n*-butyl ether, di-*n*-pentyl ether, and di-*n*-octyl ether, it was found that little lubricity improvement occurred in the range tested ($\leq 0.2\%$ ether blends). Only the di-*n*-octyl ether was able to reduce the wear scar diameter obtained during high frequency reciprocating rig testing to below 460 μm .

In addition to those properties highlighted, blends of ethers and diesel fuel (crude oil and Fischer–Tropsch derived) were also evaluated from the perspective of fuel stability, compatibility, and emission performance.^{51,52} These studies evaluated diesel fuel blends with di-*n*-pentyl ether and di-*n*-hexyl ether and reported satisfactory performance.

Prospects for Industrial Application. The inclusion of an etherification unit in an LTFT refinery can potentially be justified on the basis of the improved yield and quality of the distillate produced. The present study used only model compounds to improve our understanding of the catalysis and reaction network. To assess the prospects for industrial application, the impact of the differences between the model and industrial feeds must be evaluated, as well as some industrially relevant parameters, such as catalyst deactivation and product yield.

a. Distillate Yield. The distillate yield can be improved in two ways, by the etherification of naphtha range alcohols to distillate range ethers and by the dimerization of naphtha range olefins. Of the 1-alcohols, 1-heptanol is arguably the heaviest naphtha range alcohol, with a normal boiling point of 176 °C. In terms of the linear ethers, di-*n*-pentyl ether is the lowest boiling distillate range ether (Table 6). The range of alcohols that can be etherified to improve distillate yield is therefore limited to C₅–C₇. Olefin dimerization is one of the significant side-reactions. Although it is an undesirable side-reaction from the point of view of improving the ether yield, it helps to improve the distillate yield. In this respect, conducting alcohol dehydration under some pressure is doubly beneficial for increasing the distillate yield (Figure 7), because it improves both the ether yield and the olefin dimerization yield.

b. Processing Conditions. Apart from the thermodynamic equilibrium limitations imposed on the etherification reaction, there is a clear trade-off between conversion and ether selectiv-

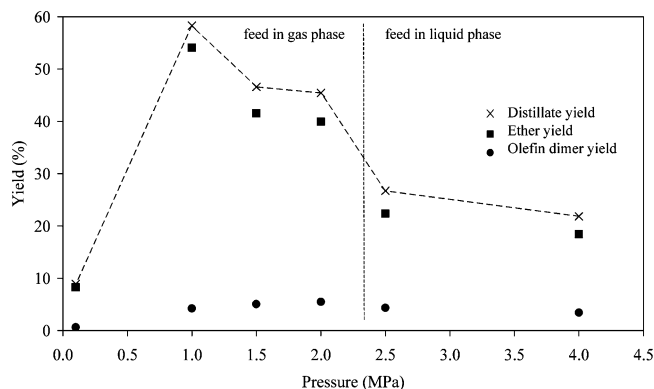


Figure 7. Distillate yield (x) as a function of the operating pressure during the dehydration of 1-hexanol over η -alumina at 300 °C, showing the contributions of ether yield (■) and olefin dimer yield (●).

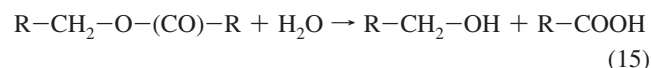
ity. This causes the ether yield to pass through a maximum as the temperature, pressure, and space velocity are increased. The optimum processing conditions for alcohol conversion over alumina have not been determined, but are likely to be around 300 °C and 1 MPa, where the highest ether yield was obtained experimentally.

c. Distillate Quality. Linear ethers have a beneficial effect on cetane number and to a lesser extent on density and lubricity. This has been discussed before. The olefin dimers that are formed as side-products will typically have a low degree of branching and should also have a good cetane number.

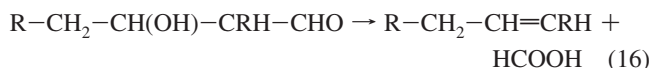
d. Processing Industrial LTFT Feed. There are four important differences between the model feed materials that were studied and industrial LTFT feed. First, there are other oxygenates present in the LTFT feed, which served as justification for the selection of alumina as catalyst for this study. On the basis of previous studies,^{22,23} it is unlikely that the other oxygenate species will affect the alumina catalyst, but some oxygenate-based side-reactions may result in downstream processing problems due to the formation of carboxylic acids. This aspect will be discussed separately. Second, there are olefins in the feed, which will increase the probability of side-reactions involving olefins, such as olefin dimerization. This is not a problem, because alumina is only mildly acidic, and it is unlikely that much heavy olefin oligomers will be formed. Third, the bulk of the feed will be paraffins, which will dilute the reaction mixture and reduce bimolecular reactions. This will improve catalyst lifetime and reduce the catalyst deactivation rate significantly, because deposits will be reduced. It has the further advantage of acting as an energy carrier, thereby reducing the adiabatic temperature decrease due to etherification and dehydration. This is an important industrial consideration and has been discussed previously.²³ Dilution of the feed will unfortunately also reduce the conversion rate somewhat. The fourth difference is the fact that the industrial feed will be a mixture. The linear ethers formed by alcohol dehydration will consequently be a mixture of symmetrical and unsymmetrical ethers. Although this is not a problem per se, the distillate properties will be affected. For example, the blending cetane number will be lower on account of the unsymmetrical ethers (Table 6). Furthermore, it has been reported that the rate of alcohol dehydration over alumina increases with carbon chain length of the alcohol feed.^{47,53} This has also been found in our study (see alcohol conversion at 300 °C in Table 2) and may introduce some bias in the product distribution.

e. Carboxylic Acid Formation. There are two oxygenate side-reactions that could potentially result in downstream refining problems. Esters that are formed may be hydrolyzed

at reaction conditions to produce an alcohol and a carboxylic acid (eq 15).



This reaction does not involve C–C bond cleavage, and the carboxylic acids are of the same chain length as the alcohols in the feed. As long as the feed contains only heavier alcohols, ester hydrolysis does not pose a problem, because the heavier carboxylic acids are not very corrosive. As a matter of fact, the longer chain carboxylic acids are useful to improve lubricity.⁴⁹ However, short chain carboxylic acids can be produced by aldol condensation of the aldehydes (eq 12) followed by the carbonyl to carboxylic acid decomposition reaction (eq 16).



f. Catalyst Selection. The present study considered only alumina as catalyst. This may not be the optimum catalyst for the etherification of industrial LTFT feed, because both etherification and olefin dimerization are desirable reactions for increasing the yield and/or quality of distillate. This may call for a more acidic catalyst that would more readily catalyze olefin dimerization. Nevertheless, even if a more applied investigation shows that alumina is the best catalyst for this application, the selection of the alumina catalyst is equally important. It has been pointed out that many of the side-reactions are catalyzed on different sites (Brønsted acid sites and basic and/or redox sites) than that needed for alcohol etherification. The purity and nature of the alumina catalyst determine side-product formation, and an alumina catalyst should be selected that would minimize undesirable side-reactions.

Conclusions

The yield and quality of distillate produced from low temperature Fischer–Tropsch (LTFT) syncrude can be improved by dehydration of the alcohols in LTFT naphtha over an η -alumina catalyst to produce fuel ethers and olefins. Although other acid catalysts, such as acidic resins, can also be used for this purpose, alumina has been selected due to its robustness in the presence of water and other oxygenate classes (carbonyls and carboxylic acids) that are present in Fischer–Tropsch syncrude. The following specific conclusions could be drawn from the experimental investigation:

(a) GC-FID response factors for the linear ethers were determined to quantify these compounds properly. It was shown that the response factors could be expressed in terms of the equivalent carbon number (ECN) concept, and an ECN of -0.6 ± 0.1 was found for the ether oxygen atom in di-*n*-butyl ether and heavier linear ethers. Further support for this experimental value was provided by the mechanistic observation that it is actually the sum of the contributions of the primary alcohol oxygen (ECN = -0.5) and two olefinic carbons (ECN = $2 \times [0.95 - 1.0] = -0.1$) formed during ether decomposition into an alcohol and an olefin. The value of -0.6 found in our study differs from the ECN value of -1.0 that was proposed in literature.

(b) The reaction network that was observed during the dehydration of $\text{C}_5\text{--C}_{12}$ 1-alcohols over η -alumina indicated the presence of three different catalytic sites. Most of the alcohol dehydration took place over Lewis acid sites. In parallel, some alcohol dehydration and olefin conversion took place over Brønsted acid sites, and some dehydrogenation to produce aldehydes and esters took place over basic and/or redox sites.

(c) The main side-reactions over η -alumina were alcohol dehydrogenation and olefin dimerization. These reactions took place over Brønsted acid sites and basic and/or redox sites.

(d) The 2-olefins produced during alcohol dehydration from 1-alcohols are predominantly *cis*-2-olefins. This indicated that most 2-olefins are produced by dehydration–hydration–dehydration over Lewis acid sites on the alumina catalyst and not by double bond isomerization over Brønsted acid sites.

(e) The highest yield of distillate (58%) and the highest yield of fuel ethers (54%) were obtained during 1-hexanol conversion over η -alumina at 300 °C, 1 MPa, and WHSV of 1 h^{−1}. Although these were unoptimized conditions, it demonstrated that distillate and ether yield passed through a maximum with increasing temperature, pressure, and space velocity.

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Supporting Information Available: GC-FID response factors for alcohols from the literature have been listed in Table S1. A breakdown of the selectivity to various olefinic products has been provided for 1-alcohol dehydration over alumina at 250 °C (Table S2), 300 °C (Table S3), and 350 °C (Table S4). The influence of flow rate on linear α -olefin, aldehyde, and other side-product formation is provided (Table S5). The influence of pressure on 1-hexanol conversion and selectivity at 300 °C and 1–4 MPa is given (Table S6) together with the vapor pressure curves of 1-hexene, 1-hexanol, and di-*n*-hexyl ether (Figure S1). Calculations are provided to show that plug flow behavior was ensured under operating conditions resulting in a liquid phase. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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