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Higher-Alcohols Biorefinery

Improvement of Catalyst for Ethanol Conversion

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Abstract

The concept of a biorefinery for higher-alcohol production is to integrate ethanol and methanol formation via fermentation and biomass gasification, respectively, with conversion of these simple alcohol intermediates into higher alcohols via the Guerbet reaction. 1-Butanol results from the self-condensation of ethanol in this multistep reaction occurring on a single catalytic bed. Combining methanol with ethanol gives a mixture of propanol, isobutanol, and 2-methyl-1-butanol. All of these higher alcohols are useful as solvents, chemical intermediates, and fuel additives and, consequently, have higher market values than the simple alcohol intermediates. Several new catalysts for the condensation of ethanol and alcohol mixtures to higher alcohols were designed and tested under a variety of conditions. Reactions of methanol-ethanol mixtures gave as high as 100% conversion of the ethanol to form high yields of isobutanol with smaller amounts of 1-propanol, the amounts in the mixture depending on the starting mixture. The most successful catalysts are multifunctional with basic and hydrogen transfer components.

Index Entries: Biorefinery, alcohols; Guerbet reaction; methanol-ethanol mixtures; catalyst.

Introduction

Currently, most biorefineries are based mainly on a single product line with potentially one or two byproducts. Thus, an ethanol plant produces ethanol from corn starch, with distiller's grain as a byproduct. Greater product flexibility and, consequently, greater opportunities for profitability would derive from a plant producing a variety of alcohols, especially higher alcohols whose market prices range from $0.77 to $1.87/kg.

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Alcohols with three to eight carbons are highly useful as solvents and chemical intermediates and are potentially useful as fuel oxygenate additives. The primary alcohols, such as 1-propanol, 1-butanol, 2-methyl-1-propanol, and 2-methyl-1-butanol, are now commercially produced from olefins in a multistep process that includes the oxo (hydrocarbonylation) reaction and subsequent hydrogenation and separation steps. The market for several of the higher alcohols is currently large and highly dependent on oil prices since they are derived from petroleum feedstocks. Lower-cost processes for higher alcohols could involve very efficient condensation reactions, starting with renewable CO_2-neutral ethanol and very inexpensive methanol. Expansion into the fuel additive market would likely be accelerated if superior performance and low-cost production could be demonstrated. Like ethanol, the higher alcohol fuel additives reduce engine emissions and improve performance but, unlike ethanol, do not generate high-volatility Reid vapor pressure and water-partitioning properties.

The condensation of inexpensive methanol and ethanol offers a relatively simple way to produce higher alcohols. This reaction is known as the Guerbet reaction and produces higher-value 1-butanol from self-condensation of ethanol or mixtures containing mainly 2-methyl-1-propanol (isobutyl alcohol) and 1-propanol from ethanol plus methanol. The Guerbet reaction is actually a multistep process occurring on a multifunctional catalyst at temperatures >300°C. The steps in the catalytic reaction involve dehydrogenation of the short-chain alcohols to aldehyde intermediates; condensation of the aldehyde intermediates to longer-chain aldehydes; and, finally, catalytic reduction to the larger alcohols. Earlier patents and studies used bases in combination with a hydrogenation/dehydrogenation catalyst component.

Development of a biorefinery concept for production of higher alcohols from ethanol depends on improvement of the catalyst required for the conversion. This article reviews the Guerbet condensation reactions developed for conversion of simple alcohols into higher alcohols and describes the testing of catalysts based on highly reactive catalytic carbons that function as the redox component of the catalytic system. The described research demonstrated the feasibility of a process for producing higher-alcohol mixtures from ethanol and methanol mixtures using novel catalytic processes. Methanol can be produced from biomass and other feedstocks via gasification and subsequent conversion of the syngas in high yield. Reactions of ethanol with itself and other alcohols will be described in future articles.

Guerbet Reactions

The condensation of methanol with ethanol produces a mixture of 1-propanol and 2-methyl-1-propanol (isobutyl alcohol), as well as small amounts of other branched alcohols, including 2-methyl-1-butanol, and nonalcohol components, depending on the catalyst and reactant ratios *(1–10)*. The reactions proceed through the formation of formaldehyde and acetaldehyde (Eqs. 1 and 2), which condense and form propenal (Eq. 3), which is reduced to 1-propanol (Eq. 4). Further condensation of formaldehyde with propanal gives the branched 2-methyl-1-propanol (isobutyl alcohol) (Eqs. 5 and 6).

Other reactions are the acetaldehyde condensation to butanal (Eq. 7) followed by reduction to alcohol (Eq. 8) or reaction with formaldehyde to form 2-methylbutanal, which is reduced to the corresponding alcohol (Eq. 9). Other reactive combinations give condensation products, provided that one of the reactants has hydrogens on the carbon adjacent to the carbon bearing the hydroxyl group, so that the carbanion intermediate can form and add to the carbonyl formed on the other reactant.

$$CH_3OH \rightarrow CH_2{=}O + H_2 \qquad (1)$$

$$CH_3CH_2OH \rightarrow CH_3CH{=}O + H_2 \qquad (2)$$

$$CH_2{=}O + CH_3CH{=}O \rightarrow HOCH_2CH_2CH{=}O \rightarrow CH_2{=}CHCH{=}O + H_2 \qquad (3)$$

$$CH_2{=}CHCH{=}O + 2H_2 \rightarrow CH_3CH_2CH_2OH\ (\text{1-propanol}) \qquad (4)$$

$$CH_3CH_2CH{=}O + CH_2{=}O \rightarrow HOCH_2CH(CH_3)CH{=}O \qquad (5)$$

$$HOCH_2CH(CH_3)CH{=}O + 2H_2 \rightarrow CH_3CH(CH_3)CH_2OH\ (\text{2-methyl-1-propanol}) \qquad (6)$$

$$2CH_3CH{=}O \rightarrow CH_3CH{=}CHCH{=}O + H_2O \qquad (7)$$

$$CH_3CH{=}CHCH{=}O \xrightarrow{H_2} CH_3CH_2CH_2CHO \xrightarrow{H_2} CH_3CH_2CH_2CH_2OH \qquad (8)$$

$$CH_3CH_2CH_2CH{=}O + CH_2{=}O \rightarrow \rightarrow CH_3CH_2CH(CH_3)CH_2OH \qquad (9)$$

There are two potential advantages of using a mixture of methanol and ethanol. First, the much lower cost of methanol allows its use in large excess so that very high conversions of ethanol might be obtained. Second, dehydrogenation of methanol produces formaldehyde, which is an especially reactive additive to carbanion intermediates in the condensation reactions.

These branched alcohol products are also useful in solvents, plasticizers, and monomers. For example, isobutyl alcohol is converted into the acetate ester, which is used extensively as a lacquer solvent. Isobutyl alcohol is also used in lubricating oils and in the production of amide resins. Propyl alcohol (59 million kg/yr) is used heavily in herbicide syntheses and in solvents for coatings and inks.

To effect the aldol condensation, reactions of liquid alcohols in a batch autoclave typically used a basic catalyst, such as sodium ethoxide or other alkali metal alcoholate *(11,12)*, phosphate *(13)*, or carbonate *(14)*, and a relatively high temperature (230°C). To aid in the dehydrogenation and hydrogenation steps, nickel *(12)*, copper chromite *(14)*, platinum, palladium, ruthenium, or rhodium was used in a finely divided state. Moderate yields of alcohol products were obtained; however, several problems remain in commercializing the Guerbet reaction for higher-alcohol production. The starting alcohol is often converted into a large amount of carboxylic acid by a side reaction. Even when this is minimized by using an appropriate catalyst system, the catalyst systems are deactivated by the water byproduct of the reaction. Essentially, this is a hydrolysis of the sodium alkoxide to the less active hydroxide; thus, successive batch reactions required the addition of new sodium alkoxide.

The key to effecting economical condensation reactions of the Guerbet type is the use of a solid base catalyst bed in a continuous or flow-through reactor for the gas-phase reaction. In this mode, the water eliminated during the condensation does not accumulate in the reactor as it does in the batch reactor. Fuchs *(15)* described a reaction of mixed alcohols and hydrogen over MgO/CuO to give a mixture of alcohols (US patent no. 2,050,788). Matsuda *(8)* used a Cu-Ni alkaline catalyst in a similar reaction (US patent no. 4,518,810). Clark *(9)* described a gas-phase reaction with a catalyst composed of a platinum group metal and alkali metal impregnated on alumina for formation of the linear alcohols, but branched alcohols were not reported. Ueda et al. *(14)* reported using a magnesium oxide catalyst for the gas-phase reaction of ethanol and methanol. Conversions of 60% (ethanol basis) were obtained at 390°C at atmospheric pressure, with a selectivity of 80% for alcohols. The catalytic activity decreased with time, however, and methanol was converted into unwanted gases: CO, H_2, and CH_4. A magnesium oxide catalyst (no hydrogen-activating metal) was also patented (US patent nos. 5,095,156 and 5,364,979) *(16,17)*. The major problem with these processes is the high methane production and the loss of activity of the mixed metal oxides used in these reactions and sintering during attempted regeneration.

To improve process economics, further work is needed to improve catalyst lifetimes. A more stable system employed a noble metal-loaded potassium L-zeolite catalyst for the condensation of ethanol with methanol to produce a 1-propanol and 2-methyl-1-propanol (US patent no. 5,300,695) *(18)*. However, yields were small compared with the large amounts of CO and CO_2 produced from the methanol. More recently, Exxon patented a noble metal-loaded alkali metal-doped mixed metal (Zr, Mn, Zn) oxide (US patent nos. 6,034,141 and 5,811,602) *(19,20)*. The catalyst was used in a syngas atmosphere. As with other catalysts, the higher temperatures resulted in decomposition of methanol. Changes in catalyst composition were noted at higher temperatures, but the stability of the catalyst was not discussed. Recently, compositions including Ni, Rh, Ru, and Cu were investigated *(21,22)*.

Novel Catalysts for Higher-Alcohol Production

The formation of higher alcohols directly in one step from smaller alcohols via the Guerbet reaction was investigated by passing the alcohol vapors through a catalytic bed and condensing the higher-alcohol products in a series of cold traps. The catalysts were tested in a tubular flow-through reactor with ethanol or with methanol-ethanol (5:1 mainly) mixtures in a nitrogen carrier gas in a matrix of temperature and pressure conditions. The liquid products were collected in dry ice–isopropanol traps and analyzed by gas chromatography (GC)–flame ionization detection. The gases were collected and analyzed by GC-thermal conductivity detector.

Novel, multifunctional fixed-bed catalysts for use in a continuous Guerbet process for higher-alcohol synthesis were prepared. To achieve high conversions in the Guerbet reaction over a stable multifunctional catalyst, we investigated the use of several catalytic carbons to function as the redox component of the catalytic system. Two commercial activated carbons were converted into more basic forms, denoted CM and FM. A highly active proprietary catalytic carbon (SO) prepared at the Energy & Environmental Research Center (EERC) was also treated to a more basic form. Thus, all three carbons were hypothesized to contain the needed redox and basic catalytic components for the Guerbet reaction. The activities of these modified carbons were compared with those of MgO catalysts on various supports and with those using a very high surface area aerogel magnesium oxide.

Materials and Methods

Preparation of Carbon-Based Catalysts

A commercial catalytic carbon (Centaur), a commercial activated carbon (Calgon 400), and the EERC SO carbon were impregnated with magnesium nitrate and calcined to produce the MgO-loaded carbons, denoted CM, FM, and SOM, respectively. Magnesium oxide (10 or 20 wt%)–impregnated carbons were prepared as follows. An aqueous solution of magnesium nitrate hexahydrate was impregnated on the carbon using the incipient wetness method. The resulting carbon was dried at 110°C. The dried carbon was placed in a 40-cm stainless steel reactor (2.5cm). The reactor was slowly heated to 360°C in a gentle flow of nitrogen. The carbon was heated at this temperature for 3 h to decompose the nitrate to oxide.

MgO-supported carbon catalyst was also prepared by impregnating an aqueous magnesium sulfate solution. The dried impregnated carbon was washed with concentrated ammonium hydroxide solution to convert the sulfate into magnesium hydroxide. This washed carbon was dried and heated in a tubular reactor as just described to convert the hydroxide to oxide.

Preparation of MgO Catalysts

Magnesium oxide was prepared by hydrolyzing an aqueous solution of magnesium sulfate with ammonium hydroxide. It was thoroughly washed with water until free of cations and anions and dried at 50°C under vacuum for 12 h. The dried product was then heated at 600°C in air *(13)*.

Magnesium oxide was also prepared by boiling 25 g of commercially available magnesium oxide in 500 mL of water with vigorous stirring in a

1-L flask equipped with a reflux condenser. After cooling, the slurry was filtered and the cake dried in an oven at 120°C. The dried product was broken into pieces and heated at 500°C under vacuum for 12 h. The product was stored under nitrogen *(23)*.

Ultrahigh-surface-area magnesium oxide (aerogel) was prepared according to the procedure described previously *(11,23)*. Magnesium turnings and analytical-grade methanol were used for the preparation of magnesium methoxide. Ten percent magnesium methoxide was prepared by stirring 7.2 g of magnesium (0.30 mol) with 300 mL of methanol in a 500-mL round-bottomed flask attached to a nitrogen supply. To prevent hydrolysis, a slow flow of nitrogen was maintained throughout the reaction. The stirring was carried out until all of the magnesium was gone (24 h).

The methoxide solution was placed in a round-bottomed flask, 300 mL of toluene was added, and the mixture was vigorously stirred. To the stirred mixture, 4.5 mL of water was added slowly. A white precipitate was observed on addition of water. After a few minutes, the mixture became clear and produced a syrup-like solution. The resulting mixture was stirred overnight to ensure completion of hydrolysis.

The hydroxide gel solution was transferred into an autoclave (300-mL glass-lined Parr reactor). The reactor was flushed with nitrogen and then pressurized with 200 cm^3 of nitrogen. The reactor was slowly heated from room temperature to 265°C. The temperature was allowed to equilibrate for 10 min before the reactor was vented to release the pressure. The operating pressure was 7.2 MPa. The pressure was released over a period of 0.5–0.8 min. The reactor was immediately removed from the heater and then flushed with nitrogen for 5–10 min. It was next allowed to cool to room temperature. The product was removed from the reactor and dried in an oven at 120°C for a few hours.

The dried product was activated by heating *in vacuo*. The dried product was placed in a quartz tube and evacuated. The quartz tube was then heated in a tubular furnace using a ramp-and-soak method as follows: ramped from room temperature to 220°C at 1°C/min; soaked at 220°C for 5 h, ramped from 220 to 500°C at 1°C/min, soaked at 500°C for 5 h. About 18 h was required for the heat treatment of the sample. The sample was allowed to cool to room temperature and then stored under nitrogen. The product was very light chunky powder. However, these chunks were very fragile; therefore, they could not be directly used for packed-bed reactors.

The ultrahigh-surface-area gel containing nickel and copper was prepared by adding nickel nitrate or copper nitrate (Ni or Cu was 3 wt% of metal of dried weight of MgO) to the gel prior to autoclave treatment *(12)*. For this product to be packed into a tube reactor, it was converted into a strong-enough granular form. This was accomplished as follows: Slurry was prepared by adding aerogel to an alcoholic solution of nickel nitrate hexahydrate. The amount of Ni in Ni/MgO was 3 wt%. Lava rock crushed to +8 mesh size was impregnated with this gel. The rock was thoroughly mixed and dried to remove solvent, and then activated by heating at 600°C for 2 h.

In another experiment, glass wool was added to the hydrolyzed magnesium methoxide gel prior to heating in the autoclave. The quartz wool coated with high-surface-area magnesium oxide was impregnated with nickel nitrate hexahydrate and activated as already described.

Continuous Catalytic Conversion of Methanol-Ethanol Mixtures

Flow-Through Reactions at Ambient Pressure

A tubular stainless steel reactor, 40 cm long (ID = 1 cm), was used for conducting catalytic runs at atmospheric pressure. The reactor was packed with the desired catalyst. The inlet of the reactor was attached to a pump and source of nitrogen gas. The outlet was attached to two ice-cooled traps. The reactor was placed in a tubular furnace maintained at 360°C. After the reactor had attained the desired temperature, the desired methanol-ethanol mixture was pumped into the reactor at the desired rate (0.1 or 0.5 mL/min). To facilitate the flow of alcohol vapors through the catalyst bed, a gentle flow (66 cm^3/min) of nitrogen was passed through the reactor. The products were condensed in the ice-cooled traps. After the desired time (60 min), alcohol flow was stopped. The flow of nitrogen was continued for an additional 10 min through the reactor to flush out any remaining product. The reactor was cooled to room temperature, and the catalyst was removed and stored under nitrogen. No liquid was present in the reactor. The distillate was analyzed by GC and GC-mass spectrometry (MS).

Flow-Through Reactions Under Pressure

In a flow-through reaction under pressure, the outlet of the reactor was attached to traps via a needle valve. The reactor was pressurized with 1.4 MPa of nitrogen, and the needle valve was closed. The alcohol mixture was pumped at 0.5 cm^3/min for 15 min. The pressure inside the reactor increased to 1.8–2.1 MPa. The valve was slightly opened to allow the product to condense into two ice-cooled traps by maintaining the pressure inside the reactor. The run was continued for another 15 min.

Batch Reaction

In a batch reaction, the reactants and catalyst were placed in a 15-mL tube reactor. The reactor was evacuated and sealed and then heated at 360°C for 30 min. The products were centrifuged, and liquid was collected and analyzed.

Product Analyses

Analyses of the starting material and products were carried out by GC and GC-MS analyses. For GC analyses, a Shimadzu gas chromatograph, GC-17A, was used. A 60-m-long narrow bore (0.25-mm) DB5 with 0.25-µm phase thickness supplied by J & W Scientific was used. The GC parameters were as follows: split injection (split ratio of 50:1), carrier gas of hydrogen at 1 cm^3/min at 30°C. The heating program was as follows: initial temperature of 30°C, initial time of 2 min, rate of 30–250°C at 3°C/min, final time of 5 min. A variety of straight chain and branched alcohols (C_1–C_{10}) were calibrated using anisole as the internal standard. Reaction products from each run were mixed with 0.1 g of anisole (internal standard) and analyzed by GC. Conversions of the ethanol component were calculated by subtracting the ethanol recovered in the product mixture from the starting amount; this is reported in Tables 1, 2, and 4–10 as the percentage of ethanol conversion (EtOH conversion). Theoretical yields of each alcohol product were calculated by assuming that all of the ethanol that reacted was converted into that alcohol, and the percentage of theoretical is also reported in these tables for each alcohol component.

In many of the experiments, a small amount of the 2-methylpropanal (isobutyraldehyde) intermediate was formed. The amounts were determined and are reported in Tables 1, 2, and 4–10. Only in two of the experiments were formaldehyde and acetaldehyde analyzed, but it is assumed that small amounts of formaldehyde were present in all of the products. Other aldehyde intermediates, such as propanal and 2-methylbutanal, were not present in amounts large enough for detection. Besides the major higher-alcohol products and aldehyde intermediates described above, some other minor products were determined in the chromatograms of each product. These include esters, ethers, and aromatics formed in very small amounts. The sums of these are reported in Tables 1, 2, and 4–10 as "Other." The areas of these GC peaks were converted to millimoles by using approximate response factors appropriate for the molecular weight range of the peaks.

Results and Discussion

Effect of Reactor Temperature and Starting Composition

Reactions of ethanol-methanol mixtures were carried out with recovered CM catalyst at various temperatures. Several variations of the starting composition were utilized at 360°C. The results are shown in Table 1. The reaction at 310°C gave a very low conversion of the ethanol with small amounts of the higher alcohols being formed. The poor mass balance was assumed to have resulted from the formation of acetaldehyde, which was not analyzed in this experiment.

The reactions at 360°C gave high conversions of ethanol and good yields of 2-methyl-1-propanol, based on reacted ethanol, along with some of the other C_3 and C_5 alcohols, and small yields of nonalcohol products (carboxylic acids, esters, ethers). The high-temperature (400°C) experiment also gave a high conversion and respectable yields of higher alcohols. Mass balance closures were close to 100% based on reacted ethanol. Carbonaceous deposits may form but could not be identified because the catalyst is composed of carbon as well as metal oxide.

For reactions with the CM catalyst at 360°C, the higher molar ratios of methanol to ethanol resulted in considerably more ethanol being converted into products, reaching 98% conversion when the ratio was 9.7. For the higher methanol-to-ethanol ratios, yields of 2-methyl-1-propanol were approximately the same. At the low ratio (3.3), yields of 2-methyl-1-propanol were much lower, and yields of 1-propanol and 2-methyl-1-butanol (formed from 2 mol of ethanol) were higher. Subsequent comparisons of catalysts were all conducted at 360°C with methanol-ethanol molar ratios of 7.2, corresponding to a 5:1 volume ratio.

Most of the reactions produced some 2-methylpropanal in the products. Not shown in Tables 1–6 are yields of formaldehyde and acetaldehyde, which were not measured in these initial experiments. A subsequent experiment with the SOM carbon was performed with several cold traps to determine formaldehyde and acetaldehyde concentrations in the products. The results are discussed below.

Comparison of Catalysts: Carbon-Based Catalysts

To determine the effect of the carbon structure on the catalytic conversion of methanol-ethanol mixtures to higher alcohols, three different carbons were investigated. The activity of a freshly prepared CM catalyst was compared with that of freshly prepared FM and SOM catalysts. Reactions of the pumped 5:1 methanol-ethanol mixture with all of these freshly prepared catalysts were performed in the flow reactor under identical conditions. Conversions and product composition results are given in Table 2. Very high conversions of ethanol were obtained with all three catalysts. The selectivity for 2-methyl-1-propanol was higher for the SOM and FM catalyst compared with CM. Typically, the catalyst activities degrade and selectivities for higher alcohols decrease with time. Further work is in progress to investigate these changes.

Gas Product Composition from Carbon Catalyst

For several of the experiments, gas products were collected in a gas bag following the liquid product traps. The gases were analyzed by GC with a thermal conductivity detector, and the total volume was determined from the gas flow rate. The amount of the gaseous product collected was 3.5 mmol. The major components in the gas phase were hydrogen, carbon monoxide, carbon dioxide, propane, acetylene, 1-butane, isobutane, *cis*- and *trans*-2-butenes, ethylene, methane, and oxygen. The composition of the gas mixture from a run with the SOM catalytic carbon is given in Table 3. The hydrogen is of some significance, since it derives from dehydrogenation of the alcohol but is not all retained on the carbon for subsequent hydrogenation of product aldehydes. Other gases were negligible.

Effect of Active Metal Incorporation

Earlier patents used catalysts containing a Group VIII metal to aid in the transfer of hydrogen (dehydrogenation and hydrogenation). The FM carbon catalyst in this project was similarly modified by the addition of 0.6 wt% of the active metal (nickel). The results using this catalyst are compared with those using FM catalyst in Table 4. The addition of nickel improved on

Table 1
Effects of Temperature and Starting Composition Molar Ratio on Conversion and Yields for Reactions of Methanol-Ethanol Mixtures[a]

Reactant ratio MeOH:EtOH (mmol)	Temperature (°C)	Recovered MeOH (mmol)	Recovered EtOH (mmol)	EtOH conversion (%)	2-Me propanal (mmol [%])	1-PrOH (mmol [%])	2-Me-1-PrOH (mmol [%])	2-Me-1-BuOH (mmol [%])	Other (mmol)
5.0/MeOH (97.95); EtOH (19.47)	310	94.42	16.64	15	0.00 (0)	0.44 (15)	0.59 (20)	0.00 (0)	0.20
9.7/MeOH (194.4); EtOH (20.00)	360	79.62	0.43	98	1.11 (5)	1.24 (6)	12.54 (64)	0.44 (4)	0.39
7.2/MeOH (125); EtOH (17.40)	360	88.00	0.96	94	0.84 (5)	0.65 (4)	10.64 (65)	0.28 (3)	3.40
3.3/MeOH (83.43); EtOH (25.44)	360	49.96	17.71	70	0.24 (1)	6.88 (39)	6.44 (36)	1.61 (18)	2.20
3.3/MeOH (91.28); EtOH (27.83)	400	37.36	2.40	91	0.92 (4)	4.20 (17)	14.48 (57)	1.80 (14)	2.60

[a] Catalyst, cm (recovered); carrier flow, 66cm^3/min. Percentages given in parenthesis refer to percent yield based on millimoles of product per millimole of ethanol converted.

Table 2
Effect of Carbon Precursor on Catalyst Activity and Conversions and Yields for Methanol-Ethanol Reactions[a]

Catalyst	Recovered MeOH (mmol)	Recovered EtOH (mmol)	EtOH conversion (%)	2-Me propanal (mmol [%])	1-PrOH (mmol [%])	2-Me-1-PrOH (mmol [%])	2-Me-1-BuOH (mmol [%])	Others (mmol)
CM	88.10	0.96	94	0.84 (5)	0.65 (4)	10.64 (65)	0.28 (3)	3.3
FM	89.03	0	100	1.13 (7)	0.44 (3)	13.19 (76)	0.88 (10)	1.2
SOM	82.61	0	100	1.12 (6)	0.30 (2)	14.81 (85)	0.42 (5)	0.8

[a] Flow rate, 0.1 mL/min; N_2 carrier flow, 66 cm^3/min; MeOH, 125 mmol (4.00 g); EtOH, 17.4 mmol (0.80 g); molar ratio, 7.2 temperature, 360°C; time, 60 min. Percentages given in parenthesis refer to percent yield based on millimoles of product per millimole of ethanol converted.

Table 3
Composition of Gas Formed in Methanol-Ethanol Reaction on SOM Catalyst

Gas	Weight (mg)	mmol	Composition (mmol%)
Hydrogen	3.0	1.500	8.40
Carbon dioxide	8.1	0.200	1.12
Propane	0.7	0.015	0.08
Acetylene	3.5	0.140	0.78
i-Butane	1.5	0.026	0.15
t-Butane	3.2	0.055	0.31
trans-2-Butene	1.6	0.028	0.16
cis-2-Butene	7.0	0.123	0.70
Ethene	1.2	0.040	0.22
Oxygen	2.8	0.087	0.49
Methane	4.0	0.230	1.30
Carbon monoxide	8.2	0.293	1.64
Nitrogen	424.6	15.153	84.65
Total	44.7	17.900	100.00

the high yields of the alcohol products, especially the 2-methyl-1-propanol (90%). Since the yield of 2-methylpropanal decreased substantially, the greater yield of 2-methyl-1-propanol may have resulted from the increased hydrogenation of 2-methylpropanal intermediate.

Effect of Base Composition on Activity

To determine whether a variation in base modification of the carbon catalyst has an effect on the activity, a second catalyst (CSM) was prepared from the Centaur commercial carbon by impregnating with magnesium sulfate and subsequently heating to decompose the salt to the oxide form. The resulting carbon was used as a catalyst for the conversion of the methanol-ethanol mixture; the results are given in Table 5. The CSM catalyst prepared using the alternative base precursor was less effective in converting the ethanol, and lower amounts of higher alcohols were obtained. Since the amount of 2-methylpropanal intermediate was higher, the results suggest that the sulfuric acid from the decomposition of the magnesium sulfate may have poisoned some of the catalytic sites for hydrogenation.

Magnesium Oxide Catalysts

Several patents and literature reports utilized inorganic basic catalysts for the Guerbet reaction. Several of these were prepared and utilized for the methanol-ethanol mixture. A very porous low-density aerogel form of MgO was prepared, but the material lacked any kind of strength and could not be packed by itself in a reactor tube. Thus, glass wool and lava rock were used as a support for MgO. For the lava rock support, MgO (aerogel) and nickel nitrate were slurried into ethanol and impregnated on lava rock. The product was dried at 110°C followed by activation at 160°C in nitrogen for 3 h.

Table 4
Effect of Transition Metal on Activity of Carbon Catalyst and Conversions and Yields of Methanol-Ethanol Reactions [a]

Catalyst	Recovered MeOH (mmol)	Recovered EtOH (mmol)	EtOH conversion (%)	2-Me propanal (mmol [%])	1-PrOH (mmol [%])	2-Me-1-PrOH (mmol [%])	2-Me-1-BuOH (mmol [%])	Others (mmol)
FM	89.03	0	100	1.13 (7)	0.44 (3)	13.19 (76)	0.28 (3)	1.3
Ni-FM	89.25	0	100	0.15 (1)	0.60 (3)	15.69 (90)	0.15 (2)	1.1

[a] Flow rate, 0.1 mL/min; carrier flow, 66 cm^3/min; MeOH, 125 mmol; EtOH, 17.4 mmol; temperature, 360°C; time, 60 min. Percentages given in parenthesis refer to percent yield based on millimoles of product per millimole of ethanol converted.

Table 5
Effect of Basic Precursor on Activity of Carbon Catalyst and Conversions and Yields for Methanol-Ethanol Reactions [a]

Catalyst	Recovered MeOH (mmol)	Recovered EtOH (mmol)	EtOH conversion (%)	2-Me propanal (mmol [%])	1-PrOH (mmol [%])	2-Me-1-PrOH (mmol [%])	2-Me-1-BuOH (mmol [%])	Others (mmol)
CM	88.00	0.96	94	0.84 (5)	0.65 (4)	10.64 (65)	0.28 (3)	3.4
CSM	99.26	3.26	81	2.76 (19)	0.20 (1)	9.50 (67)	0.00 (0)	1.4

[a] Flow rate, 0.1 mL/min; carrier flow, 66 cm^3/min; MeOH, 125 mmol; EtOH, 17.4; temperature, 360°C; time, 60 min. Percentages given in parenthesis refer to percentage yield based on millimoles of product per millimole of ethanol converted.

Table 6
Activity of Supported MgO Catalyst and Conversions and Yields of Methanol-Ethanol Reactions [a]

Catalyst	Recovered MeOH (mmol)	Recovered EtOH (mmol)	EtOH conversion (%)	2-Me propanal (mmol [%])	C_3 (mmol [%])	2-Me-1-PrOH (mmol [%])	2-Me-1-BuOH (mmol [%])	Others (mmol)
Glass wool/ MgO	118.90	14.71	16	0.00 (0)	2.50 (93)	0.25 (9)	0 (0)	0
Glass wool/ MgO/Ni	109.61	9.25	47	0.61 (7)	7.01 (86)	0.00 (0)	0 (0)	1.3
Lava rock/ MgO/Ni	115.54	15.17	13	0.17 (8)	0.85 (38)	0.51 (23)	0 (0)	0

[a] Flow rate, 0.1 mL/min; carrier flow, 66 cm^3/min; temperature, 360°C; time, 60 min. Percentages given in parenthesis refer to percent yield based on millimoles of product per millimole of ethanol converted.

Table 7
Intermediate Formation and Conversions and Yields for Catalytic Conversion of Methanol-Ethanol Mixture to Higher Alcohols [a]

Time (h)	EtOH conversion (%)	H_2CO (mmol)	Ethanal (mmol)	2-Me propanal (mmol [%])	1-PrOH (mmol [%])	2-Me-1-PrOH (mmol [%])	2-Me-1-BuOH (mmol [%])	Other (mmol)
1	94	1.75	0.57	0.67 (8)	0.64 (4)	10.49 (64)	0.23 (3)	3.88
2	90	0.39	0.25	0.94 (12)	1.69 (11)	8.32 (53)	0.44 (6)	3.12
4 [b]	45	0.04	1.51	1.07 (9)	3.23 (14)	8.00 (34)	1.88 (16)	6.86

[a] Catalyst, CM; flow rate, 0.1 mL/min; carrier flow, 66 cm^3/min; temperature, 360°C; time, 60 min; MeOH, 125 mmol; EtOH, 17.4 mmol. Percentages given in parenthesis refer to percent yield based on millimoles of product per millimole of ethanol converted.

[b] MeOH/EtOH ratio, 1:1; MeOH, 75 mmol; EtOH, 52.17 mmol.

For the glass wool support, the glass wool was added to the autoclave prior to aerogel preparation. The resulting catalysts were used as a catalyst for the conversion of the methanol-ethanol mixture; the results are given in Table 6. Owing to the broadness of the peak corresponding to C_3 alcohols and aldehydes, a clear distinction could not be made as to the identity or identities of the C_3 species in these products; that is, the major component could be propanal.

The results show that these high-surface MgO catalysts are inferior to the carbon-based sorbents. Even with added nickel to aid in hydrogen transfer reactions, the conversions are lower than those obtained with the carbon catalysts. Although some condensation of the aldehyde intermediates to C_3 compounds must have occurred, the condensation reaction does not proceed as well to the C_4 compounds.

Formation of Aldehyde Byproduct

To further improve the mass balance during catalytic conversion of the methanol-ethanol mixtures into higher alcohols, products were collected in two traps cooled by dry ice–isopropyl alcohol slurry, and gases from the second traps were bubbled through another trap containing a known weight of 2-(2-methoxyethoxy)ethanol cooled in a dry ice–isopropyl alcohol bath. Products from all of these traps were weighed and analyzed by GC; the results are given in Table 7.

From the reaction of the methanol-ethanol mixture with freshly prepared catalyst, 98% of the products was trapped in the two traps cooled in a dry ice–isopropyl alcohol bath. The third trap containing 2-(2-methoxyethoxy)ethanol cooled in a dry ice–isopropyl alcohol bath showed only traces of several products. Therefore, it was assumed that the remaining 2% of the material was gaseous products, as observed in previous reactions. In addition to the products described in Table 7, formaldehyde (1.75 mmol) and acetaldehyde (0.57 mmol) were also identified. When the same reaction was carried out with the used catalyst, almost 100% of the products was trapped in the first two traps. The third trap showed only traces of product as before. Other products were formaldehyde (0.39 mmol) and acetaldehyde (0.25 mmol).

Reactions using a methanol-ethanol ratio of 1:1 with catalyst recovered from the experiment described in the paragraph above were also carried out under similar conditions. The products from the first two traps amounted to 95.3 wt%. Products in the third trap were insignificant. Formaldehyde (0.04 mmol) and acetaldehyde (1.51 mmol) were observed. It is assumed that the remaining 4.7% was gaseous products.

Effect of Hydrogen in Carrier Gas

Since the product gas composition indicated that some hydrogen was not being utilized for hydrogenation of the higher-aldehyde intermediate to form additional alcohols, the effect of adding hydrogen as a carrier gas to further improve the product yield and product slate was investigated.

Recovered Centaur–20% MgO catalyst was used as the catalyst. As before, products were collected in two traps cooled in a dry ice–isopropyl alcohol bath, and gases from the second traps were bubbled through another trap containing a known weight of 2-(2-methoxyethoxy)ethanol cooled in a dry ice–isopropyl alcohol bath. Products from all these traps were weighed and analyzed by GC; the results are given in Table 8.

There did not appear to be a significant difference in the conversion and yields in the reaction in hydrogen compared with the reaction in nitrogen. Since the 2-methylpropanal was actually higher in the reaction using hydrogen, this appears to show that the gas-phase hydrogen is probably not used as effectively as the spillover hydrogen on the carbon catalyst, resulting from dehydrogenation of the ethanol and methanol.

From both of these reactions, almost 98% of the products was trapped in the two traps cooled in a dry ice–isopropyl alcohol bath. The third trap containing 2-(2-methoxyethoxy)ethanol cooled in a dry ice–isopropyl alcohol bath showed only traces of several products. Therefore, it was assumed that the remaining 2% of the material was gaseous products, as observed in previous reactions. Formaldehyde (0.65 mmol) and acetaldehyde (0.55 mmol) were also identified.

Effect of Pressure on Catalytic Conversion

The effect of pressure was investigated by carrying out a flow-through reaction under mild pressure. The results (Table 9) were compared with the previous flow-through reactions at ambient pressure as well as with a batch reaction under similar conditions. The increased pressure in the flow-through run as well as the batch run resulted in very low conversions of the ethanol. There may have been destruction of the base catalyst under this condition.

Catalytic Conversion of Recycled Products

Some of the aldehyde intermediates in the Guerbet reaction were always present in the product mixture. These can obviously be converted into higher-alcohol products in subsequent reactions, by recycling either the entire product mixture or only the lower alcohol/aldehyde portion recovered by distillation. The latter would be expected to occur in the process. To investigate the feasibility of increased conversion by recycling the entire product mixture, products obtained from a continuous run for 5 h were used. The products from 2- to 5-h runs were mixed together, and the composite was recycled through the CM catalyst under identical conditions; the data are given in Table 10.

The composite was very low in ethanol, so the conversion was naturally 100% in the recycle run. The recycled feed produced a very high yield of 2-methyl-1-propanol. The reaction also resulted in an increased formation of 2-methylpropanal. Thus, recycling of the lower alcohols containing some lower aldehydes should be effective for increasing higher-alcohol product yields, but this experiment has not yet been completed.

Table 8
Effect of Carrier Gas Composition on Conversions and Yields for Catalytic Conversion of Methanol-Ethanol Mixture to Higher Alcohols[a]

Carrier gas	Recovered MeOH (mmol)	Recovered EtOH (mmol)	EtOH conversion (%)	2-Me propanal (mmol [%])	1-PrOH (mmol [%])	2-Me-1-PrOH (mmol [%])	2-Me-1-BuOH (mmol [%])	Others (mmol)
N_2	87.1	1.02	94	0.67 (4)	0.64 (4)	10.49 (64)	0.23 (3)	3.9
H_2	84.6	0.94	95	0.94 (6)	1.42 (9)	10.72 (65)	0.61 (7)	2.5

[a] Catalyst, CM; flow rate, 0.1 mL/min; carrier flow, 66 cm^3/min of N_2 or H_2; temperature, 360°C; time, 60 min; MeOH, 125 mmol; EtOH, 17.4 mmol. Percentage given in parenthesis refers to percent yield based on millimoles of product per millimole of ethanol converted.

Table 9
Effect of Pressure on Conversions and Yields for Catalytic Conversion of Methanol-Ethanol Mixture to Higher Alcohols[a]

Conditions/ ratios (mmol)[b]	Recovered MeOH (mmol)	Recovered EtOH (mmol)	EtOH conversion (%)	2-Me propanal (mmol [%])	1-PrOH (mmol [%])	2-Me-1-PrOH (mmol [%])	2-Me-1-BuOH (mmol [%])	Others (mmol)
Ambient flow/ MeOH (250); EtOH (35)	197.81	3.47	90	1.45 (5)	2.02 (6)	19.35 (62)	0.95 (6)	2.6
2.1 MPa flow/ MeOH (312); EtOH (43)	272.1	26.79	38	1.24 (8)	1.52 (9)	11.79 (71)	0.22 (3)	2.6
Batch/MeOH (130); EtOH (18)	124.6	17.8	2	Trace (0)	Trace (0)	Trace (0)	Trace (0)	Trace

[a] Catalyst, CM (recovered); temperature, 360°C. Percentage given in parenthesis refers to percent yield based on millimoles of product per millimole of ethanol converted.

[b] Ambient flow, injected at 0.1 mL/min using a syringe pump under ambient pressure for 120 min; 2.1 MPa flow, injected at 0.5 mL/min using a syringe pump under pressure for 30 min; batch, reaction carried out in a sealed-tube reactor for 30 min.

Table 10
Conversions and Yields for Catalytic Conversion of Recycled Products [a]

Sample	Recovered MeOH (mmol)	Recovered EtOH (mmol)	EtOH conversion (%)	2-Me propanal (mmol)	1-PrOH (mmol)	2-Me-1-PrOH (mmol)	2-Me-1-BuOH (mmol)	Other (mmol)
Initial product	97.19	2.98	—	1.53	1.32	8.35	0.63	2.68
Recyled product	88.57	0	100	1.86	1.28	10.87	0.80	3.09

[a] Catalyst, CM; flow rate, 0.1 mL/min; MeOH, 125 mmol; EtOH, 17.4 mmol; carrier flow, 66 cm^3/min; temperature, 360°C; time, 1 h.

Mixed Alcohol Fuel Production

A larger quantity of the actual higher-alcohol product mixture was desired for fuel characterization tests. The mixture of higher Guerbet alcohols was prepared by catalytic conversion of a methanol-ethanol mixture (5:1 volume ratio) with the CM catalytic carbon prepared during this project. Reactions were carried out continuously, and products were collected in dry ice–cooled traps and removed every 2 h for several days. The reactions were carried out under the following conditions: catalyst = CM; reactor = 40-cm-long, 2.5-cm-stainless steel reactor; feed = methanol-ethanol (5:1); flow rate = 0.5 mL/min; carrier gas = 66 cm^3/min of nitrogen; temperature = 360°C; pressure = ambient.

The alcohol mixture was distilled to remove the majority of methanol, ethanol, formaldehyde, acetaldehyde, and water. Remaining water was removed with the use of 3A molecular sieves. The composition of the alcohol mix after removal of most of the methanol and ethanol was as follows: (2.9%) methanol, (1.9%) ethanol, (11.9%) *n*-propanol, (81.3%) 2-methyl-1-propanol, (1.4%) 2-methyl-1-butanol, and (0.7%) other components. Attempts to remove the small amounts of residual methanol and ethanol using 4A molecular sieves were not successful.

No attempt was made to separate the higher alcohols by distillation, since purification is not needed for fuel-grade products. To obtain higher-purity 2-methyl-1-propanol, an alternative to distillation is to return the product mixture to the reactor to further convert 1-propanol to 2-methyl-1-propanol with excess methanol. Further methylation of either 2-methyl-1-propanol or 2-methyl-1-butanol was never observed. Identification of the minor products is in progress.

The distilled alcohol product mixture was also esterified by refluxing with glacial acetic acid in the presence of a catalytic amount of sulfuric acid. The product was extracted with water followed by extraction with saturated sodium bicarbonate solution. It was further washed with water and dried over anhydrous sodium sulfate. The crude ester was distilled, and the distillate was stored for further use. The percent yield of esters was 86%. The mixed ester was determined by GC to be composed of (1.3%) methyl acetate, (1.3%) ethyl acetate, (11.5%) *n*-propyl acetate, (81.7%) isobutyl acetate, (1.2%) 2-methyl-1-butyl acetate, and (1.9%) other components. The composition corresponded closely to that of the parent alcohol mixture. The fuel characteristics of the alcohol mixture and the ester mixture prepared from it were reported earlier *(24)*.

Conclusion

Base-modified carbons were highly effective for producing higher alcohols. In the methanol-ethanol (5:1) reactions, 90–100% of the ethanol was converted into products with the carbon catalysts. Selectivities for the major product, 2-methyl-1-propanol, vary from 65 to 85%, based on ethanol. Less than 3% of methanol was converted into gases. Other minor products were 1-propanol and 2-methyl-1-butanol. Small amounts of aldehyde intermediates were found. Best results were obtained at 360°C and ambient pressure. Adding hydrogen to the carrier had a negligible effect on yields. Adding nickel during the impregnation step in the preparation resulted in even higher yields of alcohol products.

For comparison with the carbon-based catalysts, several MgO catalysts were prepared on silica and alumina supports, and a very high-surface MgO aerogel was also prepared. Testing these under the same conditions gave very poor yields of the desired alcohols. It is clear that the carbon structures promote the activity, very likely by catalyzing the dehydrogenation and hydrogenation steps.

Although these high yield results and the low gas make were highly encouraging, the loss of activity with time was still a concern. Conversions dropped 20–30% after several days. Runs over longer time periods are currently being investigated to determine service life of the catalysts. Regeneration of spent carbon catalysts has been investigated and will be reported elsewhere.

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