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Advances in catalytic synthesis and utilization of higher alcohols

R.G. Herman [*]

Lehigh University, Zettlemoyer Center for Surface Studies, Sinclair Laboratory, 7 Asa Drive, Bethlehem, PA 18015, USA

Abstract

Alcohols can be used directly as fuels and fuel additives or as intermediates to form high octane or high cetane ethers. Catalysts have been improved to synthesize the higher alcohols, especially isobutanol, from coal- or natural gas-derived H_2/CO synthesis gas, and reaction engineering approaches are being investigated to further increase the activities and selectivities of the reactions forming the higher alcohols. These approaches include (a) using a dual catalyst bed reactor for gas phase conversions and (b) employing a slurry phase reaction system for increasing the reaction rate of the exothermic synthesis reactions. These developments have led to higher alcohol productivities. For example, with double bed Cs/Cu/ZnO/Cr_2O_3 catalysts, productivities of isobutanol and total alcohols as high as 202 and 947 g/kg catalyst/h, respectively, have been achieved. However, declining petroleum prices over the last three years have pushed the economic break-even point to even greater productivity levels of isobutanol and of a mixture of the higher alcohols. It is shown that alcohols and certain ethers have desirable properties as octane enhancers, while other ethers could be used as additives to enhance the cetane number of diesel fuel. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Alcohol synthesis; Isobutanol; Methanol; Copper catalysts; Higher alcohols; Slurry phase

1. Introduction to alcohol synthesis

Catalytic synthesis of methanol from $H_2/CO/CO_2$ synthesis gas is one of the most active and selective industrial processes carried out on a commodity scale today [1–5]. The synthesis gas is typically obtained by steam reforming of natural gas (methane) at high temperatures such as 800–850°C over Ni-based catalysts [6] or by gasification of coal [5]. The former process results in a hydrogen-rich synthesis gas that is suitable for direct conversion to CH_3OH, while the latter results in a hydrogen-poor synthesis gas, e.g. $H_2/CO = 0.45–1$. In all cases, the resultant synthesis gas also contains CO_2, the presence of which at a low optimum concentration is necessary for high conversion of synthesis gas to methanol [7–10]. Methanol synthesis is carried out over (a) low temperature and pressure (250°C and 5–10 MPa (≈50–100 atm; ≈750–1500 psig)) copper-based catalysts that contain ZnO and an oxide support, e.g. Cu/ZnO/Al_2O_3 or Cu/ZnO/Cr_2O_3, or (b) high temperature and pressure (≈400°C and 10–20 MPa) copper-free ‘zinc chromite-type’ (ZnO/Cr_2O_3) catalysts [3,5,10–14]. Most commercial plants now utilize the low temperature/pressure catalysts.

For approximately the last 15 years, there has been intensive research centered on the development of active and selective catalysts for shifting the synthesis away from methanol and toward higher alcohols, i.e. C_2–C_4 alcohols, especially isobutanol (2-methyl-1-propanol). The resultant alcohols could be used directly as fuels, as fuel additives for octane or cetane enhancement, as oxygenate fuel additives for environmental reasons, and as intermediates to form other fuel additives such as methyltertiarybutylether (MTBE), as partially discussed elsewhere [15]. As

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[*] Corresponding author.

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Table 1
Productivities (g/kg catalyst/h) of isobutanol, total alcohols, and total hydrocarbons (HC) over alkali-promoted Zn/Cr catalysts using a $H_2/CO = 1$ synthesis gas

Promoter	Temperature (°C), Pressure (MPa)	GHSV (ℓ/kg catalyst/h)	Isobutanol	Total alcohols	Total HC	Ref.
Cs	405, 8.5	8000[a]	84	218	?	[17]
Cs	390, 7.6	7300	50	≈172	≈27	[14]
Cs	405, 7.6	18375	74	288	20	[18]
K	440, 10.3	12000	103	167	101	[19,20]
Cs	440, 10.3	12000	116	214	35	[21]
Cs + Pd	400, 6.9	?	80	166	48	[22]
Cs + Pd	440, 10.3	?	142	227	77	[22]

[a] The gas hourly space velocity is expressed as h^{-1}.

has been demonstrated with a continuous flow of a methanol/isobutanol reactant mixture in a two-stage reactor system using different acid catalysts, isobutanol can be dehydrated to isobutene, followed by coupling with methanol to form MTBE [16].

2. Gas phase synthesis of higher alcohols

In the first half of this century, ZnO/Cr_2O_3 catalysts promoted by alkali were used in a number of processes to produce mixtures of higher alcohols, but these processes were very non-selective [11]. Large quantities of hydrocarbons were usually formed. The catalysts were subsequently improved, in part by using a heavy alkali ion dopant, in terms of alcohol selectivity and productivity, as indicated in Table 1 [14,17–22]. In the data presented in this table, eight linear and branched alcohols, along with a small quantity of secondary alcohols, were considered by Herman and Lietti [14], while Epling et al. [22] tabulated only the oxygenates methanol, ethanol, isopropanol, n-propanol, and isobutanol. Beretta et al. [18] included 14 C_1–C_7 alcohols in the analysis reported. Thus, it is evident that isobutanol is a principal alcohol formed over these ‘zinc chromite-type’ catalysts under these high temperature conditions. In these examples, different Zn/Cr ratios and alkali-doping levels were utilized, but these results were typically the best observed in each study of these catalysts. The high reactor temperature required for these catalysts still tends to form appreciable yields of hydrocarbons.

During the 1980s, it was found that low temperature copper-based, zinc oxide-containing catalysts promoted by heavy alkali were much more active and selective toward the synthesis of higher alcohols than were the copper-free catalysts [1,4,23–34], forming principally C_2–C_4 alcohols in addition to methanol. The dominant alcohol in the mixture was methanol, while the second most abundant alcohol formed was the branched isobutanol. It was shown that the higher alcohols were formed by a unique carbon-chain growth mechanism, referred to as oxygen retention reversal aldol condensation, centered on β-carbon addition [4,33–38]. The growth step of forming isobutanol from n-propanol is shown in Eq. (1), where the β-carbon is defined as the carbon adjacent to the carbon bonded to oxygen.

$$\begin{aligned} &CH_3CH_2CH_2\,OH + {*}CO/2H_2 \\ &\quad \Rightarrow (CH_3)_2\,CH * CH_2\,OH + H_2O \end{aligned} \tag{1}$$

A dominant factor in guiding the product selectivity was the relative reaction rate for each C–C bond forming step, e.g. $C_1 \Rightarrow C_2 \Rightarrow C_3 \Rightarrow C_4$. Studies by Smith et al. [28,35,36] of the kinetics of the reaction steps showed that the slow, rate-determining step in forming the higher alcohols from synthesis gas was the $C_1 \Rightarrow C_2$ step, as earlier proposed by Frolich and Cryder [39] and more recently confirmed by Hilmen et al. [40]. Note that in this C–C bond-forming process of forming ethanol from methanol, there is no β-carbon to assist in the ‘formose-type’ chemistry that is observed over these catalysts. The subsequent $C_2 \Rightarrow C_3$ and $C_3 \Rightarrow C_4$ synthesis steps proceed at faster rates, and this leads to a depletion of ethanol in the reaction mixture. Branched alcohols are terminal products, and this leads to an enrichment in the product mixture of branched alcohols such as isobutanol.

In Eq. (1), the oxygen that is incorporated into the alcohol product is derived from the oxygenated C_1 intermediate formed from the $^*CO/H_2$ reactants, as shown by isotopic labelling studies [32,41]. The promotional effect for higher alcohol synthesis depended upon the alkali cation, with the productivity increasing in the series $K^+ < Rb^+ < Cs^+$ [25,29], corresponding to increasing basicity. It is noted that for higher alcohol synthesis, the initial synthesis gas is essentially free of CO_2, and the H_2/CO molar ratio is ≤ 1. Elevated levels of CO_2 tend to inhibit the synthesis of higher alcohols.

During this same period of time, it was shown that higher alcohols were also formed over alkali-promoted transition metal sulfide catalysts, particularly MoS_2 [41–49]. The reaction conditions needed were in a similar range, e.g. $H_2/CO \approx 1$, 275–325°C, and 7.5–10 MPa, to that employed with the low temperature copper-based oxide catalysts. In contrast to the alkali-promoted Cu-based catalysts, it was shown that the higher alcohols formed over the sulfide catalysts were linear and C–C bond formation proceeded via a CO-insertion mechanism [4,35,41,49]. Labelling studies demonstrated [49] that the formation of n-butanol was formed from n-propanol as depicted by Eq. (2).

$$CH_3CH_2CH_2OH + {*CO}/2H_2 \Rightarrow CH_3CH_2CH_2 * CH_2OH + H_2O \qquad (2)$$

In addition to the alcohols formed over the alkali- promoted sulfide catalysts, the product contained some 15–20% hydrocarbons (or even more), principally consisting of methane. The carbon number distribution of both the alcohols and the hydrocarbons followed the Anderson–Schulz–Flory (ASF) distribution, with methanol being the principal product, but with the $C_1 \Rightarrow C_2$ growth step being appreciably rapid. Again the Cs^+ promoter was found to be the best promoter among the alkali metal cations. An advantage of the sulfide catalysts is the absence of poisoning induced by sulfur impurities in the synthesis gas, unlike the copper-based catalysts. In addition, the sulfide catalysts are not as sensitive to the presence of CO_2 in the synthesis gas, but large quantities of CO_2 tend to retard the conversion of CO to products. In addition to forming appreciable quantities of hydrocarbons and facing a limited selectivity to higher alcohols because of the ASF distribution, the sulfide-based catalysts are, to-date, less active than the oxide-based catalysts, especially the Cu/ZnO-based catalysts. An innovation is needed to make the sulfide catalysts more active and selective, perhaps by increasing the alkali dispersion and moderating the hydrogenation ability of the catalysts.

A recent approach taken to increase the productivity of isobutanol formation from synthesis gas was to combine ZnO with an ‘isosynthesis’ component, i.e. ZrO_2, and promote the catalyst with a redox oxide and a strong base [50–52]. Isosynthesis is a high pressure process directed toward converting synthesis gas to aliphatic branched hydrocarbons, especially C_4 hydrocarbons [53]. The alcohol synthesis catalysts being developed also require not only a high reaction temperature but also a high pressure, i.e. 25 MPa, to achieve alcohol formation. Examples of these catalysts and the observed productivities are given in Table 2. High productivities and selectivities of isobutanol were observed with these catalysts. For example, it was reported that 59% of the product formed over the Li/Pd/Zr/Zn/Mn catalyst was isobutanol (including H_2O but excluding CO_2) [50]. With the K/Pd/Zr/Zn/Mn catalyst, 44% of the CO was converted to products, but the selectivity was 40–50% to CO_2 [51]. The synthesis rate for the alcohols was remarkable, but an appreciable yield of hydrocarbons was also obtained. Without the presence of Pd, the alcohol productivity was still high, with methanol being the dominate product, but the isobutanol formation rate was appreciably lower than when Pd was added to the catalyst [52]. A disadvantage of these catalysts is the high reaction temperature required to achieve high alcohol productivities.

3. Challenges for higher alcohol synthesis and newer engineering concepts

Advances that need to be made in the synthesis of higher alcohols from synthesis gas include:

- Productivity of higher alcohols needs to be increased. Over the oxide catalysts, the initial step in the C–C bond-forming process is too slow, i.e. the $C_1 \Rightarrow C_2$ step that leads from methanol to ethanol is the bottleneck to forming isobutanol in high space time yields.

Table 2
Productivities (g/ℓ catalyst/h) of isobutanol, total alcohols, and other products over alkali-promoted Zr/Zn/Mn catalysts using a $H_2/CO = 1$ synthesis gas

Promoter	Temperature (°C), Pressure (MPa)	GHSV (h^{-1})	Isobutanol	Total alcohols	Other products	Ref.
Li/Pd	420, 25	20000	744		?	[50]
K/Pd	427, 25	20000	≈630	1010	≈235	[51]
K	370, 25	23250	35	≈869	?	[52]
K	430, 25	23250	142	≈876	?	[52]

- Selectivity needs to be improved over some of the catalysts under development to minimize the quantity of side-products formed, especially the formation of hydrocarbons that is especially pronounced over sulfide catalysts.

Approaches to achieve higher space time yields of higher alcohols that are being investigated include:

- Using Cs-promoted, Cu-free Zn/Cr catalysts at elevated temperatures in the range of 375–450°C [14,17,22] where methanol formation is suppressed by the thermodynamics of the reaction. However, the higher temperatures are a disadvantage because they increase the productivity of hydrocarbons along with that of the alcohols and tend to decrease the alcohol selectivity.
- Injection of ethanol or n-propanol into the synthesis gas stream entering a fixed-bed continuous flow reactor to react directly with the C_1 intermediate on the catalyst surface [14,28,40,54]. This technology needs further study, and it is noted that it would also need a source of ethanol or n-propanol or utilize extensive recycling.
- Coupling two catalyst beds in series at different reaction temperatures to optimize the chemistry of the different C–C bond-forming steps, e.g. the $C_1 \Rightarrow C_2$ step and the subsequent growth steps [18,55–57]. This is under exploratory investigation.
- Carry out the synthesis using a catalyst in a slurry phase reactor rather than in fixed bed configuration [58–62], which has some advantages, e.g. high heat transfer of the exothermic heat of reaction, but is more technologically challenging than utilizing a fixed-bed gas phase tubular reactor. This is based on the earlier Chem Systems approach for methanol synthesis at high conversion rates in a slurry phase reactor [63–66]. Injection of methanol, ethanol, and/or n-propanol could also be employed to enhance the formation of higher alcohols [60].

4. Dual catalyst bed reactors for isobutanol synthesis

Although the chain growth to higher oxygenates *via* aldol condensation over basic oxide catalysts is governed by kinetic factors, thermodynamic constraints dictate the product composition as far as the yields of methanol and side-products esters are concerned. By operating at higher temperatures, it is expected that the selectivities of higher oxygenates will be increased due to thermodynamic, as well as kinetic, reasons at the expense of methanol. A reason for this is that methanol has an unfavorable equilibrium constant for high temperature operation (with methanol increasingly decomposing back to synthesis gas as temperature is increased). A second reason is that branched alcohols, i.e. the 2-methyl products, are unreactive and are terminal products, while linear alcohols, i.e. ethanol, n-propanol, and n-butanol, can undergo further coupling reactions [4,14,27,36,37,41]. Thus, the yields of branched alcohols tend to increase with temperature, while linear alcohols exhibit a maximum. It is concluded that operating at high temperatures will favor the isobutanol/methanol molar ratio and the 2-methyl branched/linear alcohols molar ratio. However, operation at very high temperatures leads to little of the synthesis gas being converted to methanol (for thermodynamic reasons), which is the intermediate leading to higher alcohols.

The concept of the double bed configuration is to maximize the formation of methanol from synthesis gas over the first catalyst bed at lower reaction temperature and to maximize the C–C bond-forming steps and subsequent formation of isobutanol over the second bed at higher reaction temperature [18]. This concept is schematically shown in Fig. 1. Since copper-containing catalysts are low temperature alcohol synthesis catalysts and zinc chromite-type

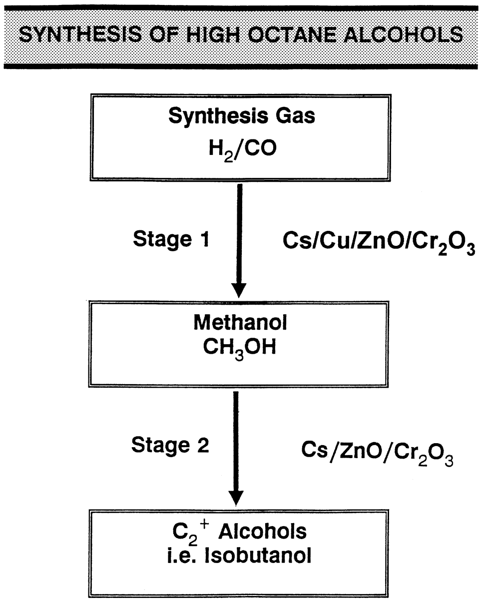

Fig. 1. A schematic of a two-stage catalyst reaction system for the gas phase synthesis of higher alcohols from synthesis gas, where the catalysts can be in the same reactor but different temperatures.

catalysts are high temperature catalysts, these two catalysts were utilized in the laboratory-scale dual catalyst beds reactor. This configuration is designated as $Cs/Cu/ZnO/Cr_2O_3||Cs/ZnO/Cr_2O_3$, as follows from Fig. 1. Testing was carried out with a $H_2/CO = 0.75$ synthesis gas at 7.6 MPa, and a comparison of the productivities obtained with the dual bed reactor to those observed with the single bed catalysts is given in Table 3 [18]. It is clear that the isobutanol productivity was more than doubled (to 138.8 g/kg catalyst/h) by using the dual bed reaction as compared with only using the $Cs/Cu/ZnO/Cr_2O_3$ catalyst.

Since it is known that the exothermic methanol synthesis reaction is thermodynamically limited by high temperature, the effect of reaction pressure was probed to determine if it had a significant effect on the synthesis rate of isobutanol [57]. For these studies, a synthesis gas with $H_2/CO = 1$ was utilized, and the pressure was varied in the range of 7.6–12.4 MPa. The space time yields observed for methanol, ethanol, n-propanol, and isobutanol are shown in Fig. 2. It is clear that increasing pressure greatly increased the productivity of methanol, resulting in nearly tripling of the space time yield (Fig. 2A). At the same time, the isobutanol space time yield increased by ca. 60%. Thus, pressure had a positive effect on the synthesis of the alcohols, but the effect was most pronounced for methanol formation. Little effect on total hydrocarbon (HC) formation was noted (with CH_4 increasing but C_2H_4 decreasing), with space time yields remaining in the range of 28–40 g HC/kg catalyst/h. At 12.4 MPa, the CO conversion to products, exclusive of CO_2, was 11.6%.

The effect of the flow rate of the reactants on the productivities of the single bed and double bed catalysts has been investigated [55] at 7.6 MPa. The largest effects of the flow rate on the synthesis of higher alcohols were observed over the 4 mol% $Cs/ZnO/Cr_2O_3$ and the double bed $Cs/Cu/ZnO/Cr_2O_3||Cs/ZnO/Cr_2O_3$ catalysts. Analysis of the data demonstrates, as shown in Fig. 3, that as the GHSV of the $H_2/CO = 0.75$ reactants was progressively increased over the double bed catalysts, all of the principal products increased, especially methanol. However, it is noted that at GHSV = 5450 ℓ/kg catalyst/h, the largest residence time studied, the principal product was isobutanol. At this flow rate, the CO conversion, exclusive of CO_2 formation was 12.0%. Fig. 4 shows that the conversion decreased as the reactant flow rate increased. With the decreasing residence time of the reactants in the catalyst beds, the weight ratio of the 2-methyl branched C_4–C_7 alcohols relative to the linear C_1–C_6 linear alcohols also decreased. Thus, longer residence times enhance the selectivity of the 2-methyl branched alcohols relative to the linear alcohols, but the highest productivities of branched alcohols occur at higher GHSV because of the larger quantity of reactants being passed over the catalysts per unit time. Appreciable quantities of C_{7+} oxygenates were formed during these experiments, especially at GHSV = 12 000 ℓ/kg catalyst/h, with both the single bed catalysts and the double bed catalysts, but maximizing the productivities of these products has not been investigated.

Since high temperature tends to favor the formation of various side-products that include CH_4 and DME, a study was carried out in which the Stage 1 promoted zinc chromite-type catalyst (see Fig. 1) that requires high temperature was replaced by a second portion of the copper-containing catalyst. This allowed the reaction temperature to be reduced because of the higher intrinsic activity of the copper-based catalyst compared with the copper-free catalyst. As seen in Table 4, appreciably higher productivities of isobutanol were

Table 3

Higher alcohol synthesis (productivities expressed in g/kg catalyst/h) over the 3 mol% $Cs/Cu/ZnO/Cr_2O_3$ catalyst, the 4 mol% $Cs/ZnO/Cr_2O_3$ catalyst (Harshaw Zn-0311 T doped with Cs), and the double bed combination of the two catalysts (1 g of each separated by 20 cm in a downflow tubular reaction) with $H_2/CO = 0.75$ at 7.6 MPa and with GHSV = 18 375 ℓ/kg catalyst/h [18]

Product[a]	$Cs/Cu/ZnO/Cr_2O_3$ 325°C	$Cs/ZnO/Cr_2O_3$ 405°C	$Cs/Cu/ZnO/Cr_2O_3$ Top = 325°C $Cs/ZnO/Cr_2O_3$ Bottom = 405°C
MeOH	1200	173.4	178.8
EtOH	68.7	2.7	7.1
PrOH	83.2	11.5	23.5
BuOH	15.2	0.9	4.2
PentOH	9.6	0.6	3.1
HexOH	10.0	0.3	2.4
2Me-PrOH	65.6	74.1	138.8
2Me-BuOH	21.0	8.3	32.9
2Me-PentOH	14.4	5.3	21.7
2Me-HexOH	13.5	0.9	24.0
2-BuOH	9.6	2.5	5.2
3Me-2-BuOH	10.1	0.9	7.2
3-PentOH	10.2	1.2	7.7
2Me-3-PentOH	16.0	5.5	23.1
Me-Formate	20.4	1.1	11.3
Me-Acetate	11.7	0.8	1.7
DME	5.3	4.7	4.8
C_7^+ Oxygenates	53.9	78.0	81.5
CH_4	10.4	4.1	12.1
C_2-C_4 HC	8.1	15.6	27.9
CO Conversion (%) (CO_2-free)	11.7	4.5	6.6

[a] The productivities of small amounts of aldehydes and ketones have been summed to those of the corresponding primary and secondary alcohols, respectively. Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl; DME, dimethylether; HC, hydrocarbon, etc.

achieved, while the quantities of side-products were significantly reduced [56]. It is noted that the isobutanol (2Me-PrOH)/methanol mass ratios were about 0.35 and 0.5 for the lower bed temperatures of 340 and 370°C, respectively. The selectivities of the isobutanol and methanol were especially notable. At the bottom bed temperature of 340°C, 67% of the C in the products was in these two alcohols. If n-propanol is included along with isobutanol and methanol, then 80% of the carbon found in the alcohol and hydrocarbon products was obtained in these three alcohols. Further engineering optimization of this process could be carried out. For example, kinetic modelling indicated that the 1/1 bed sizes used in this study were not the optimum for achieving the highest space time yields of isobutanol [56].

It is noted that the dual bed reactor studies were carried out at 7.6 MPa. This contrasts with the high pressure studies summarized in Table 2, which were carried out at 25 MPa. However, the total alcohol productivities were comparable. For example, as shown in Table 2, the high pressure studies at 370°C gave 35 and ≈869 g/l catalyst/h of isobutanol and total alcohols, respectively (at 9.8% CO conversion on a CO_2-free basis) [52], while the lower pressure studies at the same temperature for the bottom bed (Table 4) gave 180 and 645 g/kg catalyst/h of isobutanol and total alcohols, respectively [56]. At the lower pressure, decreasing the temperature of the bottom bed to 340°C (Table 4) increased the space time yields of both isobutanol and total alcohols to 202 and 947 g/kg catalyst/h, respectively, because of the increased synthesis rate of the methanol building block in the higher alcohol synthesis (at 8.5% CO conversion on a CO_2-free basis) [56].

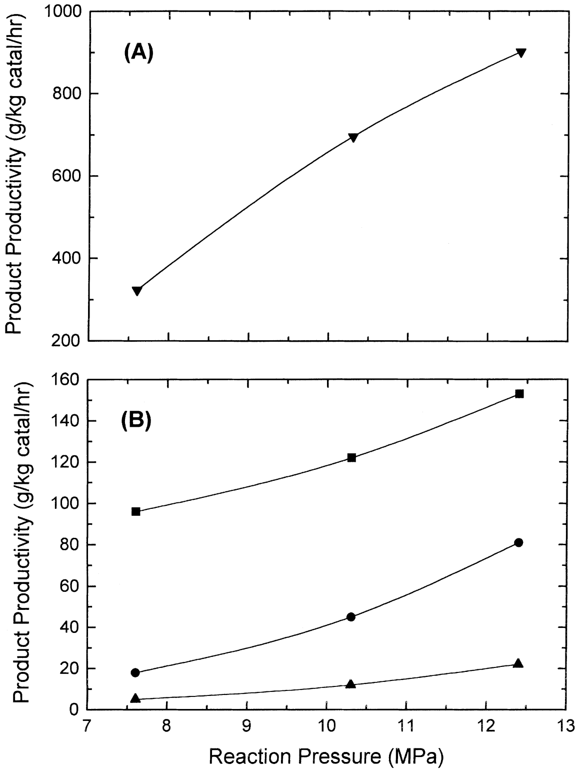

Fig. 2. Space time yields of (A) methanol (▼) and (B) ethanol (▲), n-propanol (●), and isobutanol (■) as a function of reaction pressure using the $Cs/Cu/ZnO/Cr_2O_3||Cs/ZnO/Cr_2O_3$ double bed reactor with $H_2/CO = 1.0$ synthesis gas with GHSV = 18 375 ℓ/kg catalyst/h. The temperatures of the top and bottom catalyst beds (1 g each) were 325 and 405°C, respectively.

5. Status of the slurry phase synthesis process

The slurry phase synthesis gas conversion reaction was developed by Chem Systems in the 1970s for the synthesis of methanol [63–66], and the U.S. Department of Energy and Air Products and Chemicals joined in 1979 to further develop this process technology for methanol synthesis and other exothermic reactions [61]. The reactions of interest include the conversion of synthesis gas to Fischer–Tropsch hydrocarbons, isobutanol, and dimethylether over different types of catalysts. This technology has now been developed to the stage where catalyst concentrations of up to 50 wt% can be dispersed in an inert hydrocarbon oil.

Advantages of the slurry phase reactor system include the following:

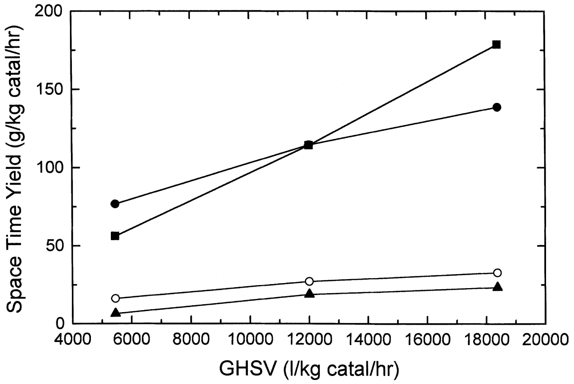

Fig. 3. Space time yields of methanol (■), n-propanol (▲), isobutanol (●), and 2-methyl-1-butanol (○) over the $Cs/Cu/ZnO/Cr_2O_3||Cs/ZnO/Cr_2O_3$ double bed catalysts with $H_2/CO = 0.75$ synthesis gas as a function of the synthesis gas flow rate (GHSV). The temperatures of the top and bottom catalyst beds were 325 and 405°C, respectively.

- High heat transfer rate, which is beneficial for the highly exothermic alcohol synthesis reaction and allows the reaction to be run at higher conversion rates (with no diffusion limitations) than commercially practiced in the methanol synthesis process.
- Good temperature control and thermal moderation of the reaction system, which prevents hot spots that induce sintering and deactivation of the catalyst.
- Ability to add fresh charges of catalyst to the slurry phase reactor on-line and withdraw portions of used

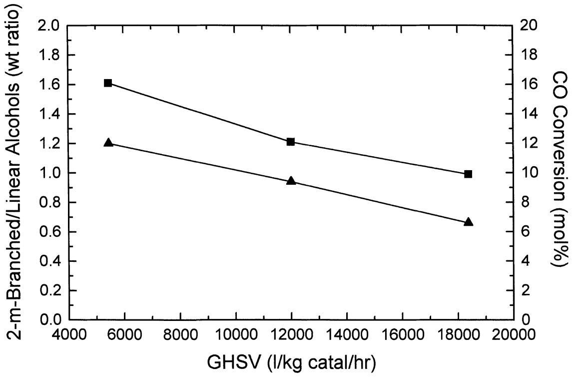

Fig. 4. The ratio of the 2-methyl branched C_4–C_7 alcohols to the linear C_1–C_6 alcohols (■) and the CO conversion (▲) over the $Cs/Cu/ZnO/Cr_2O_3||Cs/ZnO/Cr_2O_3$ double bed catalysts with $H_2/CO = 0.75$ synthesis gas as a function of the synthesis gas flow rate (GHSV). The temperatures of the top and bottom catalyst beds were 325 and 405°C, respectively.

Table 4
Higher alcohol synthesis (productivities expressed in g/kg catalyst/h) over the double bed configuration of two equal portions of a 3 mol% $Cs/Cu/ZnO/Cr_2O_3$ catalyst (1 g beds separated by 20 cm in a downflow tubular reaction) with $H_2/CO = 0.75$ at 7.6 MPa and with GHSV = 18 375 ℓ/kg catalyst/h [56]

Product[a]	Top Bed = 325°C Bottom Bed = 340°C	Top Bed = 325°C Bottom Bed = 370°C
MeOH	574	369
EtOH	15	5
PrOH	93	47
BuOH	0	1
PentOH	0	1
2Me-PrOH	202	180
2Me-BuOH	7	6
2Me-PentOH	5	5
2-BuOH	26	20
3Me-2-BuOH	1	0
3-PentOH	11	9
2Me-3-PentOH	13	2
Me-Formate	<0.6	–
Me-Actate	<0.7	–
DME	<0.5	–
CH_4	14	22
C_2–C_4 HC	24	22
CO Conversion(%) (CO_2-free)	8.5	6.2

[a] The productivities of small amounts of aldehydes and ketones have been summed to those of the corresponding primary and secondary alcohols, respectively. Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl; DME, dimethylether; HC, hydrocarbon, etc.

catalyst, which can increase plant on-stream days and less downtime.

A pilot plant scale demonstration of isobutanol synthesis has been carried out by Air Products and Chemicals in the U.S. DOE Alternative Fuels Process Development Unit located in LaPorte, TX (initially designed to produce methanol at the rate of 10 t/day [61]). This was carried out in a 0.45 m diameter stainless-steel reactor with a design slurry height of 12.2 m, a schematic of which is shown in Fig. 5 [59]. This reactor is designed to operate at up to 1800 psig (≈12.5 MPa) and 350°C, with a heat removal rate of 2.8 MMBtu/h [59]. The charge to the reactor consisted of 502 kg of Cs-promoted $Cu/ZnO/Al_2O_3$ catalyst in a 40 wt% oil slurry, and a Shell synthesis gas (nominally 30% $H_2 + 66\%\ CO + 3\%\ CO_2 + 1\%\ N_2$) was utilized for the testing [60]. Each run under a given set of reaction conditions was carried out for one or two days, and the steady-state conversions were monitored. The results are given in Table 5.

At 300°C under the conditions employed, the productivities of isobutanol were in the range of 17–26 g/kg catalyst/h. The testing results shown in Table 5 were obtained sequentially, and the last set of results was obtained while injection of a mixture of methanol, ethanol, and n-propanol was carried out. The injection composition was nominally 84% methanol, 5% ethanol, and 11% n-propanol. This injection increased the space time yield of isobutanol by 2.8 times that obtained without the alcohol addition, indicating that these alcohols were incorporated into the isobutanol product. This sequence of experiments was carried out in parallel in a laboratory autoclave, and all results were very similar to the much larger pilot plant scale [60].

6. Fuel additive characteristics of oxygenates

Oxygenates tend to be high energy fuels, and they directly provide oxygen to the fuel mixture when used as additives. Advantages of using alcohols as fuel additives include (a) expansion of the gasoline volume,

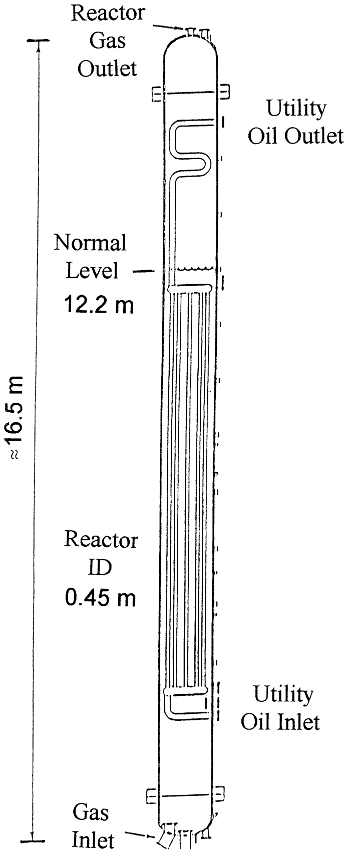

Fig. 5. A schematic of the slurry phase reactor at the U.S. Department of Energy/Air Products and Chemicals alternative fuels process development unit located in LaPorte, TX, which on the basis of methanol has a capacity of producing 600 lb mol/h.

(b) enhanced octane rating, (c) environmental benefits, and (d) possible utilization of existing gasoline infrastructure and vehicles. From Table 6, it is evident that alcohols are high octane fuels but have poor cetane characteristics. For the ethers, the structure of a particular ether directs its fuel properties. For example, methyl isobutyl ether (MIBE) has a poor blending octane number but a high cetane number. This is opposite to the properties of MTBE. MIBE has a secondary carbon in its structure, while MTBE has a tertiary carbon that is bonded directly to the ether oxygen. It is noted here that the high cetane MIBE can be formed directly from methanol and isobutanol over acid catalysts [16,75,76], but catalysts with higher activity and selectivity are needed.

7. Status of commercial feasibility

In considering the development of catalysts for higher alcohol synthesis, it was indicated that high alcohol selectivity is the most important parameter to achieve from a commercial viewpoint [77]. In addition, the higher alcohol/methanol molar ratio is important. The required synthesis gas conversion level was projected to be on the order of 5–10% [77] or 15–20% [78], while the total alcohol productivity should be at least 200–500 g/kg catalyst/h [77]. From the data in Table 4 for the lower bottom bed temperature of 340°C, the following results were obtained with the double bed catalyst:

Alcohol selectivity	94 mol%
Higher alcohol/methanol molar ratio	0.30
CO conversion (CO_2-free basis)	8.5%
Total alcohol productivity	947 g/kg catalyst/h

From a viewpoint of forming ethers as fuel additives, using data from an early Chem Systems report, a subsequent projection was made that 57 g of isobutanol/kg catalyst/h would have to be achieved to be industrially viable for subsequent synthesis of MTBE from isobutanol rather than butene derived as a by-product of petroleum refining [79]. Table 3 shows that this has been achieved over the methanol synthesis catalysts that were Cs-promoted. Tables 3 and 4 show that the dual catalyst bed configuration produces isobutanol at rates that are double or triple this target. It was pointed out that the projection of a relatively high price for isobutanol was not realized because the price of petroleum remained stable, the supply of isobutanol did not become limiting, and MTBE prices remained fairly steady [79]. Thus, a new projection in 1994 for producing isobutanol from synthesis gas for synthesis of MTBE indicated that an isobutanol productivity of 400 g/kg catalyst/h would be necessary to be economically competitive in the MTBE market place [79].

A more recent economic study was carried out by Bechtel for a stand-alone liquid phase mixed alcohol plant using natural gas feed that yielded $H_2/CO = 2.02$ synthesis gas by partial oxidation that was shifted to $H_2/CO = 3.3$ [80]. Presuming a high per pass conversion of 45% and recycling to achieve 98% overall conversion (with methanol and MTBE prices

Table 5
Productivity (g/kg catalyst/h) of isobutanol and of the C_2–C_6 alcohols from the pilot plant scale slurry phase reactor over a $Cs/Cu/ZnO/Al_2O_3$ catalyst at 300°C in a 40 wt% slurry [60]

Pressure (psia)	GHSV (ℓ/kg catalyst/h)	Isobutanol (g/kg catalyst/h)	C_2–C_6 Alcohols (g/kg catalyst/h)
765	5000	25.8	70.0
765	3000	18.7	45.5
765	8200	16.6	50.5
1315	8200	20.8	86.9
1750	8200	23.2	95.9
1750	3000	23.8	60.6
1315	5000	19.2	64.2
1315	5000	54.0[a]	183[a]

[a] Achieved with full recycle of a MeOH, EtOH, and PrOH mixture (see text).

of $0.35/ gallon and $0.53–0.85/gallon, respectively), isobutanol and methanol productivities of 181 and 314 g/kg catalyst/h would be required, respectively. Note the productivities of these alcohols reported in Table 4, which approximately meets these targets. If low cost natural gas is available (current economic projections often use a cost of $1/MMBtu; does stranded natural gas qualify?), coproduction of excess methanol becomes attractive, especially if the price of methanol returns to the $1–2/gallon range. This latter range is not likely in the near-future because the price of methanol in the U.S. during the last decade has generally been in the range of $0.26–$0.70/gallon [81], although it did peak at $1.78/gallon in October 1994 [82]. Recent spot prices for methanol have been in the range of $0.25–0.35/gallon (last half of 1998), caused principally by the cost of natural gas averaging only about $2/MMBtu. This compares with the 1998 U.S. prices of ethanol and aviation gasoline of about $1.50 and $2.25 per gallon, respectively [83].

The market potential and economics of scale for fuel oxygenates are huge. Worldwide consumption of petroleum is ≈65 million barrels/day and over 55% is used in the transportation sector [84]. Thus, over 1.5 billion gallons of petroleum are utilized for producing transportation fuels each day. At the present time

Table 6
Selected properties of oxygenate fuels and additives and selected hydrocarbon fuels[a]

Oxygenate (or fuel)	Blending octane number (R+M)/2	Cetane number	Boiling point (°C)	Blending RVP (psi) [68]
Methanol	116 [67], 108 [68]	3, 5 [69]	65	31^+
Ethanol	113 [67], 115 [68]	8	78	18
i-Propanol	108.5 [67], 106 [68]		82	14
n-Butanol	87 [67]	25	118	
i-Butanol	102 [68]	13	108	5
t-Butanol	101 [67], 100 [68]		83	
DME		55–60 [69]	−25	
DIPE	104.5 [67], 105 [68]		68	5
MIBE	64 [70]	53 [71]	58	
MTBE	109 [67], 110 [68], 108 [72]	<10	55	8
ETBE	110 [67], 112 [68]		73	4
IPTBE	100.5 [67], 113 [68]		87	
TAME	105 [67], 104.5 [68],105.5 [73]		86	≈1.5
Butane	94 [72]	≈10 [69]	−0.5	55 [74]
Gasoline	<87>		38–204	
Diesel fuel		>42 (40–60)	163–399	

[a] In this table, the following abbreviations are used: R, research octane No.; M, motor octane No.; RVP, Reid vapor pressure; DME, dimethylether; DIPE, diisopropylether; MIBE, methylisobutylether; MTBE, methyltertiarybutylether; ETBE, ethyltertiarybutylether; IPTBE, isopropyltertiary butylether; and TAME, tertiaryamylmethylether.

(1998), the price of petroleum has been suppressed to much less than \$20/barrel [85]. With the costs of raw materials rather constant, but with increases in labor and capital costs with time, the break-even point of developing competing technologies with current processes tends to continue to recede. However, the roles of environmental concerns and governmental regulations are also factors to be considered in planning research and development programs in the areas of clean fuels, of which higher alcohols can play a key role.

In a study of alternative transportation fuels that included methanol and ethanol, it was noted that the alcohols provide environmental benefits relative to conventional gasoline, but projected disadvantages included higher fuel costs and lower net energy efficiency, which was attributed largely to the potential impact of increasing energy imports [86]. However, alcohols are produced from domestic U.S. energy resources, and engine tests of linear alcohols/gasoline blends (2.5 and 5.0% oxygen) showed that the blends had higher brake thermal efficiencies than the neat gasoline [87]. The environmental significance of alcohols as fuel additives was also recently pointed out in a study of the effects of oxygenates on emissions from heavy-duty diesel engines [88]. It was reported that adding only 1–2 wt% n-octanol to No. 2 diesel fuel decreased particulate emission by 10–21%. At the same time, it decreased CO and NO_x emissions but increased hydrocarbon emissions. Further studies of the environmental impact of using mixtures of higher alcohols as diesel fuel additives are needed.

8. Conclusions

In addition to developing new and improved catalysts for conversion of H_2/CO synthesis gas to higher alcohols, especially isobutanol, reaction engineering approaches are being investigated to increase the space time yields of the higher alcohols. These include (a) using a dual catalyst bed reactor for gas phase synthesis of alcohols, (b) utilization of a slurry phase synthesis process to increase the CO conversion level of the exothermic alcohol synthesis reactions, and (c) injection of lower alcohols into the reaction stream to increase the synthesis rate of the higher alcohols. Progress has been made in higher alcohol synthesis using the first two approaches, while the third technique has not been systematically studied. While higher space time yields of higher alcohols have been achieved and have met designated benchmarks, improvements in the catalysts and synthesis processes are still required in the face of depressed petroleum prices. It is shown that while alcohols have octane enhancing qualities, some ethers also have high octane numbers while other have high cetane numbers.

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