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SYNTHESIS OF DIMETHYL ETHER AND ALTERNATIVE FUELS IN THE LIQUID PHASE FROM COAL-DERIVED SYNTHESIS GAS

Topical Report

Task 3.2: Screen Novel Catalyst Systems
Task 3.3: Evaluation of the Preferred Catalyst System

Contractor

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Executive Summary

As part of the DOE-sponsored contract "Synthesis of Dimethyl Ether and Alternative Fuels in the Liquid Phase from Coal-Derived Syngas" (Contract No. DE-AC22-90PC89865), experimental evaluations of the one-step synthesis of alternative fuels were carried out. The objective of this work was to develop novel processes for converting coal-derived syngas to fuels or fuel additives. Building on a technology base acquired during the development of the Liquid Phase Methanol (LPMEOH) process, this work focused on the development of slurry reactor based processes.

The experimental investigations, which involved bench-scale reactor studies, focused primarily on three areas:

1. One-step, slurry-phase syngas conversion to hydrocarbons or methanol/hydrocarbon mixtures using a mixture of methanol synthesis catalyst and methanol conversion catalyst in the same slurry reactor.

2. Slurry-phase conversion of syngas to mixed alcohols using various catalysts.

3. One-step, slurry-phase syngas conversion to mixed ethers using a mixture of mixed alcohols synthesis catalyst and dehydration catalyst in the same slurry reactor.

The experimental results indicate that, of the three types of processes investigated, slurry phase conversion of syngas to mixed alcohols shows the most promise for further process development. Evaluations of various mixed alcohols catalysts show that a cesium-promoted Cu/ZnO/Al_2O_3 methanol synthesis catalyst, developed in Air Products' laboratories, has the highest performance in terms of rate and selectivity for C_{2+}-alcohols. In fact, once-through conversion at industrially practical reaction conditions yielded a mixed alcohols product potentially suitable for direct gasoline blending. Moreover, an additional attractive aspect of this catalyst is its high selectivity for branched alcohols, potential precursors to iso-olefins for use in etherification.

1.0 BACKGROUND

The objective of this task was to experimentally evaluate novel processes for converting coal-derived synthesis gas to fuel oxygenates. Building on a technology base acquired during the development of the LPMEOH process, the present work focused on developing slurry reactor based processes.

The experimental investigations focused primarily in three areas:

1. One-Step, Slurry-Phase Syngas Conversion to Hydrocarbons or Methanol/Hydrocarbon Mixtures
2. Slurry-Phase Conversion of Syngas to Mixed Alcohols
3. One-Step, Slurry-Phase Syngas Conversion to Mixed Ethers

1.1 One-Step, Slurry-Phase Syngas Conversion to Hydrocarbons or Methanol/Hydrocarbon Mixtures

The New Zealand Synthetic Fuels Corporation currently converts syngas, derived from natural gas reforming, to gasoline via intermediate methanol:

$$\begin{aligned} CO + H_2 &\rightarrow CH_3OH \\ CH_3OH &\rightarrow \text{gasoline.} \end{aligned}$$

In this process, the overall conversion is done in three steps in three separate reactors: (1) syngas conversion to methanol using a $Cu/ZnO/Al_2O_3$ catalyst; (2) methanol dehydration to a mixture of methanol and dimethyl ether using an Al_2O_3 catalyst; and (3) conversion of the methanol/dimethyl ether mixture to gasoline over HZSM-5 zeolite.[1] All three steps are done using packed bed reactors.

The focus of the present work was to evaluate the possibility of combining these reaction steps in one slurry reactor by using a mixed catalyst system consisting of $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst and HZSM-5. Combining the reaction steps in this manner has the potential to save considerable capital costs by reducing the number of reactors required for the overall conversion. In addition, the overall conversion of syngas to gasoline releases a large quantity of heat: approximately 2800 j/(g methanol) for methanol synthesis and 1250–2000 j/(g product) for methanol conversion. The highly exothermic nature of the overall conversion makes this reaction scheme well suited for a slurry reactor, which affords excellent heat management capabilities. One-step conversion in a packed bed reactor probably would not be feasible because of the high heat release.

The proposed process is a way of converting coal-derived syngas to gasoline in one step. Alternatively, the process could be operated to produce mixtures of methanol and gasoline-range hydrocarbons which may also be useful as a transportation fuel. The possibility exists that hydrocarbons present in methanol fuel may enhance the properties of the methanol fuel (e.g., better cold-starting, flame luminosity, etc.).

There are two key challenges in making the proposed one-step process economically viable. First, since selectivity and productivity for each reaction step involved in the overall conversion depend uniquely on reaction conditions, the reaction steps optimally operate at different temperatures and pressures. Table 1-1 shows typical operating temperatures and pressures for the three reaction steps in the gas-to-gasoline process.[2,3]

TABLE 1-1
Optimal Ranges of Operating Conditions for Gas-to-Gasoline Process

Reaction Step	Temperature (°C)	Pressure (atm)
methanol synthesis	250–300	50–100
methanol dehydration	300–420	15–25
gasoline synthesis	350–420	15–25

In view of Table 1-1, operation of all three reaction steps at the same conditions would necessarily entail operation at a condition which is not ideal for all three reactions, thus requiring a compromise. However, a synergism is anticipated if all three reactions are done concurrently. Specifically, in-situ reaction of methanol to hydrocarbons will alleviate the constraint that thermodynamic equilibrium imposes on the extent of conversion of syngas to methanol. The net performance will depend on the opposing effects of a compromise in reaction conditions and the advantages of the reaction synergism.

The second key challenge in the development of this process is identifying a slurry liquid that is compatible with the methanol synthesis catalyst and also stable in the presence of the highly acidic zeolite. Previous studies of slurry liquids done during the development of the LPMEOH process have shown that only certain types of slurry liquids are compatible with the $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst.[4] The preferred liquids for the methanol synthesis process consist of saturated hydrocarbons of paraffinic and/or naphthenic structure. However, such compounds are subject to acid-catalyzed cracking in the presence of HZSM-5, which is a very effective cracking catalyst. The extent to which some potential slurry liquids cracked in the presence of zeolite was investigated in the present study. From these liquid stability studies, a preferred slurry liquid was identified and methanol conversion to hydrocarbons over HZSM-5 was done in a slurry reactor. In addition, the overall conversion of syngas was done using $Cu/ZnO/Al_2O_3$ and HZSM-5 in the same reactor.

1.2 Slurry-Phase Conversion of Syngas to Mixed Alcohols

Alcohols are known to be effective oxygenated gasoline components. Table 1-2, which shows the average of the research and motor octane numbers for some alcohols,[5] indicates that C_1-C_4 alcohols are good octane improvers.

TABLE 1-2
Average Blending Octane Numbers for Selected Alcohols

Alcohol	Blending Octane (R+M)/2
methanol	115
ethanol	113
1-propanol	105
isobutanol	101

Studies have also shown that the use of mixed alcohols in gasoline results in lower hydrocarbon and CO tailpipe emissions.[6] However, a potential drawback is that alcohols in gasoline are sensitive to phase separation in the presence of water; moisture is ubiquitous in the gasoline distribution system. Alcohol blends with a high methanol content are particularly sensitive to this phase instability. For the effective use of alcohol as a gasoline additive, a considerable fraction of C_{2+} cosolvent alcohols is necessary for phase stability in the presence of H_2O. Thus, a commercially viable process for the production of mixed alcohols from syngas must have a relatively high selectivity to C_{2+} cosolvent alcohols. For example, the Environmental Protection Agency (EPA) waiver granted to Texas Methanol Corporation for the Lurgi Octamix mixed alcohols products specified that the methanol to cosolvent alcohol split be 2:1 or, in other terms, a mix of 67% methanol and 33% C_{2+}-alcohols by weight.

Existing proposed processes for the production of mixed alcohols from syngas are based on conversion in packed bed reactors.[7,8] However, the conversion of syngas to alcohols is highly exothermic. Table 1-3 shows the heats of reaction for the synthesis of selected alcohols from CO and H_2.

TABLE 1-3
Heats of Reaction for Synthesis of Selected Alchols from CO and H_2 $x\,CO + 2xH_2 = C_xH_{2x+1}OH + (x\text{-}1)H_2O$

$C_xH_{2x+1}OH$	ΔH_{rxn}(@298), kcal/mole
methanol	-17
ethanol	-53
1-propanol	-85
isobutanol	-131

The heat of reaction per mole of product alcohol increases substantially with molecular weight. Removal of this high reaction heat is difficult in packed bed reactors. Slurry reactors offer much better heat management capabilities enabling a higher per-pass conversion, potentially better catalyst stability through the elimination of "hot spots," and the ability to process unshifted synthesis gas. Another potential advantage in the use of a slurry reactor is an enhancement in the selectivity to higher alcohols induced by secondary conversion (see below reaction), as a result of reactor back mixing.

$$\text{lower alcohols} \xrightarrow{CO/H_2} \text{higher alcohols}$$

The purpose of this study was to investigate slurry-phase mixed alcohols synthesis on a lab scale. A $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst and the same catalyst promoted with cesium were investigated under reaction conditions conducive for producing higher alcohols. The effects of temperature, gas-hourly space velocity (GHSV), and feed composition were investigated. In addition, a commercial alkali-promoted $Cu/ZnO/Al_2O_3$ mixed alcohols catalyst and a Cu-Co based mixed alcohols catalyst were evaluated in the slurry reactor. Other investigations involved the use of $Cu/ZnO/Al_2O_3$ and another catalyst component in the same reactor in attempts to increase syngas conversion to C_{2+}-alcohols.

1.3 One-Step, Slurry-Phase Syngas Conversion to Mixed Ethers

Methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), and tert-amyl methyl ether (TAME) have emerged as the most important oxygenates for gasoline blending. Properties of these ethers that make them good gasoline components include excellent miscibility with gasoline, high blending octane number, relatively low blending vapor pressure, and a tendency to reduce tailpipe emissions. Current production of ethers is based mainly on petroleum and natural gas feedstocks. MTBE, ETBE, and TAME are currently produced by reaction of an iso-olefin with an alcohol. For example, in the case of MTBE, isobutylene is selectively reacted with methanol in the presence of an acidic ion exchange resin catalyst. A coal-based route to ethers is of considerable interest.

Besides the reaction of an olefin with an alcohol, ethers can also be produced by intermolecular dehydration of alcohols:

$$R\text{-}OH + R'\text{-}OH \rightarrow R\text{-}O\text{-}R',\ R\text{-}O\text{-}R,\ R'\text{-}O\text{-}R' + H_2O,$$

where R and R' are alkyl groups. In the absence of any carbon-carbon bond rearrangement, the structure of the ethers produced by this route will depend directly on the structure of the reactant alcohol molecules. As indicated by the above stoichiometry, in the case where R and R' are different alkyl groups, the formation of three different ethers is possible. In general, for direct dehydration of a mixture of n different alcohols, the formation of $n(n+1)/2$ different ethers is possible. In addition, side reactions, such as intramolecular dehydration of alcohols to olefins, are possible. Thus, product selectivity is considered to be a major issue in developing such a process. Some of the ethers produced by the above scheme may be useful as octane or cetane improvers in transportation fuels.

This work focused on investigating the feasibility of converting mixed alcohols, generated in-situ from syngas, to mixed ethers in a single slurry reactor. This study involved the use of a mixed catalyst system consisting of a mixed alcohols synthesis catalyst and a dehydration catalyst in the same reactor. The major portion of the work involved the use of mixtures of cesium-promoted $Cu/ZnO/Al_2O_3$ and Al_2O_3. The effect of the proportion of the two catalysts on product selectivity and productivity was investigated. In addition, some initial experiments involved the dehydration of a vaporized stream of mixed alcohols over Al_2O_3.

2.0 EXPERIMENTAL

2.1 Apparatus

The reactions were carried out in two 50 ml micro-autoclave reactors (Autoclave Engineers Microclaves). The reactors were connected to a feed gas manifold and were operated in a continuous, once-through mode.

A simplified schematic of the flow system for one of the reactors is shown in Figure 2-1. The feed gases were supplied from cylinders of premixed gases. Four feed gases were supplied to the reactors: two types of synthesis gas, reduction gas, and nitrogen. The synthesis gases were purified by passage through packed beds of activated carbon to remove any iron or nickel carbonyls present. Vaporized liquid was added to the gas feed by a high-pressure syringe pump which injected liquid to a feed preheater/vaporizer. The exit gases from the reactor passed through a gas-liquid separator which refluxed the vaporized and entrained slurry liquid back to the reactor. Pressure in the reactor was controlled by a back pressure regulator and reactor exit stream flow rate was measured using a wet test meter. All lines downstream from the reactor were electrically heat-traced to prevent the possible condensation of reaction products.

Analysis of the feed and product gas streams was done on-line by gas chromatography (GC). The components of the synthesis gas (H_2, CO, CO_2, and N_2) were quantified by a Hewlett-Packard 5890 GC equipped with dual TCD detectors and packed columns. Hydrogen analysis was done using N_2 carrier gas and a column packed with activated carbon at 50°C. Carbon monoxide and N_2 were separated on a 13X molecular sieve column at room temperature with He carrier. Carbon dioxide analysis was done using a Porapak Q column at 130°C with He carrier. TCD data was acquired and quantified by a Hewlett-Packard 5850 Chemstation.

Analysis of organic products was done by another Hewlett-Packard 5890 GC with a single FID detector and a 0.53 mm I.D. capillary column with a 5 mm DB-1 film. FID data was acquired by a Hewlett-Packard 3396A integrator.

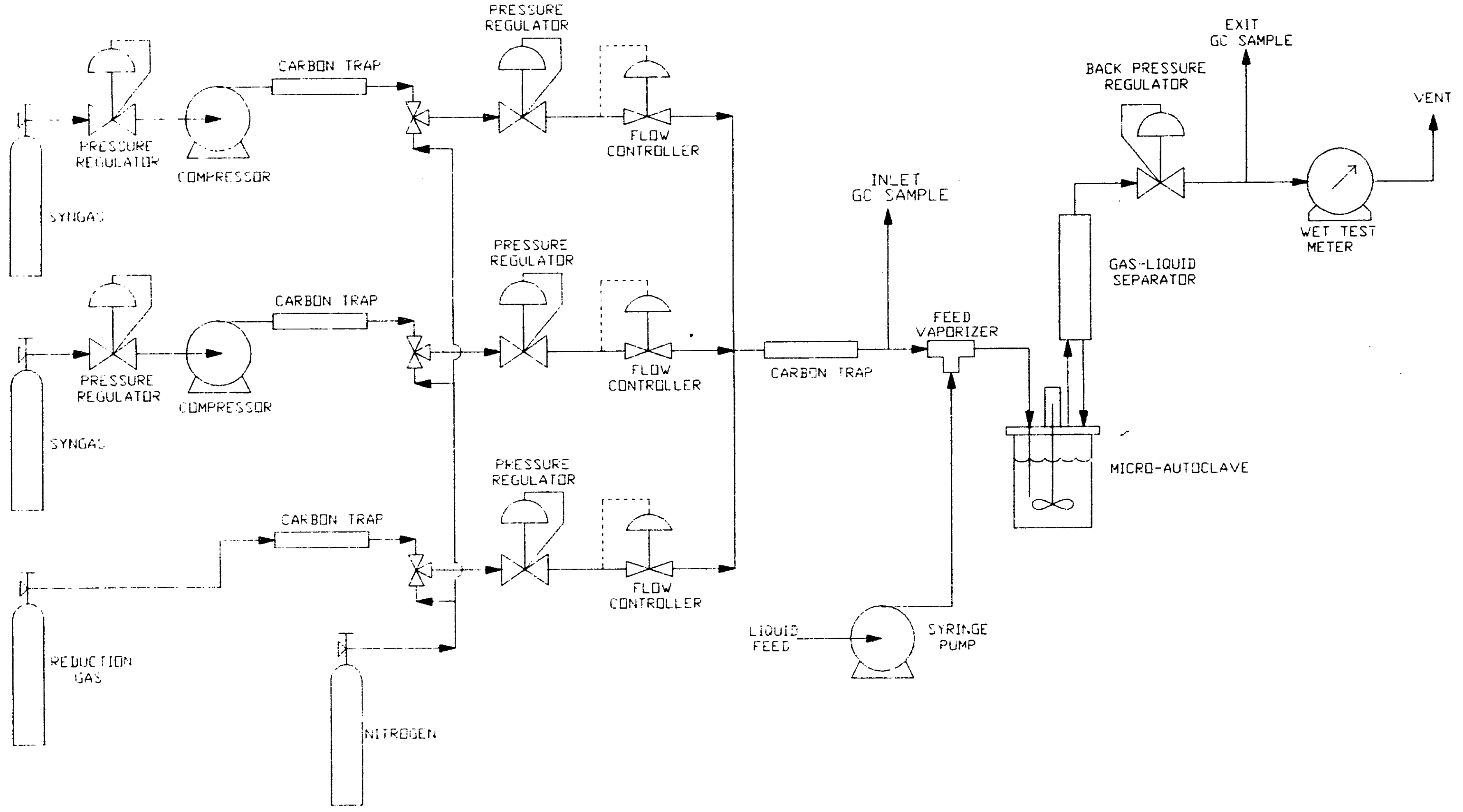
2.2 Catalyst Materials

For the one-step syngas conversion to methanol/hydrocarbons study, the methanol synthesis catalyst used was a powder form of BASF S3-86, which is a commercial $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst. The zeolites used, HZSM-5, was obtained from Zeochem.

A few different catalysts were used in the syngas to mixed alcohols investigations. Most of the studies involved the use of a cesium-promoted BASF S3-86, a catalyst which was formulated at Air Products. This catalyst was produced by incipient wetness impregnation of BASF S3-86 with an aqueous solution of cesium formate to yield a cesium loading of 1.1 wt%. The impregnated catalyst was further treated by calcination and was reduced to the active form in the reactor prior to mixed alcohols synthesis studies. In some experiments a co-catalyst was used along with the cesium-promoted BASF S3-86. One material, Rh supported on La_2O_3, was produced by impregnating La_2O_3 with aqueous $Rh(Cl)_3$ solution, followed by drying and calcination. Another co-catalyst, lanthanum strontium manganite ($La_{0.9}Sr_{0.1}MnO_3$), was obtained from HUA Associates. Another

FIGURE 2-1

FLOW SCHEMATIC OF MICRO-AUTOCLAVE REACTOR



alkali-promoted Cu/ZnO/Al_2O_3 mixed alcohols catalyst was obtained from the Lurgi Corporation. This is the same catalyst formulation used in Lurgi's Octamix process, which is a packed-bed process for producing mixed alcohols from syngas currently offered for license. Finally, a Cu-Co based mixed alcohols catalyst, obtained from an external source under a confidentiality agreement, was also investigated for use in a slurry reactor. A Cu-Co based catalyst is used in the mixed alcohols production process developed by IFP (Institut Français du Petrole).

For the mixed ethers synthesis studies, the mixed alcohols catalyst component used was the cesium-promoted BASF S3-86 catalyst described above. The Al_2O_3 component was Catapal SB, a γ-Al_2O_3 obtained from Vista Chemical.

3.0 RESULTS AND DISCUSSION

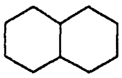
3.1 One-Step, Slurry-Phase Syngas Conversion to Hydrocarbons or Methanol/Hydrocarbon Mixtures

3.1.1 Reaction Liquid Studies

As mentioned previously, studies of slurry liquids done during the development of the LPMEOH process[4] indicate that only certain liquids are compatible with the $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst. One class of liquids which appears to be universally compatible with $Cu/ZnO/Al_2O_3$ is fully-hydrogenated paraffinic or naphthenic compounds. Thus, in the screening of liquids, attention was focused on this general class of compounds. However, a disadvantage to the use of paraffinic or naphthenic compounds is that they are subject to acid-catalyzed cracking in the presence of HZSM-5, which is an effective cracking catalyst.

Since most of the acid sites on HZSM-5 are inside the crystallites, the basic strategy used in liquid selection was to identify a paraffinic liquid composed of molecules large enough to have restricted access to the pores. The expectation is that this restricted access would minimize cracking of the paraffinic liquid molecules. The concept of using a slurry liquid composed of molecules larger than the pores of the catalyst for slurry-phase conversion of methanol to hydrocarbons has been used previously.[9]

To test the above ideas, the stability of three reaction liquids in the presence of HZSM-5 was measured. The liquids screened were Penreco Drakeol 10, Exxon Isopar V, and decalin. Drakeol 10 is a food-grade mineral oil composed of a mixture of C_{16}-C_{38} straight-chain, branched-chain, and naphthenic saturated hydrocarbons. This is the preferred liquid for use in the LPMEOH process. Exxon Isopar V consists exclusively of C_{14}-C_{18} branched-chain saturated hydrocarbons. Decalin (decahydronaphthelene) is perhydrogenated naphthalene, a C_{10} bicyclic, saturated structure:



Liquid stability was investigated using a 50 ml stirred autoclave reactor. The stability tests were done by heating a slurry of 2 g of HZSM-5 and 20 g of liquid in flowing N_2 while analyzing the off-gas for cracked hydrocarbons by the FID GC. The results of tests, conducted at a pressure of 5.3 MPa and temperatures of 250°C and 300°C, are shown in Figures 3-1 and 3-2, respectively. The results obtained at either temperature indicate that stability decreases in the following order: decalin > Isopar V > Drakeol 10.

The fact that Drakeol 10 exhibited the lowest stability to cracking is not surprising since a major portion of this liquid consists of straight-chain paraffins which have relatively easy access to the pore structure of HZSM-5. On the other hand, decalin, which is composed of the bulkiest molecules, has the most restricted access to the internal pore structure of the zeolite, and is the most stable.

FIGURE 3-1

Comparison of Liquid Stability

Catalyst: HZSM-5

250°C, 5.3 MPa

N_2 Flow: 5,000 std.lit./kg-hr

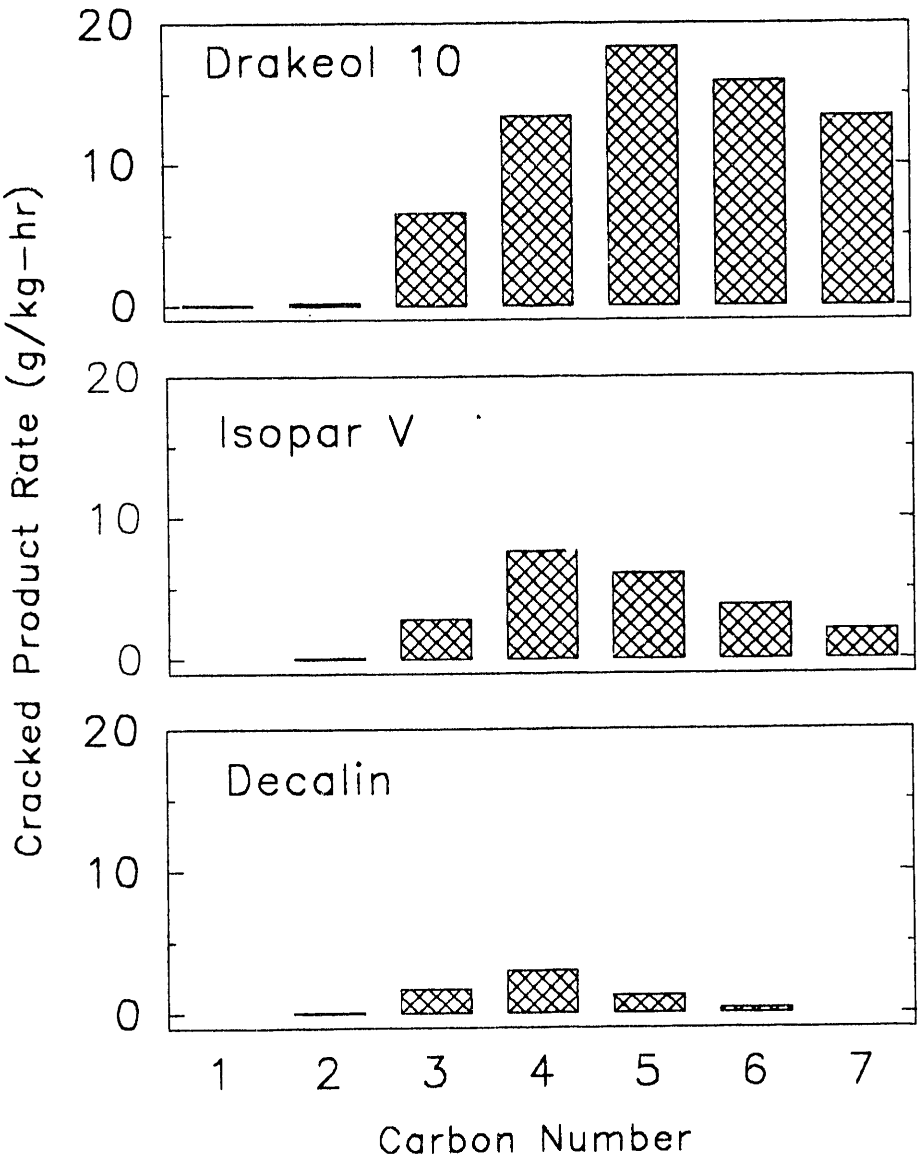


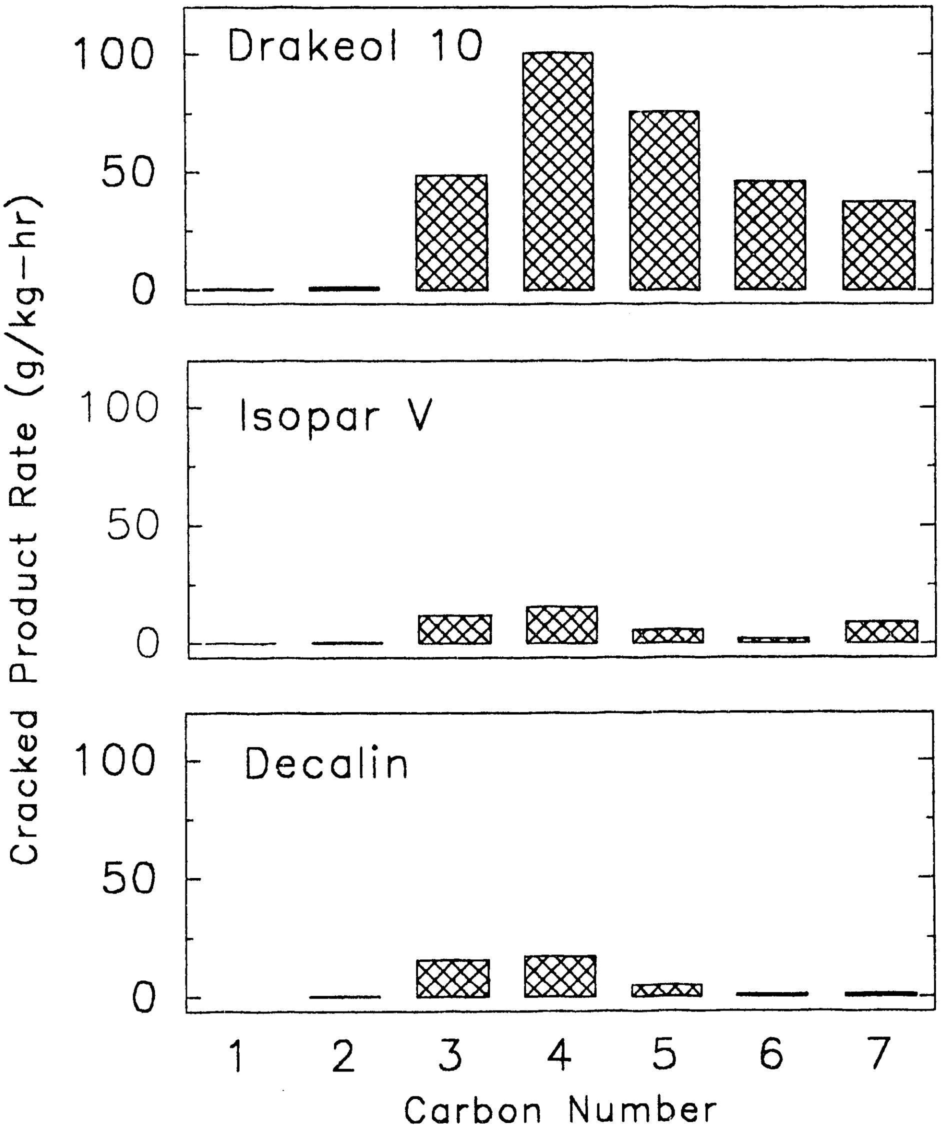
FIGURE 3-2

Comparison of Liquid Stability

Catalyst: HZSM-5

300°C, 5.3 MPa

N_2 Flow: 5,000 std.lit./kg-hr



The ease with which a molecule can enter the pore structure of a microporous material is determined by how large the kinetic diameter of the molecule is compared to the size of the pores.[10] The bicyclic decalin molecule has a larger kinetic diameter than either straight-chain or branched chain paraffins. The kinetic diameter of decalin is estimated to be greater than that of cyclohexane, which has a kinetic diameter of 6.0 Å.[10] The pores of HZSM-5 are 5.4-5.6 Å in diameter. Thus, it is not surprising that decalin was the most stable liquid since its access to the interior of the zeolite crystallites is highly restricted.

3.1.2 Surface-Passivation of HZSM-5

In an attempt to further reduce cracking of decalin in the presence of HZSM-5, passivation of the surface of the zeolite crystallites was investigated. This work was motivated by the fact that the HZSM-5 powder used consisted of finely divided particles, probably in the 0.5-5 micron range. Such particles have considerable external surface area. The possibility exists that the external surface of the crystallites may contribute significant acid sites and therefore cracking activity. These sites are readily accessible to all liquid molecules, including decalin. The aim of the passivation was to selectively deactivate the acid sites on the surface of the crystallites to achieve greater liquid stability, while leaving the internal acid sites available for conversion of methanol.

Surface passivation was done using a silanation technique employed previously by Sivasanker and Reddy.[11] These authors used N,N-dimethyltrimethylsilylamine to selectively silanate the external surface of HZSM-5. The use of this silylamine as a silica precursor is particularly advantageous because the silylamine molecules are too large to enter the pores and the amine functionality interacts strongly with the external acid sites, thereby anchoring the precursor to the surface prior to calcination.

The results for the decalin stability test, along with the results obtained for unmodified HZSM-5, are shown in Figure 3-3. It is quite clear that surface passivation resulted in much greater decalin stability since the rate of production of cracked products is much lower than that for unmodified HZSM-5. Thus, surface passivation of HZSM-5 may be a viable means of enhancing liquid stability.

3.1.3 Slurry-Phase Methanol Conversion to Hydrocarbons

Slurry-phase methanol conversion to hydrocarbons was investigated using HZSM-5 and surface-passivated HZSM-5, with decalin as the reaction liquid. The experiments were done by vaporizing methanol into N_2 carrier being fed to the 50 ml autoclave.

Figure 3-4 compares, for unmodified HZSM-5, the observed product rates obtained for N_2 flow alone and that obtained during methanol addition to the feed. The results for N_2 flow alone are included to indicate the proportion of observed products which are expected to be formed purely from cracking of the decalin. As can be seen, considerable additional hydrocarbon products were formed from 8 mol% methanol in N_2, as compared to N_2 alone, indicating that methanol was converted to hydrocarbons. Besides hydrocarbons, the other major product observed was DME. It is noteworthy that maximum in the product distribution appears at C_4, indicating a relatively low selectivity to gasoline range hydrocarbons. This is probably due, at least in part, to the low temperature (300°C) used for methanol conversion. Recall from Table 1-1 that methanol conversion is preferentially done at higher temperature (350-420°C).

FIGURE 3-3

Comparison of Decalin Stability for HZSM-5 and Surface-Passivated HZSM-5

300°C, 5.3 MPa

N_2 Flow: 5,000 std.lit./kg-hr

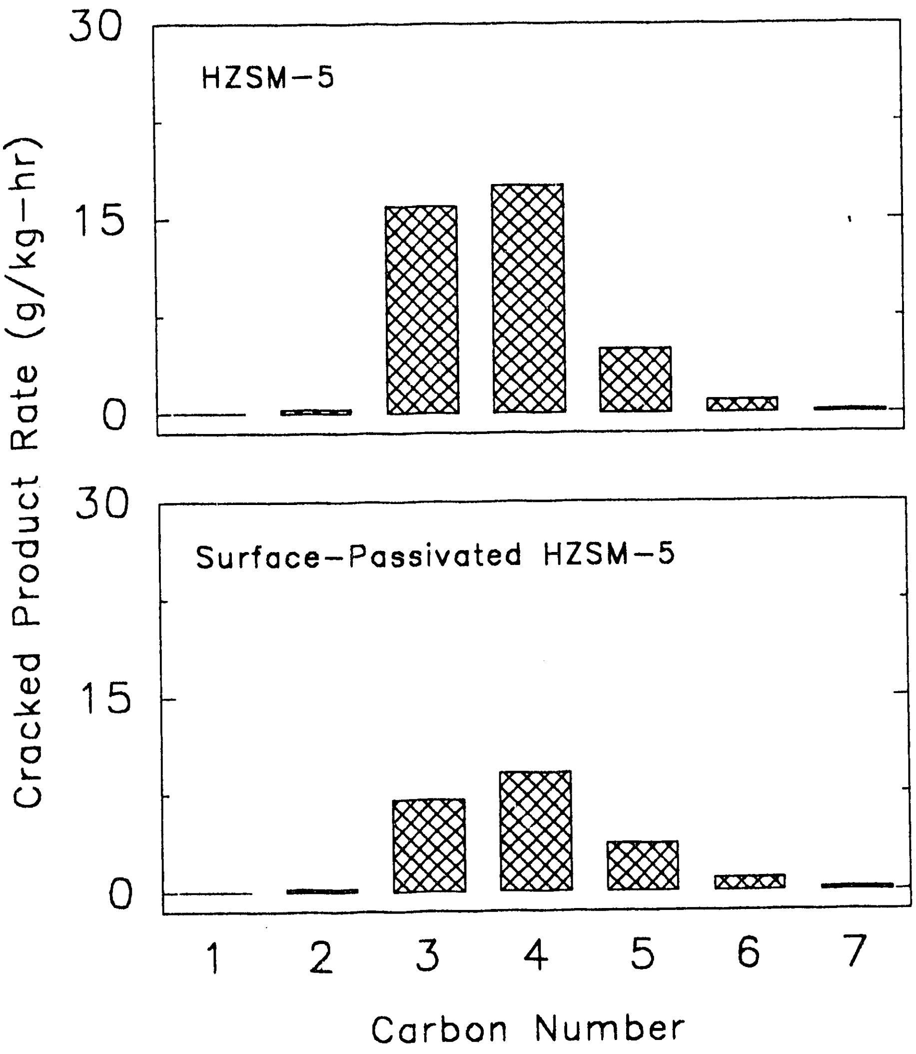


FIGURE 3-4

Slurry Phase Methanol Conversion to Hydrocarbons

Catalyst: HZSM-5
Liquid: Decalin
300°C, 5.3 MPa
N_2 Flow: 5,000 std.lit./kg-hr

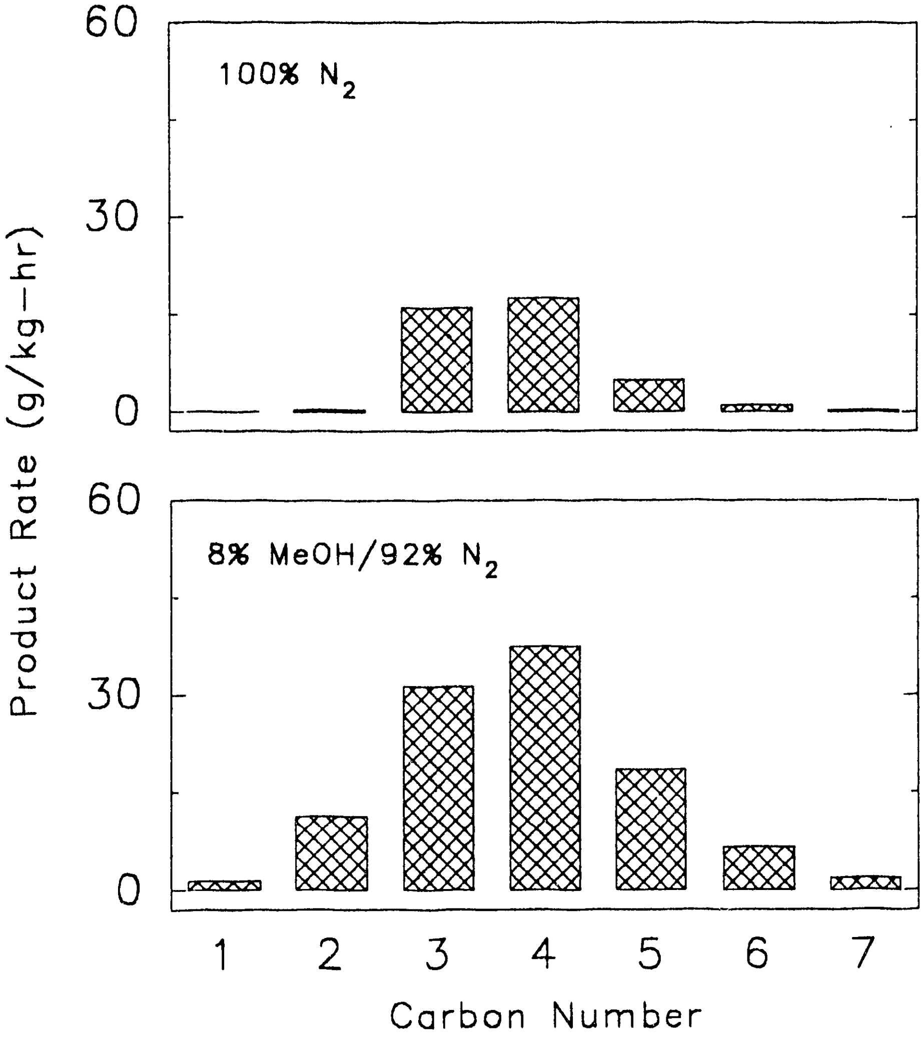


Figure 3-5 shows the product distributions observed for methanol conversion over HZSM-5 and surface-passivated HZSM-5. The product distribution obtained for surface-passivated HZSM-5 is substantially different than that for the unmodified HZSM-5. The C_2-C_7 product rate for the surface-passivated sample is essentially equal to that expected from cracking of the decalin, thereby indicating that methanol is not converted to these products. However, the methane produced is much greater than that for the unmodified HZSM-5.

The reason for the high methane selectivity for the surface-passivated sample is not clear. However, one possibility is that the surface silanation not only capped off acid sites on the external surface of the crystallites, but also may have necked down the pore openings. Such a decrease in the size of the pore openings may allow only small molecules (e.g. CH_4), formed via methanol on internal sites, to escape the zeolite structure. Further study would be necessary to determine the specific cause of the change in product distribution for the surface-passivated sample.

3.1.4 One-Step Syngas Conversion over Cu/ZnO/Al_2O_3-HZSM-5 Mixture

The slurry-phase conversion of simulated coal-derived syngas using a 50:50 (by weight) mixture of Cu/ZnO/Al_2O_3 methanol synthesis catalyst and HZSM-5 in decalin was investigated. After in-situ reduction of the Cu/ZnO/Al_2O_3 component, the autoclave was run at 250°C and 5.3 MPa using a space velocity of 5,000 std. lit./kg-hr (based on total catalyst weight). The results of this experiment are shown in Table 3-1.

TABLE 3-1
Slurry-Phase Syngas Conversion to Methanol/Hydrocarbons

Catalysts: Cu/ZnO/Al_2O_3 and HZSM-5
Liquid: Decalin
Feed Gas: 51% CO/35% H_2/13% CO_2/1% N_2
Conditions: 250°C, 5.3 MPa, GHSV=5000 std. lit./kg-hr

Time on stream (hr)	Production Rate (g/kg-hr)			
	ΣC_1-C_3 hydrocarbons	ΣC_4-C_7 hydrocarbons	DME	MeOH
1.2	18.4	8.8	333	18.5
10.1	7.9	8.7	250	15.4
14.8	8.3	6.5	201	14.8

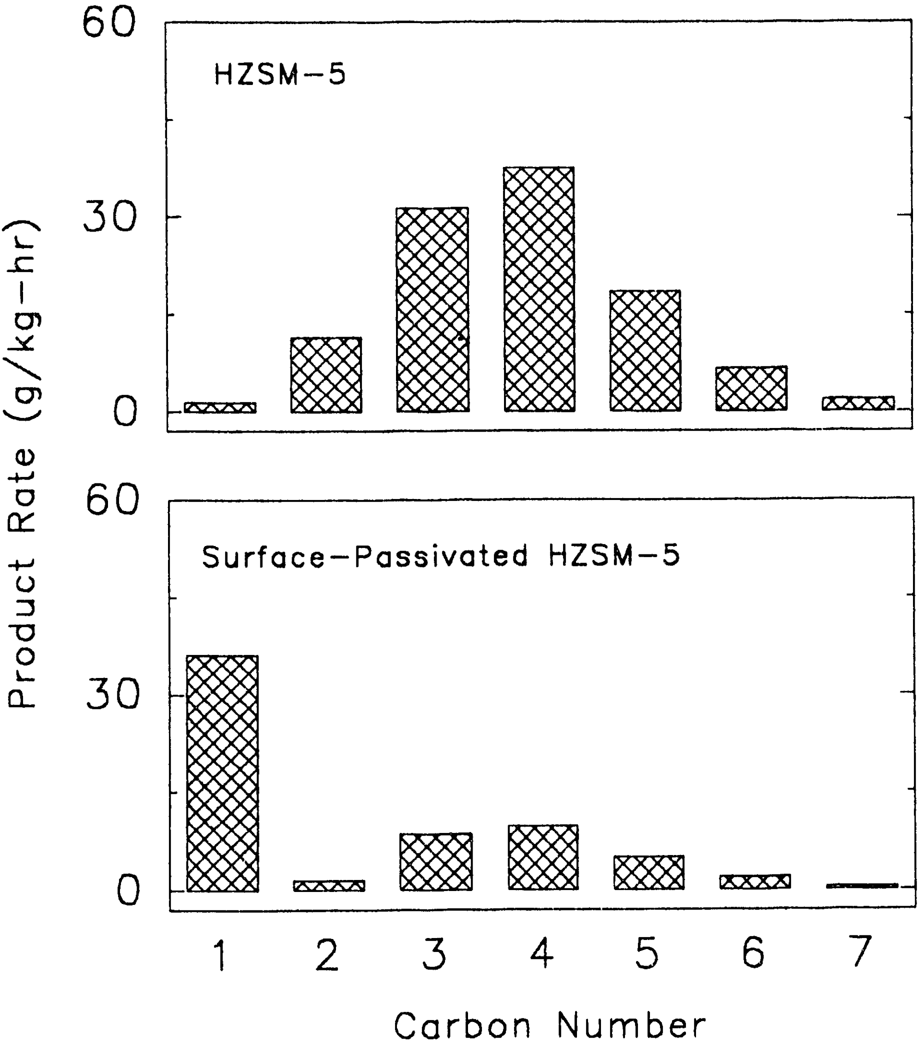
The major product was DME, while selectivity to hydrocarbons was quite low. However, the production rate of hydrocarbons was significantly greater than that expected from the decalin cracking. Though not shown in Table 3-1, CO conversion is a strong function of on-stream time, but is greater than that observed for methanol synthesis alone at these conditions (Cu/ZnO/Al_2O_3 without HZSM-5 present). The CO conversion decreased from 28% at 1.2 hours to 18% at 14.8 hours. Thus, deactivation of the mixed catalyst system appears to be significant.

Selectivity to gasoline range hydrocarbons is disappointingly low for this experiment. This is probably due to the fact that the reaction temperature used (250°C) was much lower than the optimal temperature range for methanol conversion to gasoline (350-420°C, see Table 1-1).

FIGURE 3-5

Slurry Phase Methanol Conversion to Hydrocarbons

Liquid: Decalin
300°C, 5.3 MPa
Feed: 8% MeOH/92% N_2
N_2 Flow: 5,000 std.lit./kg-hr



3.2 Slurry-Phase Conversion of Syngas to Mixed Alcohols

3.2.1 Cu/ZnO/Al_2O_3 and Cesium-promoted Cu/ZnO/Al_2O_3

3.2.1.1 Effect of Gas Composition and Gas-Hourly Space Velocity on Productivity and Product Distribution

Two syngas feeds of different composition were investigated. One feed was representative of the product gas from a Texaco coal gasifier, while the other simulated a Shell coal gasifier product gas. The nominal compositions are shown in Table 3-2. Shell gas has a much lower H_2/CO ratio (0.45) than Texaco gas (0.69), and a lower CO_2 content (3% for Shell vs. 13% for Texaco).

TABLE 3-2
Composition of Shell and Texaco Syngas

	Nominal Composition (mol%)			
Syngas	CO	H_2	CO_2	N_2
Texaco	51	35	13	1
Shell	66	30	3	1

The results for the Cu/ZnO/Al_2O_3 will be discussed first. Figures 3-6 and 3-7 show the major product alcohol rates as a function of GHSV for Cu/ZnO/Al_2O_3 for Texaco and Shell gas feeds, respectively. These data were obtained at a temperature of 300°C and a total pressure of 7.0 MPa. The major products for each catalyst are alcohols, accounting for greater than 90% by weight of the total organic products. The minor side-products were largely low molecular weight paraffins and esters.

Figures 3-6 and 3-7 show that the synthesis rate of all products increases with increasing GHSV, but the relative sensitivity to GHSV is product specific. The methanol rate increases linearly with GHSV, for both feed gases, across the range of GHSV investigated here. Moreover, the reactor exit methanol concentration shows little variation with GHSV. This indicates that the methanol synthesis reaction is close to equilibrium at these conditions. Thermodynamic equilibrium calculations, which incorporate the approximate reactor exit gas composition, support this contention. The methanol synthesis rate for Texaco gas was higher than for Shell gas across the GHSV range. This observation is consistent with thermodynamic equilibrium considerations; the higher H_2/CO ratio of the Texaco gas favors conversion to methanol. The ΣC_2-C_6 alcohols rate increases monotonically with GHSV, but unlike the result for methanol, the rate is non-linear. The ΣC_2-C_6 alcohols rate is not constrained by thermodynamic equilibrium limitations at these conditions, but rather the rate is governed by the intrinsic reaction kinetics. The ΣC_2-C_6 alcohols rate is higher for Shell gas than Texaco gas across the range of GHSV examined.

The effect of GHSV on the synthesis rate of the individual higher alcohol products is quite interesting. For both feed gases, the increase in ethanol rate with GHSV is approximately linear. By contrast, the dependence of the isobutanol rate on GHSV is not as strong. In fact, the isobutanol rate curve is fairly flat, especially toward the upper limits of GHSV investigated. Consequently, isobutanol is the major C_{2+}-alcohol product at low GHSV(<5000 std. lit./kg-hr), while ethanol is the major product at high GHSV. This behavior can be rationalized in terms of the probable reaction mechanism by which the higher alcohol products are formed, as proposed by published studies of

FIGURE 3-6

Effect of GHSV on Product Rates

Catalyst: $Cu/ZnO/Al_2O_3$

Run No.: 11472-39

300°C, 7.0 MPa, Texaco Gas

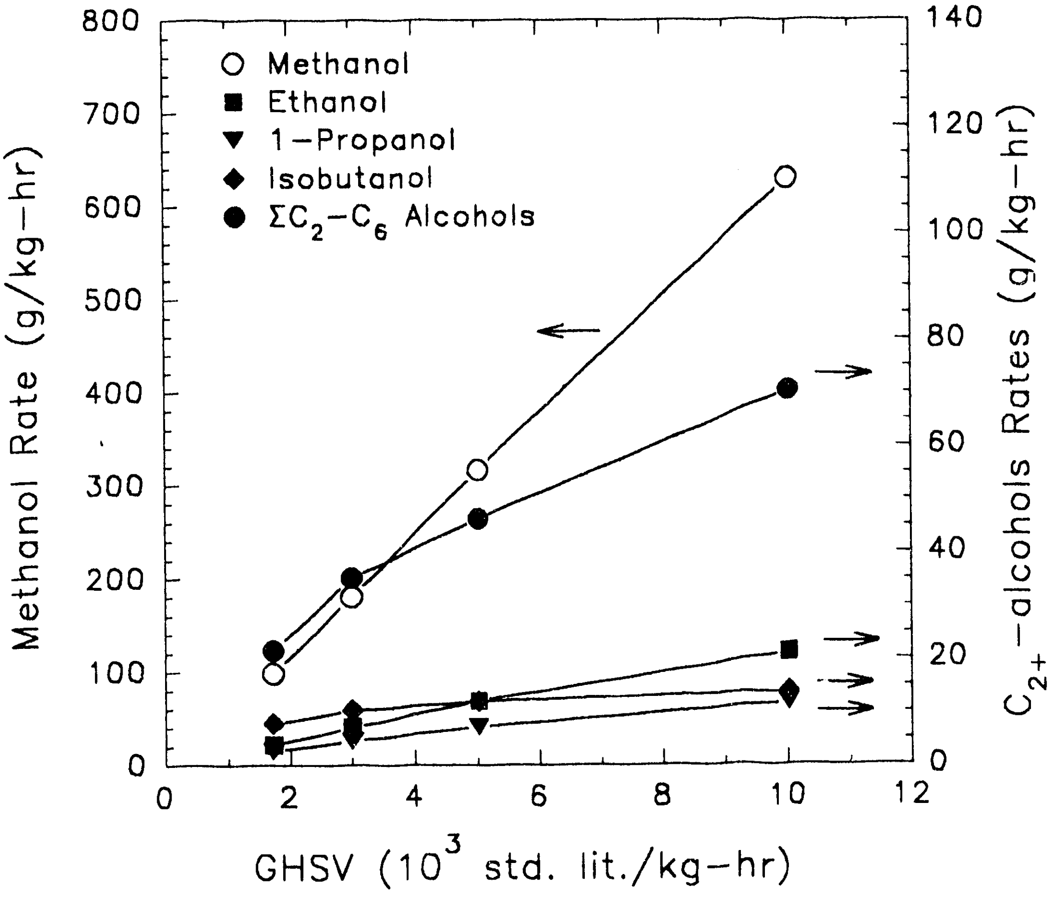
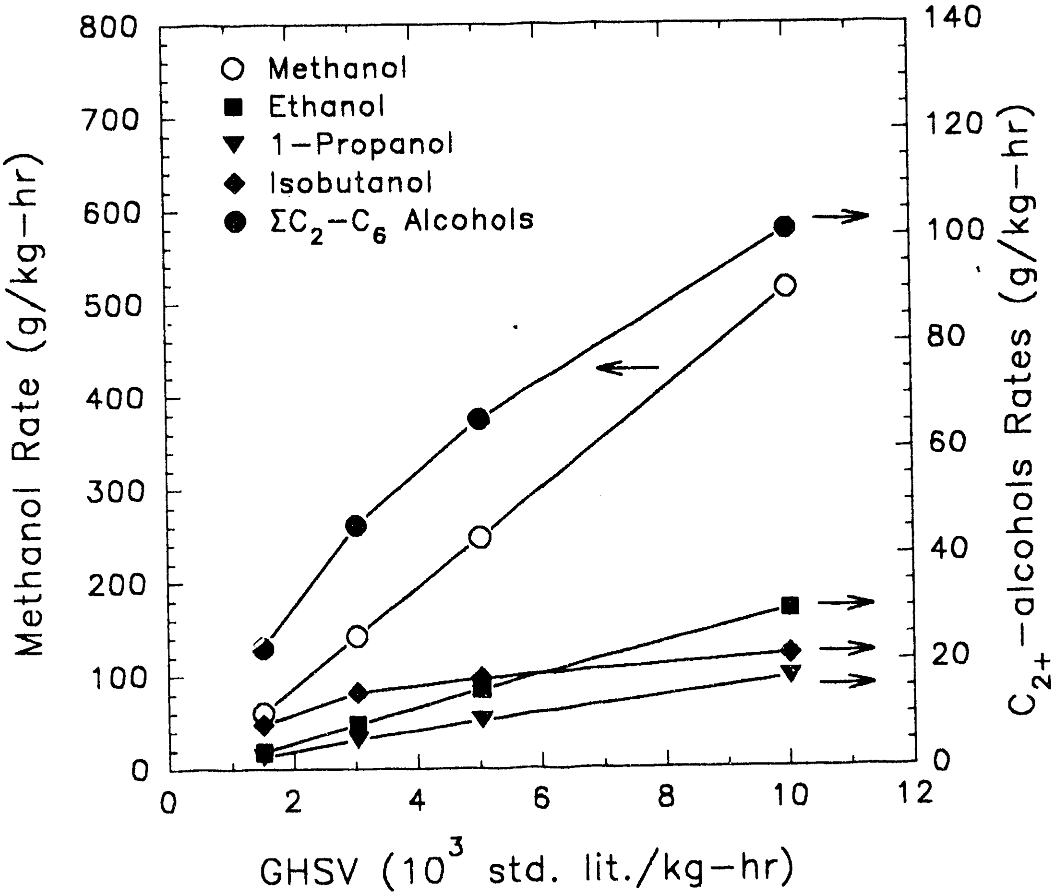


FIGURE 3-7

Effect of GHSV on Product Rates

Catalyst: $Cu/ZnO/Al_2O_3$
Run No.: 11472-39

300°C, 7.0 MPa, Shell Gas



alcohol synthesis on Cu/ZnO/Al_2O_3-based catalysts.[11,12] These studies indicate that higher alcohols are produced in a chain growth scheme by addition of primarily C_1 units to the α- or β-carbon of a lower alcohol:

$$\text{CO/H}_2\text{ or methanol} \xrightarrow{C_1} \text{ethanol} \xrightarrow{C_1} \text{1-propanol} \xrightarrow{C_1} \text{isobutanol}$$

Formation of 1-propanol occurs by C_1 addition to ethanol, and isobutanol is formed from C_1 addition to 1-propanol. In such a sequential mechanism, the expectation is that low GHSV (longer residence time) would favor formation of higher molecular weight alcohols. Thus, low GHSV favors formation of isobutanol over ethanol.

Figures 3-8 and 3-9 show the effect of GHSV on the alcohol product selectivity for the Cu/ZnO/Al_2O_3 catalyst for Texaco and Shell feed gases, respectively. The selectivities are based on the organic products only and do not consider CO that has been converted to CO_2. The major alcohols products are primary alcohols, that is, they are of the structure $R\text{-}CH_2\text{-}OH$ (where R is an alkyl group). In addition, among the C_{4+} alcohols products, branched products, in particular the "2-methyl-" isomers, dominate over linear products. This high selectivity to branched C_{4+} products is well known for Cu/ZnO/Al_2O_3-based catalysts[11,12] and can be understood in terms of the reaction mechanism mentioned above. The predominance of branched products is expected if β-addition dominates over α-addition in the chain growth scheme.

As indicated in Figures 3-8 and 3-9, the extent to which the branched products prevail over the linear isomers is greater at the lower space velocity. This is reasonable considering that long residence time (low GHSV) favors secondary reaction, such as β-addition, to the linear alcohols resulting in formation of the "2-methyl-" isomers of the linear alcohols. Not surprisingly, the total selectivity to $\Sigma C_2\text{-}C_6$ alcohols is higher at low GHSV for both feed gases. Moreover, the selectivity to $\Sigma C_2\text{-}C_6$ alcohols is higher for Shell gas as compared to Texaco gas. The selectivity to $\Sigma C_2\text{-}C_6$ alcohols increases from 9.8 wt% at 10,022 std. lit./kg-hr to 16.7 wt% at 1739 std. lit./kg-hr for Texaco gas. For Shell gas, the selectivity increases from 15.8 wt% at 10,022 std. lit./kg-hr to 24.3 wt% at 1509 std. lit./kg-hr.

Next, the results for the Cs-promoted Cu/ZnO/Al_2O_3 catalyst will be discussed. Figures 3-10 and 3-11 show the major product alcohol rates as a function of GHSV for Cs-Cu/ZnO/Al_2O_3 for Texaco and Shell gas feeds, respectively. The data were obtained at 300°C and 7.0 MPa, the same temperature and pressure used for the results on the unpromoted catalyst (Figures 3-6 through 3-9). In agreement with the results for the unpromoted Cu/ZnO/Al_2O_3, the methanol rate increases nearly linearly with increasing GHSV for both feed gases, reflecting the constraint that thermodynamic equilibrium imposes on the extent of conversion of syngas to methanol at these conditions. The $\Sigma C_2\text{-}C_6$ alcohols rate increases monotonically with GHSV for both feed gases. The effect of GHSV on the individual rates for ethanol, 1-propanol, and isobutanol shows the same basic trend as that observed for the unpromoted Cu/ZnO/Al_2O_3 catalyst. Interestingly, the isobutanol rate measured for Texaco feed gas appears to go through a weak maximum as GHSV is increased.

As also observed for the unpromoted Cu/ZnO/Al_2O_3 catalyst, the $\Sigma C_2\text{-}C_6$ alcohols rate is higher for Shell gas than Texaco gas across the range of GHSV. The relative degree to which the rate for Shell gas is higher than Texaco gas is greater for the Cs-Cu/ZnO/Al_2O_3 than the unpromoted Cu/ZnO/

FIGURE 3-8

Effect of GHSV on Alcohol Product Distribution

Catalyst: $Cu/ZnO/Al_2O_3$
Run No.: 11472-39
300°C, 7.0 MPa, Texaco Gas

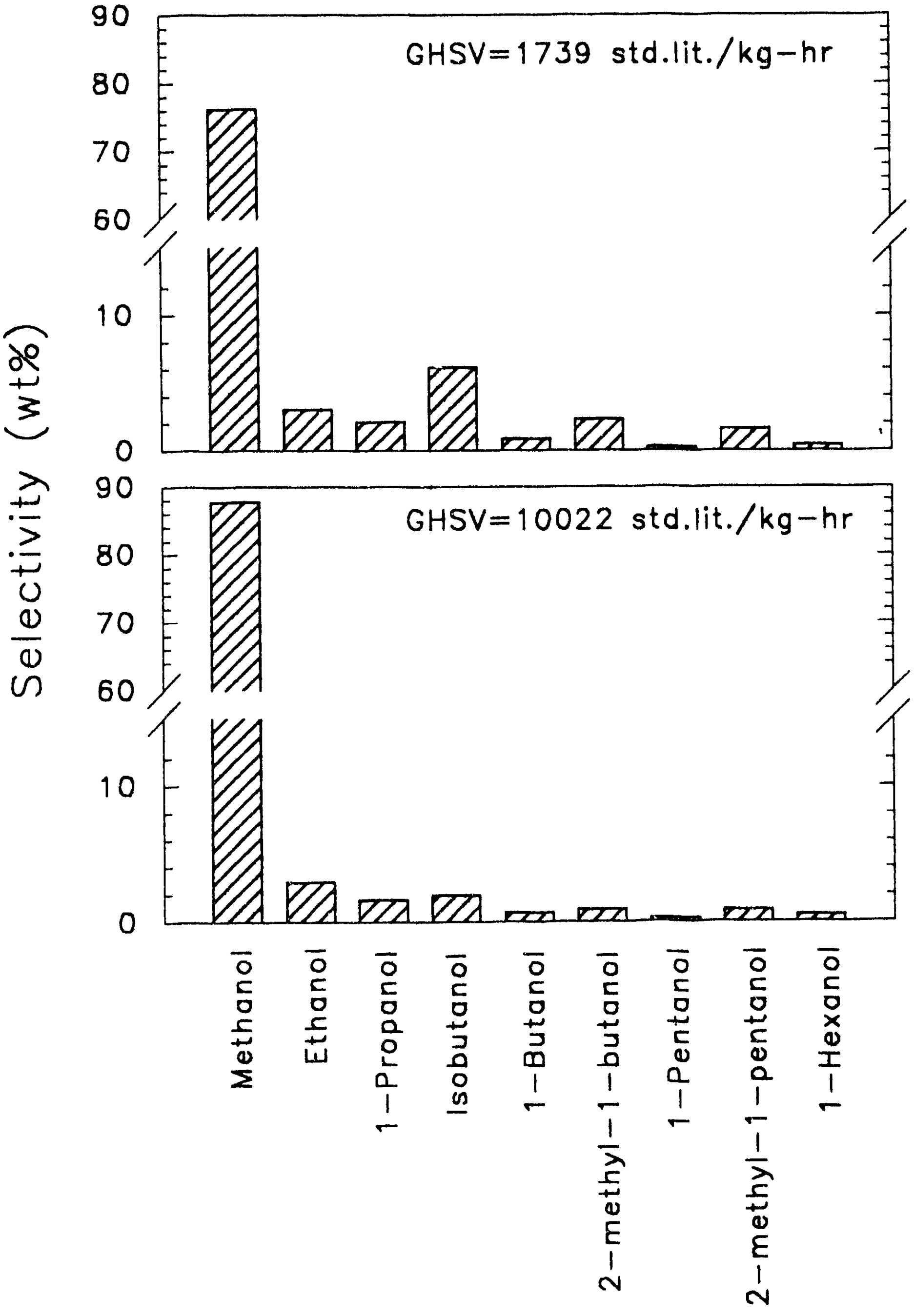


FIGURE 3-9

Effect of GHSV on Alcohol Product Distribution

Catalyst: $Cu/ZnO/Al_2O_3$

Run No.: 11472-39

300°C, 7.0 MPa, Shell Gas

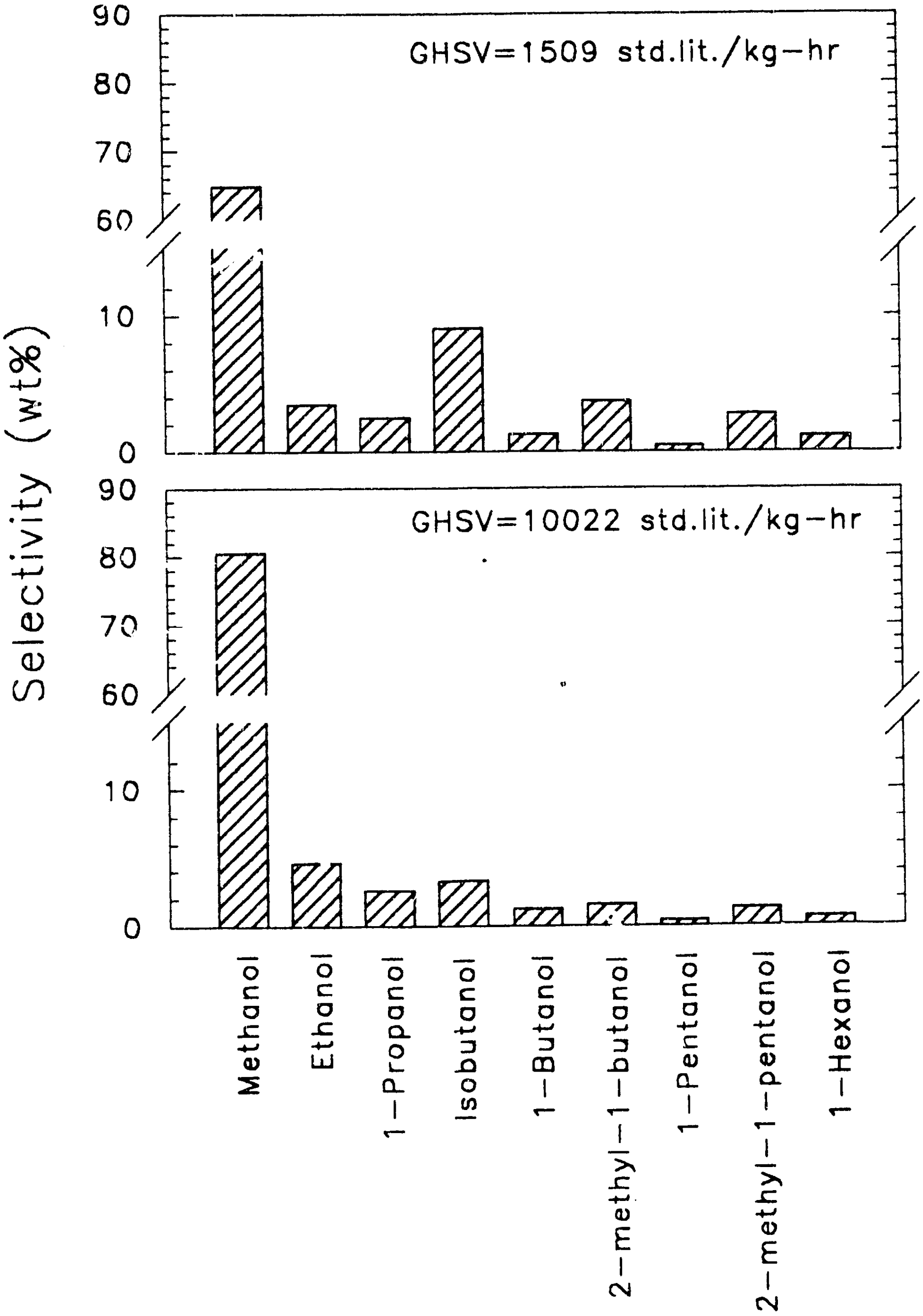


FIGURE 3–10

Effect of GHSV on Product Rates

Catalyst: Cs–Cu/ZnO/Al_2O_3
Run No.: 11168–76

300°C, 7.0 MPa, Texaco Gas

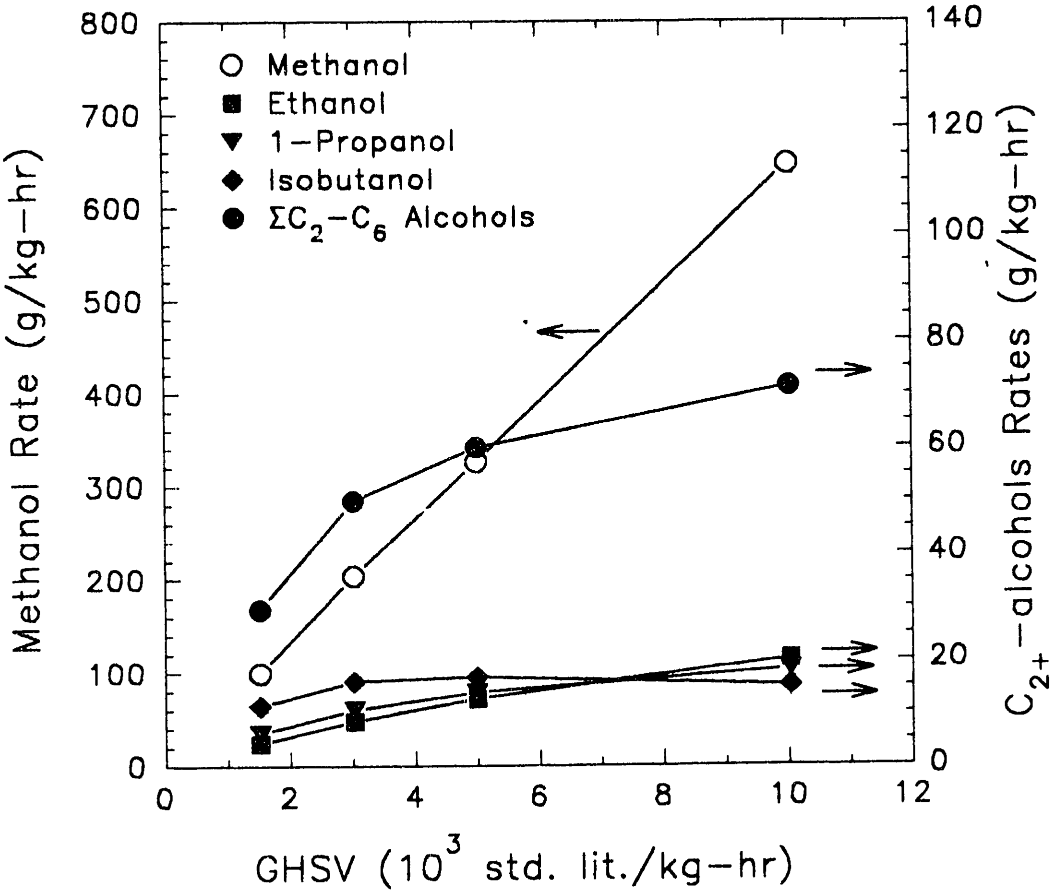


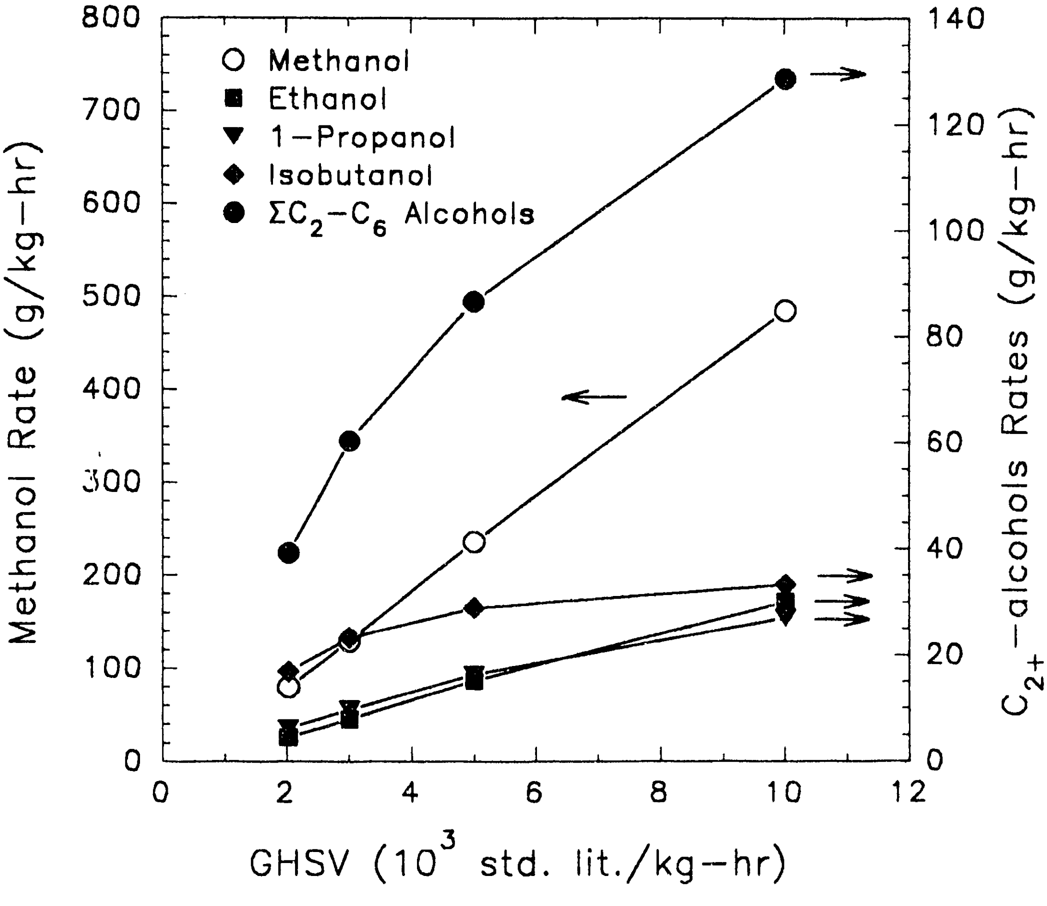
FIGURE 3-11

Effect of GHSV on Product Rates

Catalyst: Cs–Cu/ZnO/Al_2O_3

Run No.: 11168–76

300°C, 7.0 MPa, Shell Gas



Al_2O_3 catalyst. For example, at a GHSV of 10,000 std. lit./kg-hr for both feed gases, the ΣC_2-C_6 alcohols rate for Shell gas is 80% higher than that for Texaco gas for the Cs-Cu/ZnO/Al_2O_3 catalyst. By contrast, at a GHSV of 10,000 std. lit./kg-hr for both feed gases, the ΣC_2-C_6 alcohols rate for Shell gas is 43% higher than that for Texaco gas for the Cu/ZnO/Al_2O_3 catalyst.

Comparison of the alcohol rates of the two catalysts at constant feed gas composition indicates that, in general, the ΣC_2-C_6 alcohols rate is significantly higher for the Cs-Cu/ZnO/Al_2O_3 than the unpromoted Cu/ZnO/Al_2O_3 catalyst. However, one exception is that the ΣC_2-C_6 alcohols rate using Texaco gas at a GHSV of 10,000 std. lit./kg-hr is nearly the same for both catalysts, while the ΣC_2-C_6 alcohols rate at lower values of GHSV for this gas is consistently higher for the Cs-Cu/ZnO/Al_2O_3 catalyst. For both feed gases, the isobutanol rate is higher for the Cs-Cu/ZnO/Al_2O_3 catalyst than the unpromoted catalyst, across the range of GHSV investigated. Interestingly, the relative enhancement in isobutanol rate resulting from promotion of the catalyst with cesium is more pronounced in the case of the Shell gas feed in comparison to Texaco gas.

Figures 3-12 and 3-13 show the influence of GHSV on the alcohol product distribution for the Cs-Cu/ZnO/Al_2O_3 catalyst for Texaco and Shell feed gas, respectively. In agreement with results for the unpromoted catalyst, low GHSV results in an enhancement in the selectivity to higher alcohols for both feed gases. Particularly noteworthy is the increased selectivity to branched products, such as isobutanol, at the low GHSV. Also, comparison of Figures 3-12 and 3-13 indicates that the selectivity to C_{2+}-alcohols is considerably higher for Shell gas than Texaco gas, in agreement with the unpromoted Cu/ZnO/Al_2O_3 results.

The alcohol product obtained in this work will now be considered in light of what is technically acceptable for fuel use. For a mixed alcohols product to be potentially useful as a gasoline additive, it must contain a significant fraction of C_{2+}-alcohols as cosolvents for the methanol. For example, the EPA waiver granted to Texas Methanol Corporation for the Lurgi Octamix mixed alcohols products specified that the methanol to cosolvent alcohol split be 2:1 or, in other terms, a mix of 67% methanol and 33% C_{2+}-alcohols by weight. For this waiver, certain restrictions were also placed on composition of the cosolvent mix; for example, the ethanol, propanols, and butanols must comprise at least 60% by weight of the cosolvent alcohols. This waiver provides some guidelines on product composition acceptable for gasoline blending.

The product mixes obtained for the Cs-Cu/ZnO/Al_2O_3 catalyst will now be considered in view of the above mentioned EPA waiver. Table 3-3 shows the distribution of methanol and cosolvent alcohols obtained for the Cs-Cu/ZnO/Al_2O_3 for both syngas feeds at low and high GHSV. As shown, the split between methanol and higher alcohols is more favorable for the Shell gas feed. For Shell gas at a GHSV of 2028 std. lit./kg-hr, the product alcohol composition is essentially acceptable according to the EPA waiver for Octamix. Moreover, for all of the cases considered in Table 3-3, the cosolvent alcohols are comprised of at least 70 wt% ethanol, propanols, and butanols.

FIGURE 3-12

Effect of GHSV on Alcohol Product Distribution

Catalyst: Cs-Cu/ZnO/Al_2O_3

Run No.: 11168-76

300°C, 7.0 MPa, Texaco Gas

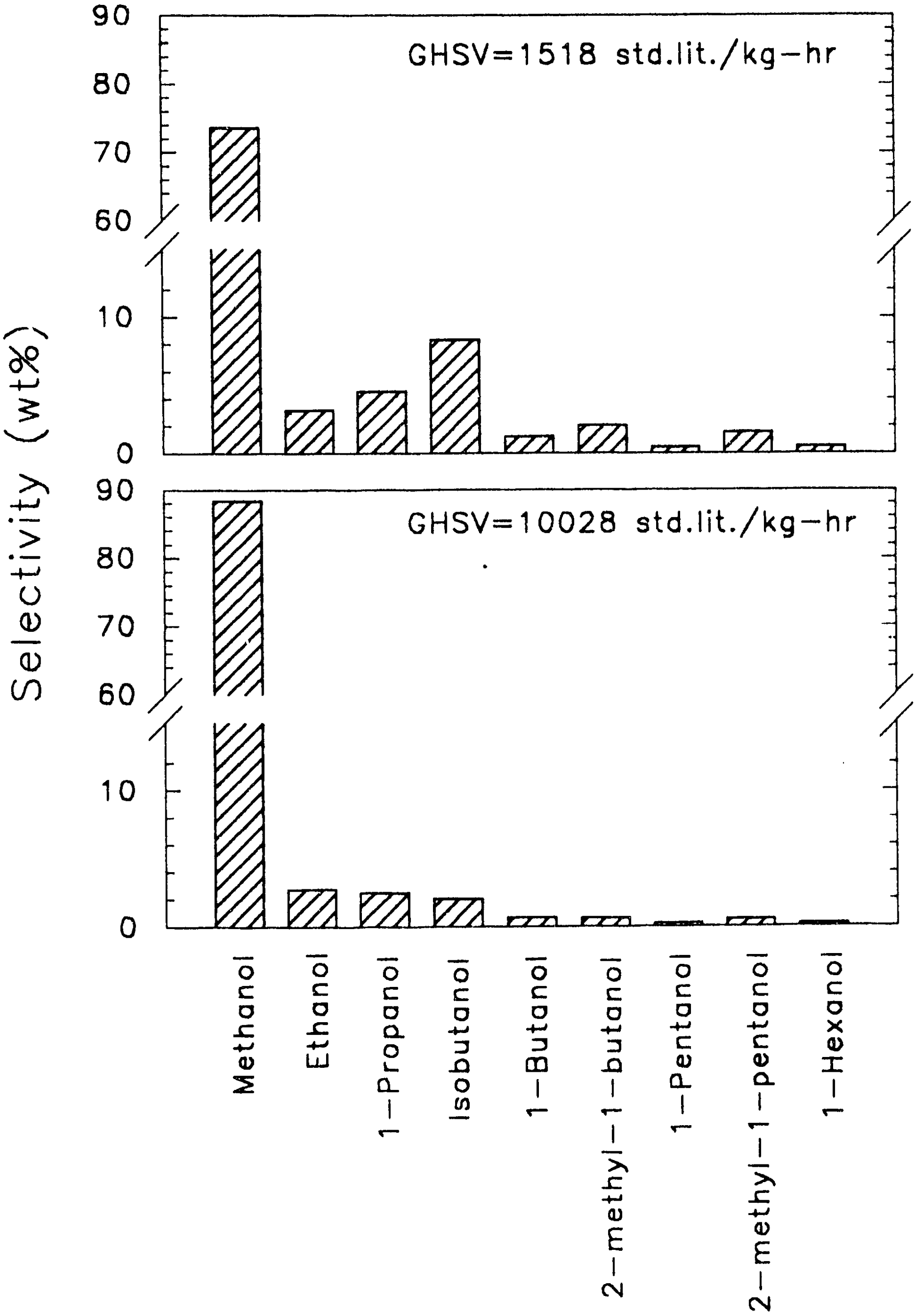


FIGURE 3-13

Effect of GHSV on Alcohol Product Distribution

Catalyst: Cs-Cu/ZnO/Al_2O_3
Run No.: 11168-76
300°C, 7.0 MPa, Shell Gas

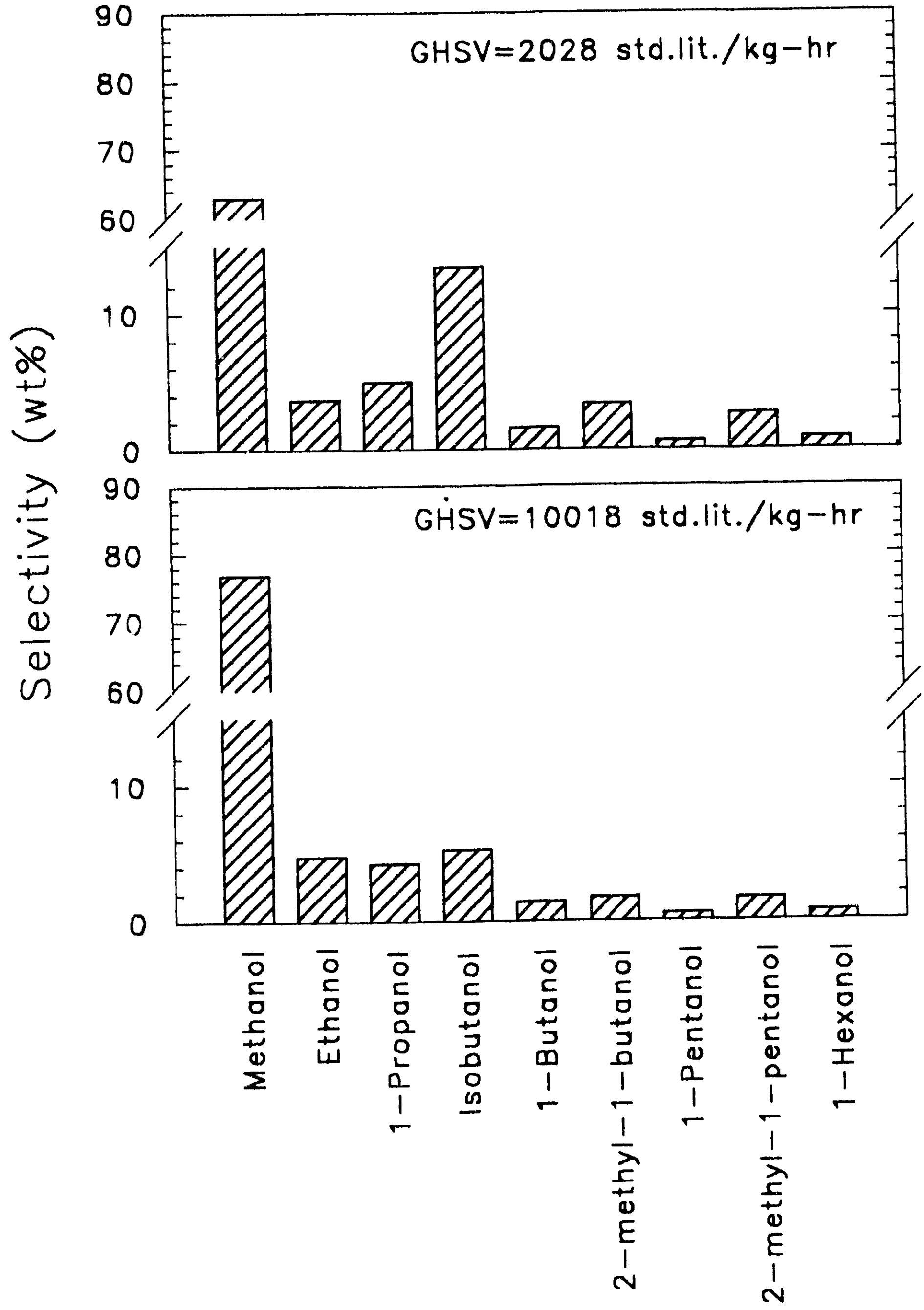


TABLE 3-3

Methanol/Cosolvent Alcohols Product Distribution for Cs-Cu/ZnO/Al_2O_3

		Selectivity Among Total Alcohols (wt%)	
Feed Gas Type	GHSV (std. lit./kg-hr)	Methanol	ΣC_2-C_6 alcohols
Texaco	1518	77	23
Texaco	5000	84	16
Texaco	10028	90	10
Shell	2028	67	33
Shell	5000	73	27
Shell	10018	79	21

The results shown in Table 3-3 indicate that potentially useful alcohol product mixes can be obtained, especially for Shell gas operating at low GHSV, using the Cs-promoted Cu/ZnO/Al_2O_3 catalyst in a slurry reactor. The fact that the product distributions shown were obtained on a once-through basis, that is, no recycle of methanol or syngas, is significant. This once-through mode of operation is particularly well-suited to a CGCC environment. Recycle of product methanol, ethanol, or propanol may also be a viable means of obtaining acceptable product distributions at higher GHSV. Results obtained for alcohol addition to the feed will be presented later.

3.2.1.2 Effect of Temperature on Product Rates and Selectivity:

The effect of temperature on the performance of the unpromoted Cu/ZnO/Al_2O_3 and Cs-Cu/ZnO/Al_2O_3 catalysts was investigated using Shell gas at a pressure of 7.0 MPa and a GHSV of 5000 std. lit./kg-hr. Figures 3-14 and 3-15 show the influence of varying the reaction temperature between 280°C and 320°C on the synthesis rates for the major product alcohols for Cu/ZnO/Al_2O_3 and Cs-Cu/ZnO/Al_2O_3, respectively.

For both catalysts, the methanol rate decreases monotonically with temperature, reflecting the constraint that thermodynamic equilibrium imposes on the synthesis of methanol in the investigated temperature range. The ΣC_2-C_6 alcohols rate is less influenced by temperature over this same temperature range for both catalysts. For each catalyst, there appears to be a maximum in the ΣC_2-C_6 alcohols rate in the vicinity of 300°C.

The influence of temperature on the rate of synthesis of the major C_{2+}-alcohol products, ethanol, 1-propanol, and isobutanol, is interesting. The ethanol rate decreases with temperature across the range, while the isobutanol rate increases, for both catalysts. The rate for 1-propanol decreases slightly with temperature, but the decrease is not as strong as that for ethanol. Unlike the methanol synthesis reaction, syngas conversion to ethanol and 1-propanol at these reaction conditions is not constrained by thermodynamic equilibrium; across this range of temperature, the rates for ethanol and 1-propanol are quite far from the equilibrium values. Thus, the decrease in rate with temperature, as observed for ethanol and 1-propanol, must be attributed to some other phenomenon. The increase in isobutanol rate which accompanies the decrease in ethanol and 1-propanol rate with increasing temperature suggests that secondary conversion of ethanol and 1-propanol to higher products, such as isobutanol, occurs at a faster rate than ethanol and 1-propanol formation and this

FIGURE 3-14

Effect of Temperature on Product Rates

Catalyst: $Cu/ZnO/Al_2O_3$

Run No.: 11472-39

7.0 MPa, Shell Gas, GHSV=5000 std.lit./kg-hr

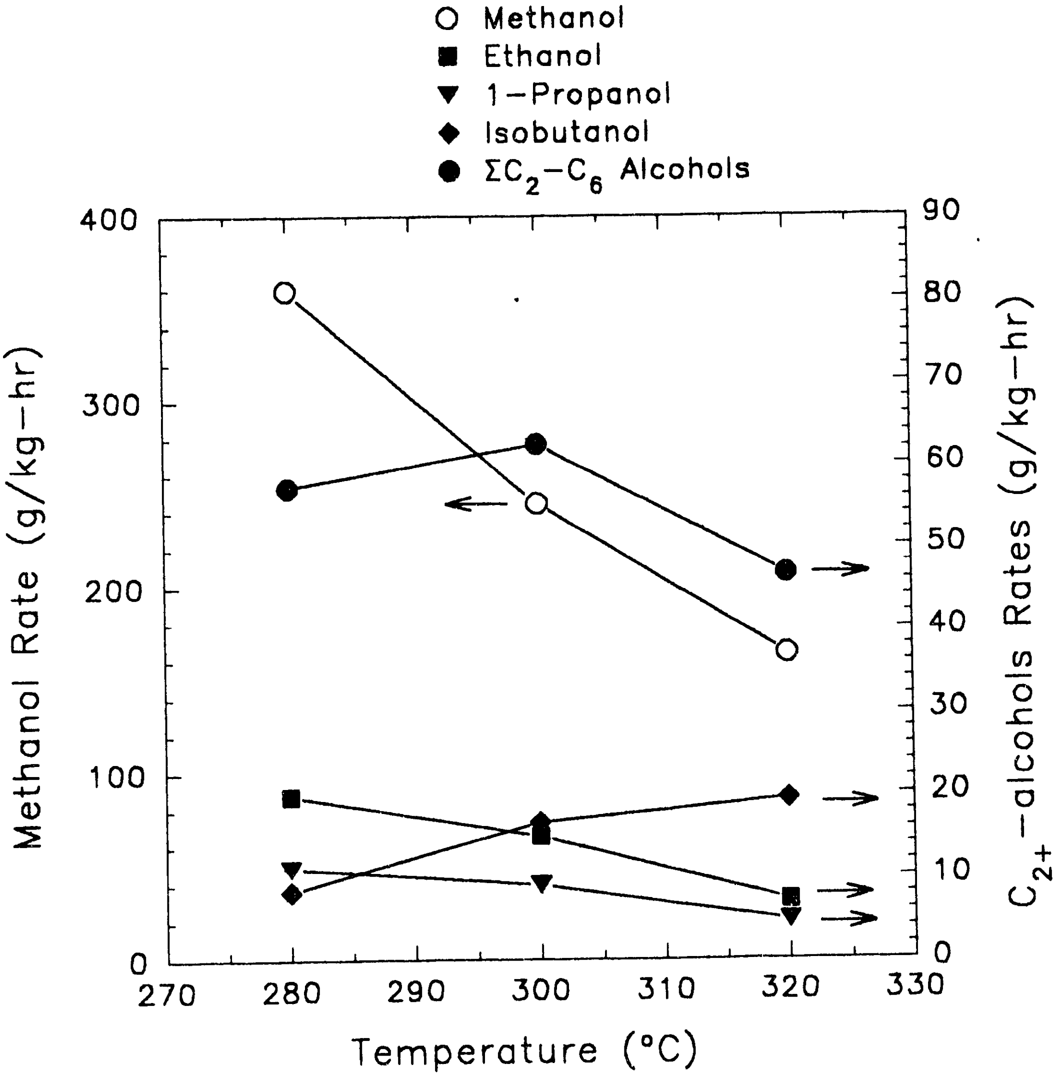


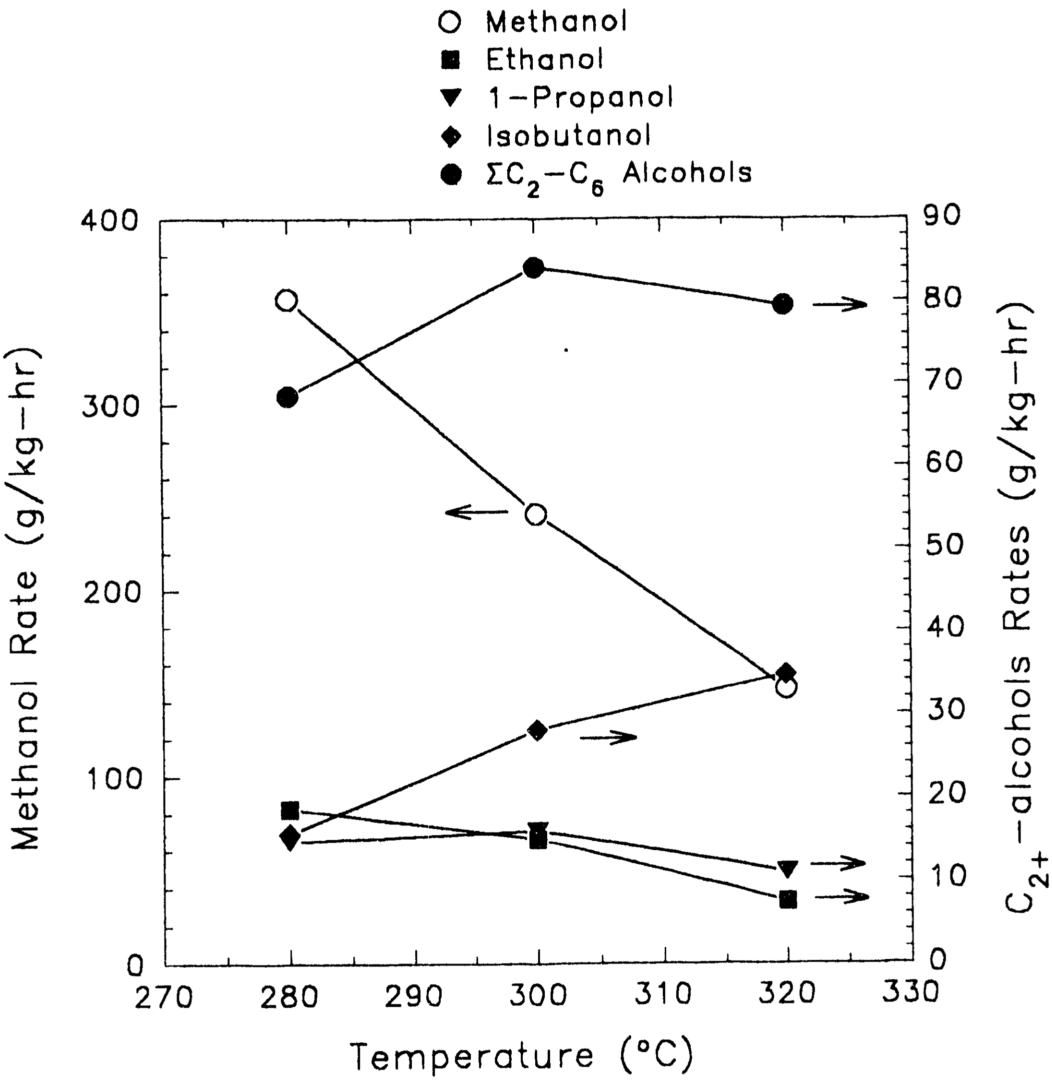
FIGURE 3–15

Effect of Temperature on Product Rates

Catalyst: Cs–Cu/ZnO/Al_2O_3

Run No.: 11168–76

7.0 MPa, Shell Gas, GHSV=5000 std.lit./kg–hr



becomes more significant at higher temperature. This hypothesis is consistent with the above mentioned mechanism for the synthesis of higher alcohols in which higher alcohol products are formed primarily from α- or β- addition of C_1 units to lower alcohols.[11,12]

Figures 3-16 and 3-17 show how temperature influences the distribution of alcohol products for Cu/ZnO/Al_2O_3 and Cs-Cu/ZnO/Al_2O_3, respectively. Obviously, for both catalysts, increased temperature results in a higher selectivity to C_2-C_6 alcohols. Also, the Cs-promoted sample has a higher selectivity to C_{2+}-alcohols than the unpromoted Cu/ZnO/Al_2O_3, at both temperatures considered. The branched chain alcohols show a particularly large increase in selectivity with increased temperature for both catalysts. At 320°C, the selectivity to isobutanol for Cs-Cu/ZnO/Al_2O_3 catalyst was 14.3 wt%. For this same catalyst at 320°C, the methanol/ΣC_2-C_6 alcohols split was 65/35 by weight, a split which is within the range for gasoline addition.

3.2.1.3 Methanol and Ethanol Addition to Feed Gas

One method of increasing product selectivity to higher alcohols during mixed alcohols synthesis is by recycle of lower alcohols products. To determine the effectiveness of each catalyst at converting methanol and ethanol to higher alcohols products, methanol and ethanol were injected into the syngas feed for each catalyst. The results of these experiments are shown in Tables 3-4 and 3-5 for unpromoted Cu/ZnO/Al_2O_3 and Cs-promoted Cu/ZnO/Al_2O_3, respectively. Both alcohols were injected at a rate of 380 g/kg-hr, which corresponds to a reactor feed concentration of 5 mol% methanol or 3.5 mol% ethanol. Also shown in Tables 3-4 and 3-5, for comparison, are the results obtained for no alcohol addition for each catalyst.

The results in Tables 3-4 and 3-5 indicate that methanol addition increased the synthesis rates of higher alcohols for both catalysts. The most significant effect was on the ethanol rate, which increased by 40% for both catalysts. A portion of the added methanol was unreacted as indicated by the increase in the methanol effluent rate over the case for no methanol addition. Effluent gas analysis indicates that a large portion of the added methanol was converted to CO and H_2, presumably by the reverse of the methanol synthesis reaction. Methanol addition resulted in a modest increase in the ΣC_3-C_6 alcohols rate for each catalyst; the rate increased by 18% and 21% for Cu/ZnO/Al_2O_3 and Cs-Cu/ZnO/Al_2O_3, respectively. In summary, the effect of methanol addition to the feed appears to be comparable for both catalysts.

TABLE 3-4
Effect of Feed Addition of Methanol and Ethanol for Cu/ZnO/Al_2O_3

Methanol or Ethanol Injection Rate=380 g/kg-hr
300°C, 7.0 MPa, Syngas GHSV=5000 std. lit./kg-hr

	Reactor Effluent Rate (g/kg-hr)				
Feed Gas	Methanol	Ethanol	1-Propanol	Isobutanol	ΣC_3-C_6 alcohols
Shell	258	15	9	15	45
Shell + 5 mol% methanol	379	21	12	16	53
Shell + 3.5 mol% ethanol	262	124	21	18	69

FIGURE 3-16

Effect of Temperature on Alcohol Product Distribution

Catalyst: $Cu/ZnO/Al_2O_3$
Run No.: 11472-39
7.0 MPa, Shell Gas, GHSV=5000 std.lit./kg-hr

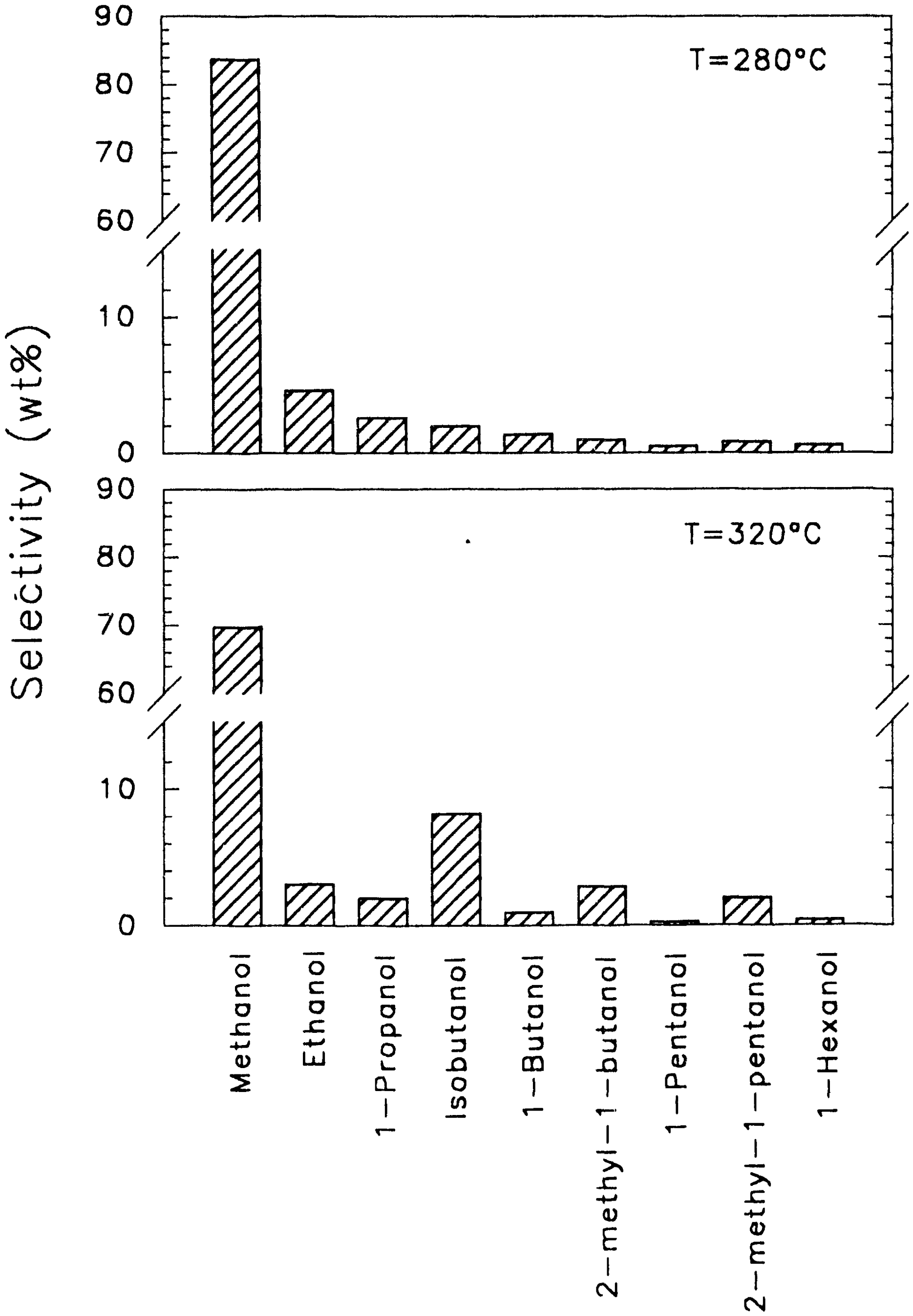


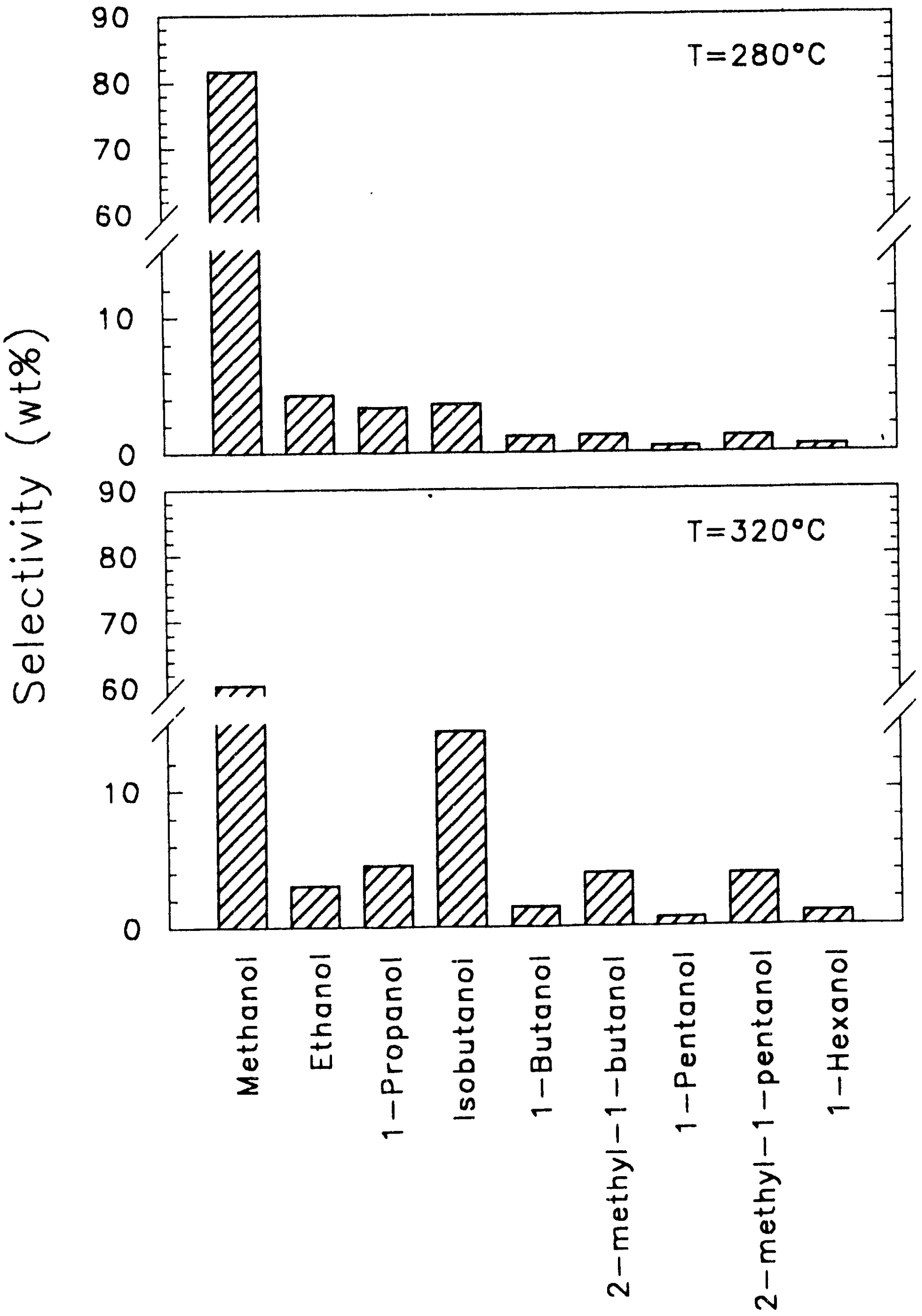
FIGURE 3-17

Effect of Temperature on Alcohol Product Distribution

Catalyst: Cs-Cu/ZnO/Al_2O_3

Run No.: 11168-76

7.0 MPa, Shell Gas, GHSV=5000 std.lit./kg-hr



The results for ethanol addition are considerably different than those for methanol addition. Tables 3-4 and 3-5 show that ethanol addition at 3.5 mol% increased the synthesis rate of C_{3+}-alcohols significantly more than that observed for methanol addition at 5 mol%. For the unpromoted $Cu/ZnO/Al_2O_3$ catalyst, ethanol addition resulted in a 53% increase in the ΣC_3-C_6 alcohols rate over the case for no ethanol addition. For this same catalyst, the 1-propanol rate increased by a factor of 2.3 while the isobutanol rate increased by 20%.

TABLE 3-5
Effect of Feed Addition of Methanol and Ethanol for Cs-$Cu/ZnO/Al_2O_3$

Methanol or Ethanol Injection Rate=380 g/kg-hr
300°C, 7.0 MPa, Syngas GHSV=5000 std. lit./kg-hr

	Reactor Effluent Rate (g/kg-hr)				
Feed Gas	Methanol	Ethanol	1-Propanol	Isobutanol	ΣC_3-C_6 alcohols
Shell	243	15	15	26	63
Shell + 5 mol% methanol	361	21	20	29	76
Shell + 3.5 mol% ethanol	241	116	64	55	162

For the Cs-promoted $Cu/ZnO/Al_2O_3$ catalyst, the influence of ethanol addition on the product distribution was much more dramatic. Ethanol addition increased the ΣC_3-C_6 alcohols rate by a factor of 2.6, an increase which is significantly more than the 53% increase observed for the unpromoted catalyst. The 1-propanol rate and isobutanol rate increased by factors of 4.3 and 2.1, respectively, upon ethanol addition.

Since other investigators have studied alcohol addition to syngas feed over Cu/ZnO-based catalysts, it is worthwhile to compare their results with those in the present work. Nunan et al.,[11] in their studies of Cs-doped Cu/ZnO, injected ethanol to H_2/CO=1:1 feed and observed the effect on the alcohol distribution at 300°C and 7.6 MPa. In agreement with the present results, their experiments showed that ethanol injection did not effect the methanol rate, but significantly increased the rates for 1-propanol and isobutanol. Kiennemann et al.,[13] studied the mechanism of higher alcohols formation on $Cu/ZnO/Al_2O_3$ catalysts by using probe molecules such as methanol. In contrast to the present work, they observed a much greater relative increase in the formation of ethanol, 1-propanol, and isobutanol, upon addition of methanol to CO/H_2=1:2 feed gas, than that observed in this study. Recall that in the present work only an 18-21% increase in C_3-C_6 alcohols was observed upon addition of 5 mol% methanol. However, it is noteworthy that the reaction conditions employed by Kiennemann et al. in their tests were much different than those used in the present work. In their experiments, a reaction temperature of 215°C and reaction pressure of 1 atm were used. Under these conditions, the formation of ethanol, 1-propanol, and isobutanol was not detected prior to methanol addition.

The results in Tables 3-4 and 3-5 indicate that recycle of methanol and, in particular, ethanol is a viable means of increasing the rate and selectivity to higher alcohols over these catalysts in a slurry reactor. However, the Cs-promoted catalyst is much more effective at converting added ethanol to higher products than the unpromoted catalyst. This is perhaps not surprising since the cesium component is believed to provide an active center upon which key steps in the chain growth process occur.[11]

3.2.2 Lurgi Octamix Mixed Alcohols Catalyst

The Lurgi Octamix mixed alcohols catalyst is an alkali-promoted Cu/ZnO-based mixed alcohols catalyst that was developed for use in a modification of Lurgi's low-pressure methanol synthesis process. Lurgi's powder catalyst was used directly in the micro-autoclave reactors to evaluate its use in a slurry reactor based process. The first two experimental runs with this catalyst showed an anomalous activity instability with on-stream time. Later inspection of the micro-autoclave internals indicated that a partial clog had developed in the impeller draft tube. After clearing the tube, a successful retest of the catalyst was done, the results of which are reported here.

3.2.2.1 Effect of time on stream

The catalyst was reduced in situ using 2% H_2 in N_2 by ramping the temperature from 100°C to 200°C at 10°C/hour, followed by a hold at 200°C for 8 hours.

Figure 3-18 shows the synthesis rate for the major products as a function of total time on syngas. The major products were methanol, higher alcohols (grouped together as ΣC_2-C_6 alcohols), and dimethyl ether (DME). The relatively high rate of production of DME is surprising for this catalyst. As shown in Figure 3-18, the methanol rate first increases, then decreases slightly with time on stream. The DME rate also decreases slightly with time. Of the major products, the higher alcohols rate shows the greatest decline with time. The ΣC_2-C_6 alcohols rate approaches a reasonably level value after about 130 hours, following which time process variable studies were done.

3.2.2.2 Effect of Reaction Temperature

The influence of temperature on rate and selectivity was investigated in the range of 250°C to 280°C using the Shell gas feed at a pressure of 7.0 MPa and a GHSV of 5000 std. lit./kg-hr. The guidelines for operation of the catalyst, supplied by Lurgi, indicated that reaction temperatures in excess of 285°C should be avoided. The effect of temperature on rate and selectivity for the major products is shown in Figures 3-19 and 3-20, respectively. For the range of temperature investigated, the DME and ΣC_2-C_6 alcohols rates increase dramatically with increasing temperature. By contrast, the methanol rate is approximately constant between 250°C and 265°C, while showing a decrease upon further increase in temperature to 280°C.

Figure 3-20 shows that increasing temperature dramatically increases selectivity to higher alcohols and DME, accompanied by a corresponding decrease in selectivity to methanol. The maximum selectivity to ΣC_2-C_6 alcohols was 7.2%, the value measured at 280°C. The 4 wt% selectivity to DME at this temperature is surprisingly high.

Figure 3-21 shows the alcohol product distribution obtained at 280°C, 7.0 MPa, and a GHSV of 5000 std. lit./kg-hr. Similar to the case for the cesium-promoted Cu/ZnO/Al_2O_3 catalyst, the selectivity to "2-methyl-" alcohol isomers is significant. The reason why the "2-methyl-" isomers are formed in significant quantities was discussed earlier. At these reaction conditions, selectivity to the various alcohols decreases with increasing carbon number. The methanol/ΣC_2-C_6 alcohols split at 280°C was 92/8, a split not favorable for direct gasoline addition. However, it is noteworthy that Lurgi's packed bed-based Octamix process incorporates methanol recycle to achieve a suitable alcohol product composition.

FIGURE 3-18

Effect of On-Stream Time on Product Rates

Catalyst: Octamix

Run No.: 12200-31

250°C, 7.0 MPa, Shell Gas, 5000 GHSV

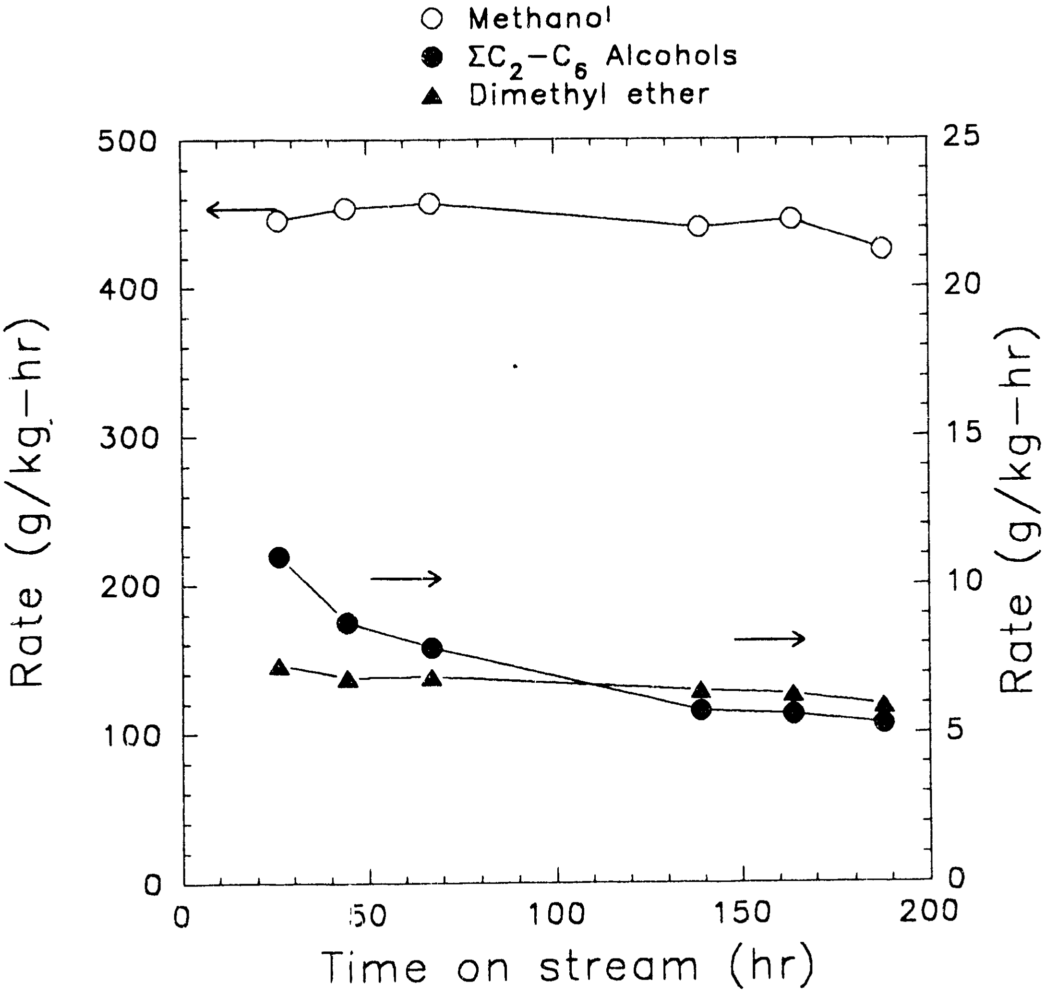


FIGURE 3–19

Effect of Temperature on Product Rates

Catalyst: Octamix

Run No.: 12200–31

7.0 MPa, Shell Gas, GHSV=5000 std. lit./kg–hr

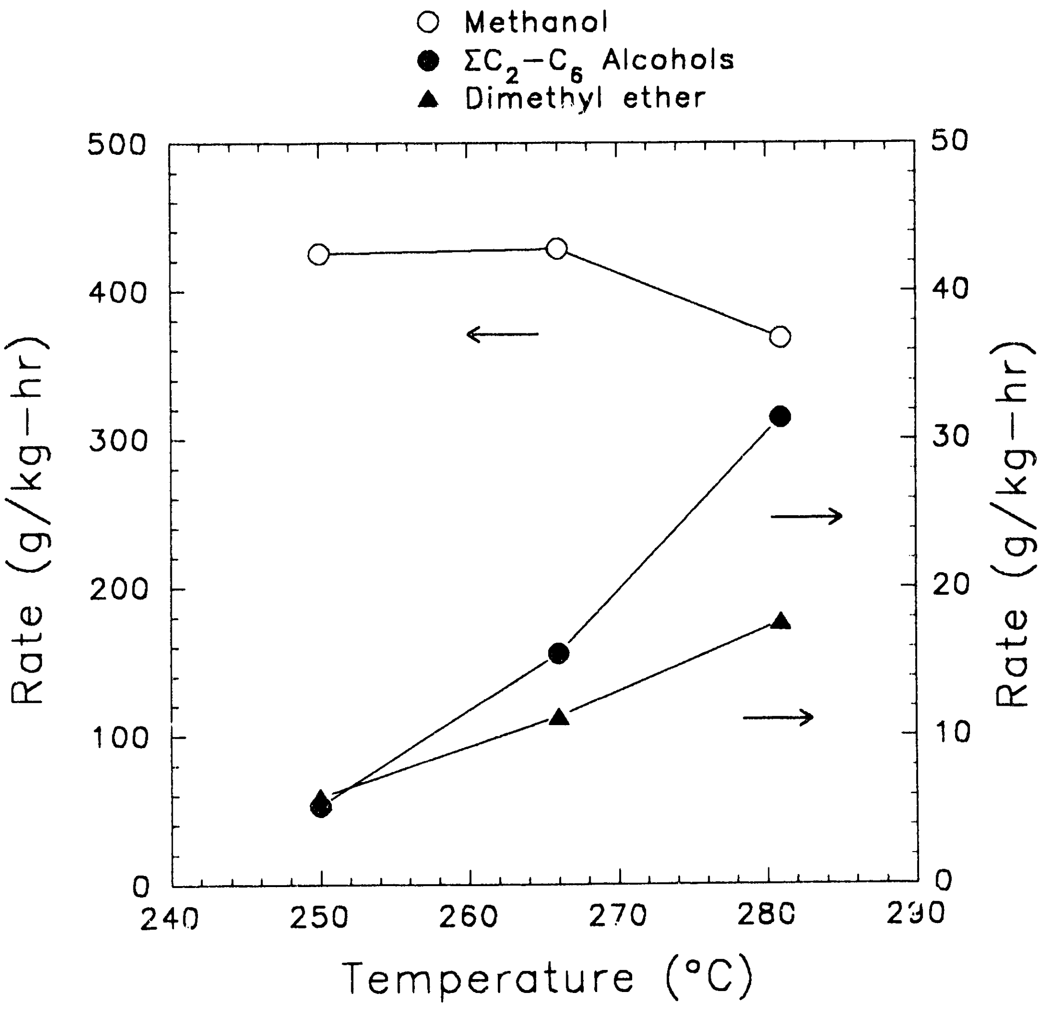


FIGURE 3–20

Effect of Temperature on Product Selectivities

Catalyst: Octamix

Run No.: 12200–31

7.0 MPa, Shell Gas, GHSV=5000 std. lit./kg–hr

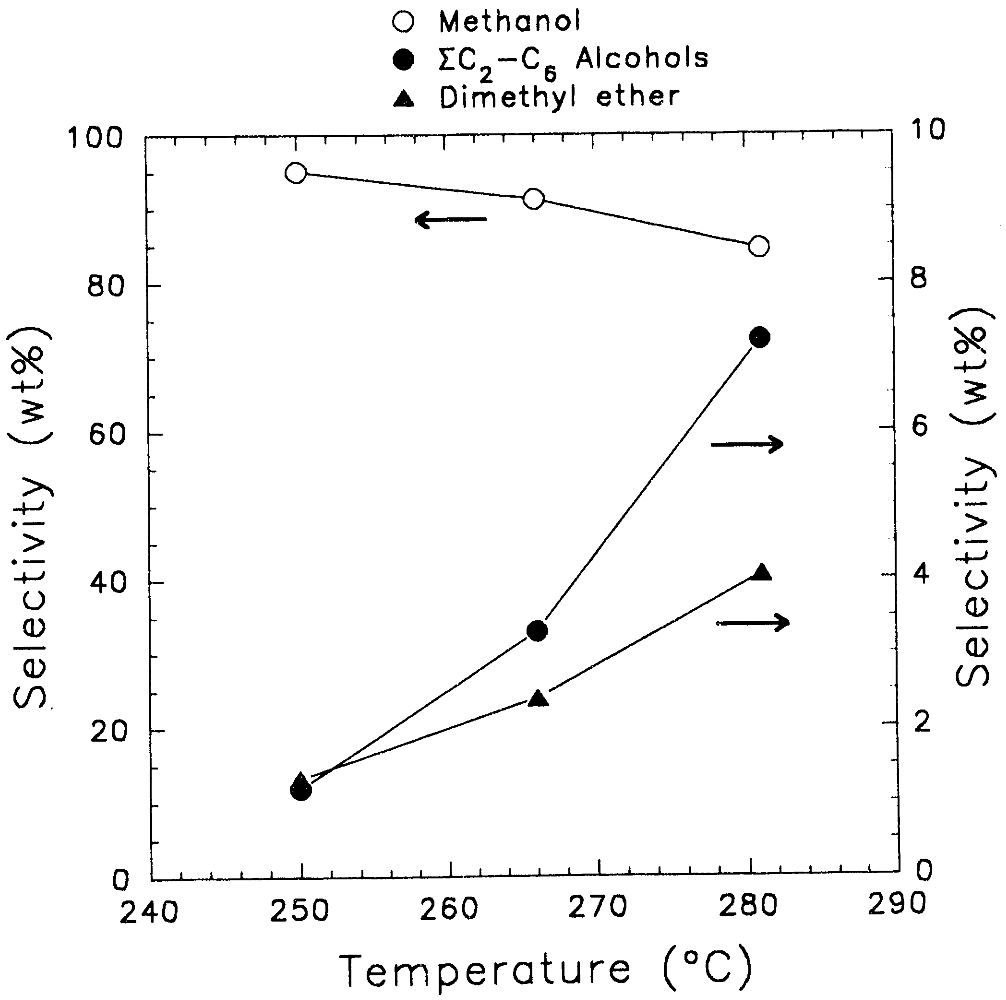
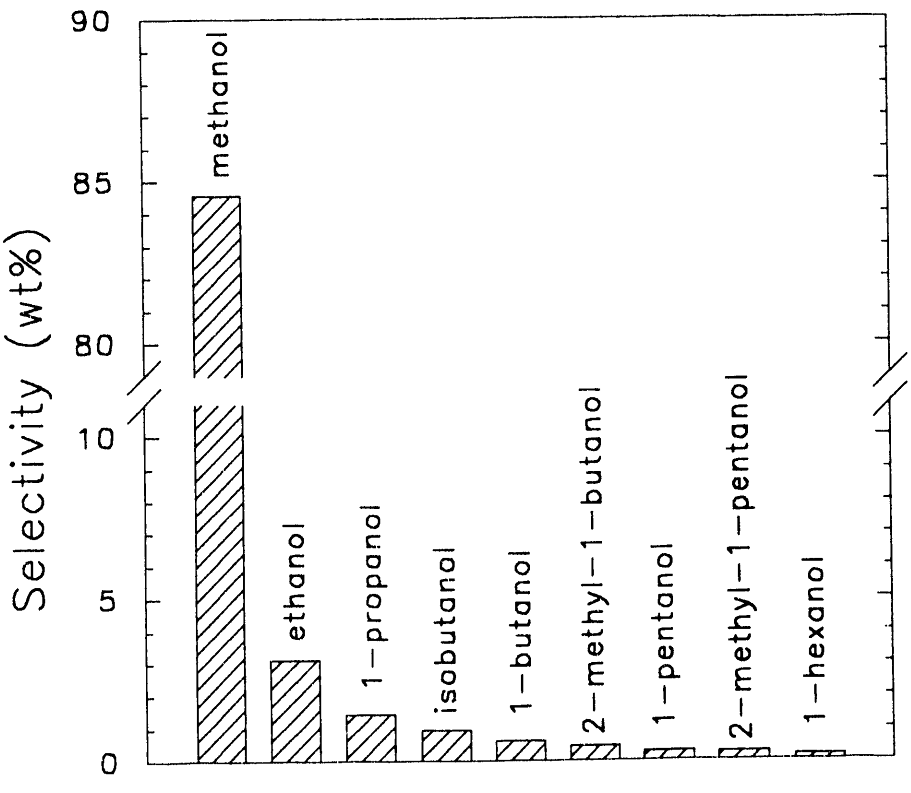


FIGURE 3–21

Alcohol Product Distribution

Catalyst: Octamix

Shell Gas, 280°C, 7.0 MPa, GHSV=5000 std. lit./kg–hr



3.2.2.3 Effect of Pressure

Figures 3-22 and 3-23 show the effect of reaction pressure on rate and selectivity, respectively. For these experiments, reaction pressures of 5.3 MPa, 7.0 MPa, and 9.7 MPa were investigated using Shell gas feed at 280°C and a GHSV of 5000 std. lit./kg-hr. Figure 3-22 shows that increasing pressure from 5.3 MPa to 7.0 MPa resulted in an increased synthesis rate for methanol, ΣC_2-C_6 alcohols, and DME. However, further increase in pressure from 7.0 MPa to 9.7 MPa had only a slight effect on the rate; the methanol and DME rates were almost invariant in this range, while the ΣC_2-C_6 alcohols rate decreased slightly. Since the effect of pressure on the rate for each of the major products is of a comparable magnitude, the selectivity shows little variation with pressure across this range, as illustrated in Figure 3-23.

3.2.2.4 Effect of Feed Gas Composition

The influence of syngas composition on the performance of the Octamix catalyst was investigated by comparing the Texaco and Shell feed gases. Figure 3-24 shows the methanol and ΣC_2-C_6 alcohols rates as a function of GHSV for both feed gases, while Figure 3-25 shows the corresponding selectivity data. These data were obtained at 280°C and 7.0 MPa using GHSVs of 5000 and 10,000 std. lit./kg-hr. As observed for the cesium-promoted $Cu/ZnO/Al_2O_3$ catalyst, the ΣC_2-C_6 alcohols rate and selectivity is much higher for Shell gas. Not surprisingly, selectivity to ΣC_2-C_6 alcohols decreases with increasing GHSV.

3.2.3 Cu-Co Mixed Alcohols Catalyst

A Cu-Co based mixed alcohols catalyst was evaluated for use in a slurry reactor. This catalyst sample was obtained under a confidentiality agreement from an external source. A sample of this material was slurried with Drakeol 10 mineral oil and activated in-situ using a stream of 2% H_2 in N_2. Following activation, the feed was changed to Shell gas at 5000 std. lit./kg-hr and the reaction conditions adjusted to 250°C and 7.0 MPa. The temperature was maintained at 250°C for 48 hours, after which the effect of temperature, pressure, GHSV, and syngas type were investigated.

3.2.3.1 Effect of Time on Stream

During the course of the investigation of various process variables, the reactor was periodically run at a fixed set of conditions to measure the catalyst stability. The results for periodic runs at 280°C, 7.0 MPa, and 5000 std. lit./kg-hr of Shell gas feed are shown in Figure 3-26. The major products were identified and grouped as methanol, ΣC_2-C_6 alcohols, and ΣC_1-C_6 hydrocarbons. These products account for 97 wt% of the total products observed; a very small selectivity low molecular weight esters accounts for the balance. No ether products were observed. The ΣC_2-C_6 alcohols and ΣC_1-C_6 hydrocarbons rates decrease monotonically with on-stream time, while the methanol rate first increases then decreases with time. The rates appear to level off after approximately 150 hours on stream.

3.2.3.2 Effect of Gas-Hourly Space Velocity

Figure 3-27 shows the effect of GHSV on the synthesis rates of the major products at 290°C and 7.0 MPa using the Shell feed gas. As shown, the methanol rate increases with GHSV, ranging from 20 g/kg-hr at 3000 std. lit./kg-hr to 32 g/kg-hr at 10,000 std. lit./kg-hr. Interestingly, the ΣC_1-C_6 hydrocarbons rate increases slightly between 3000 std. lit./kg-hr and 5000 std. lit./kg-hr, but decreases upon further increase in GHSV to 10,000 std. lit./kg-hr. The ΣC_2-C_6 alcohols rate also increases slightly from 3000 std. lit./kg-hr to 5000 std. lit./kg-hr, but appears to be approximately constant at higher GHSV.

FIGURE 3-22

Effect of Temperature on Product Rates

Catalyst: Octamix

Run No.: 12200-31

280°C, Shell Gas, GHSV=5000 std. lit./kg-hr

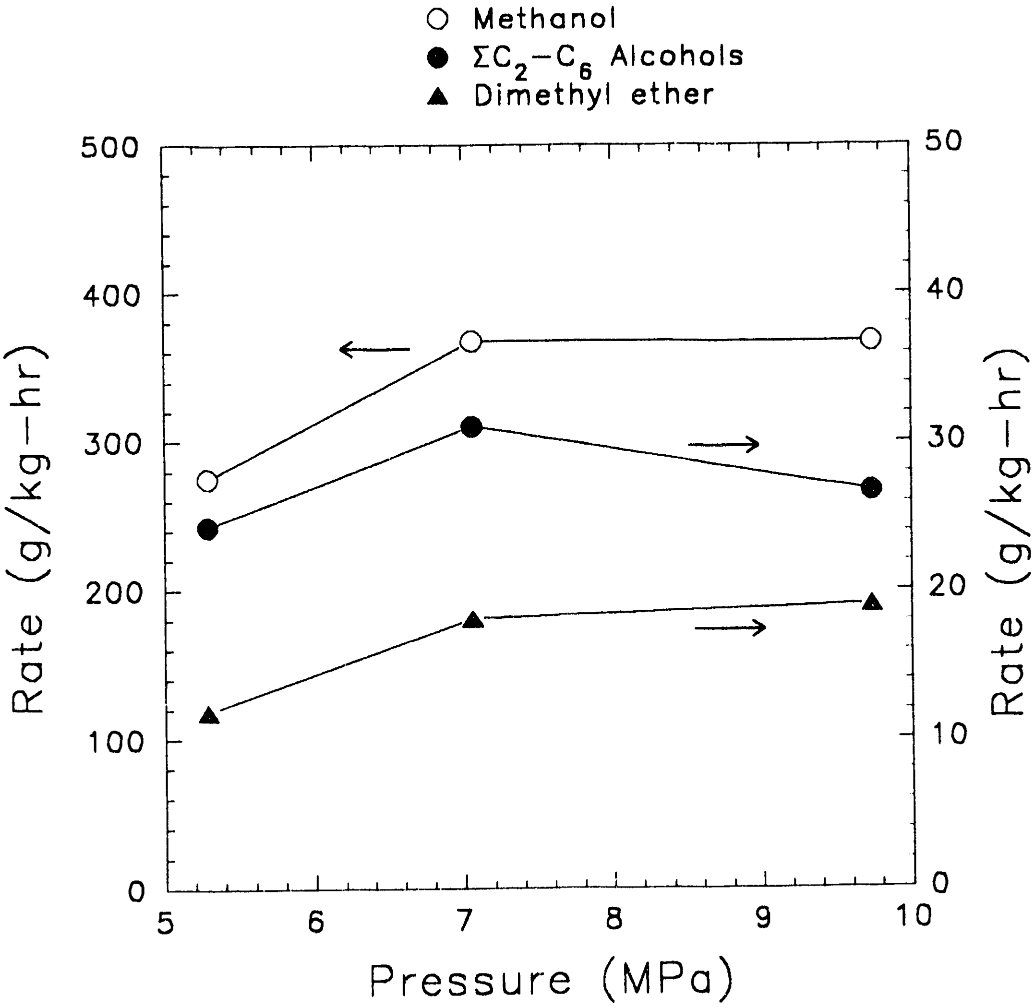


FIGURE 3-23

Effect of Pressure on Product Selectivities

Catalyst: Octamix

Run No.: 12200-31

280°C, Shell Gas, GHSV=5000 std. lit./kg-hr

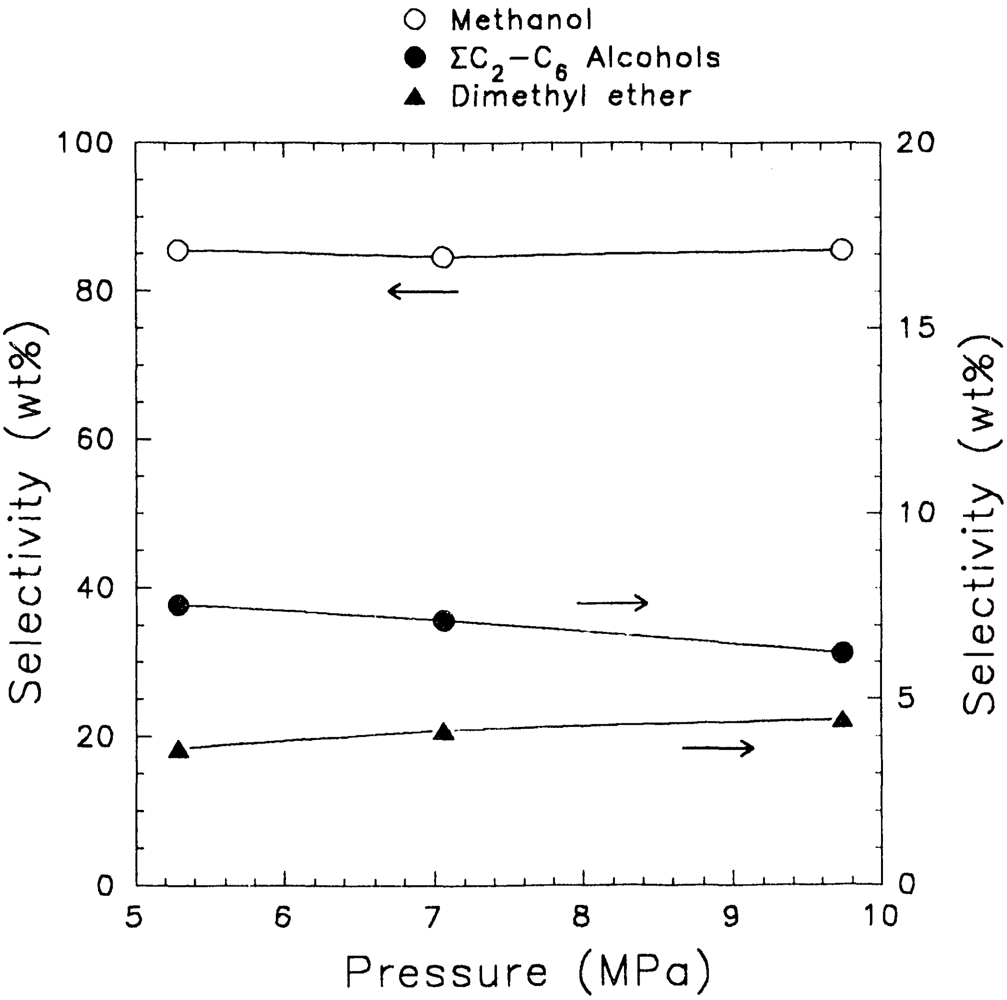


FIGURE 3-24

Effect of Syngas Composition on Product Rates

Catalyst: Octamix
Run No.: 12200-31
280°C, 7.0 MPa

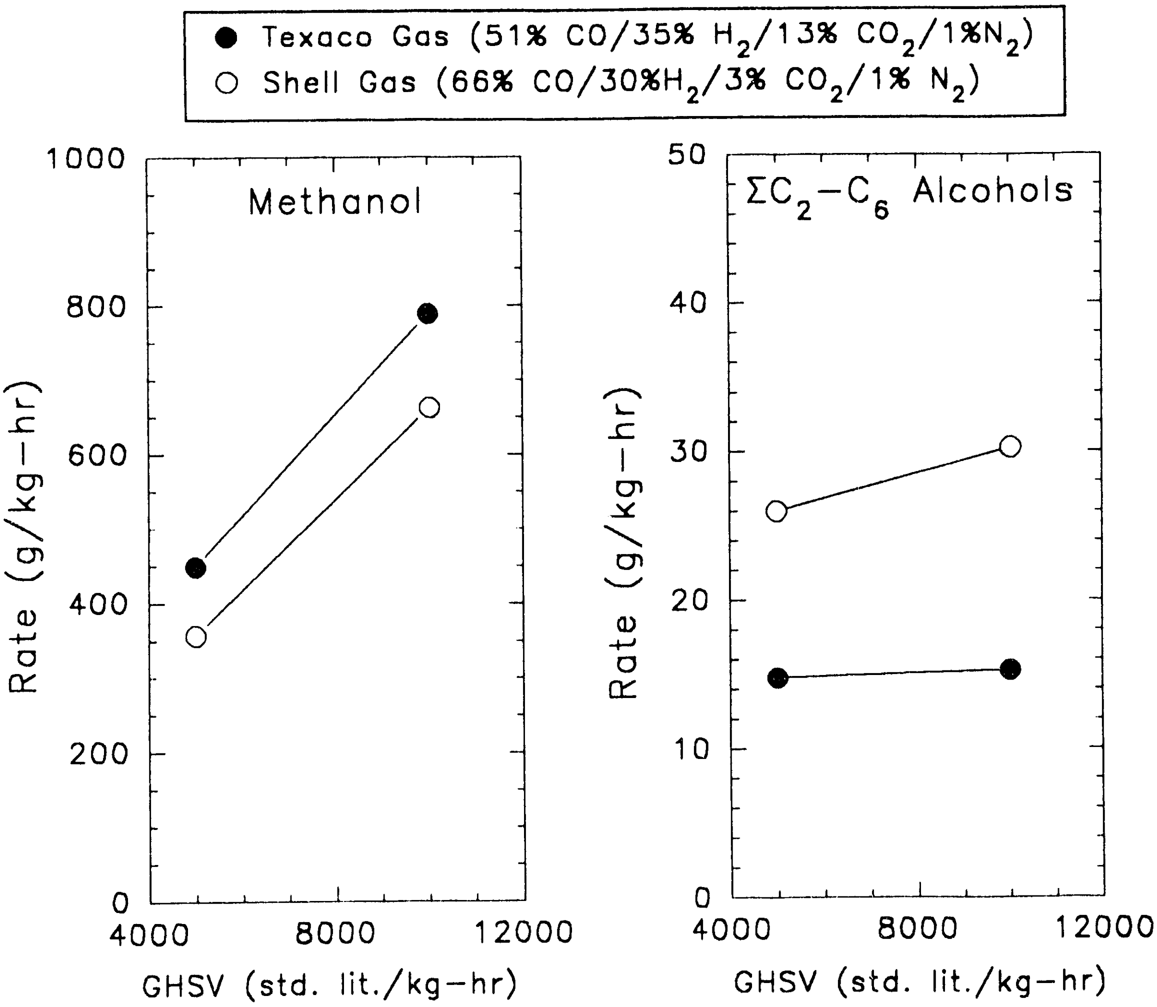


FIGURE 3-25

Effect of Syngas Composition on Product Selectivities

Catalyst: Octamix
Run No.: 12200-31
280°C, 7.0 MPa

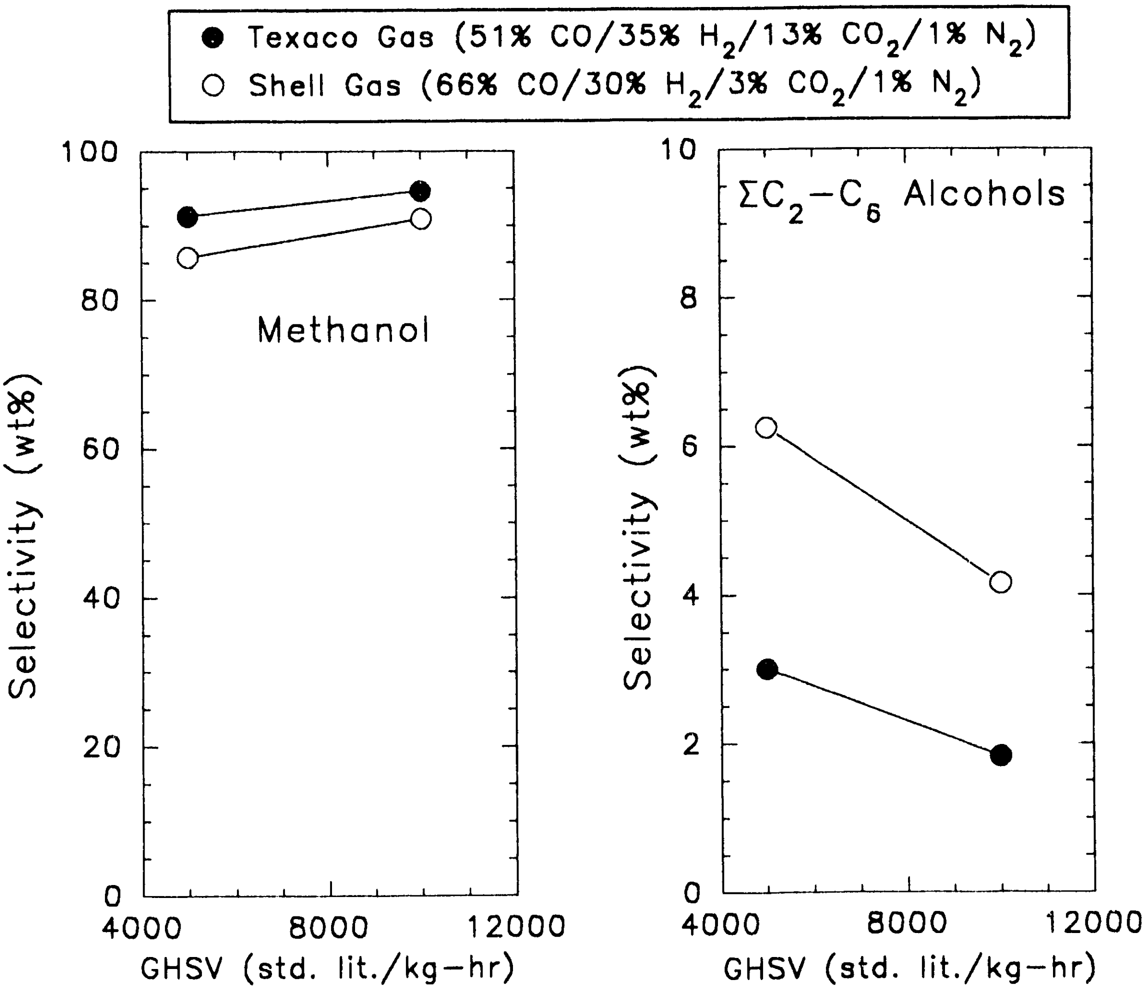


FIGURE 3-26

Effect of On-Stream Time on Product Rates

Catalyst: Cu-Co
Run No.: 12071-14
Shell Gas, 280°C, 7.0 MPa, GHSV=5000 std. lit./kg-hr

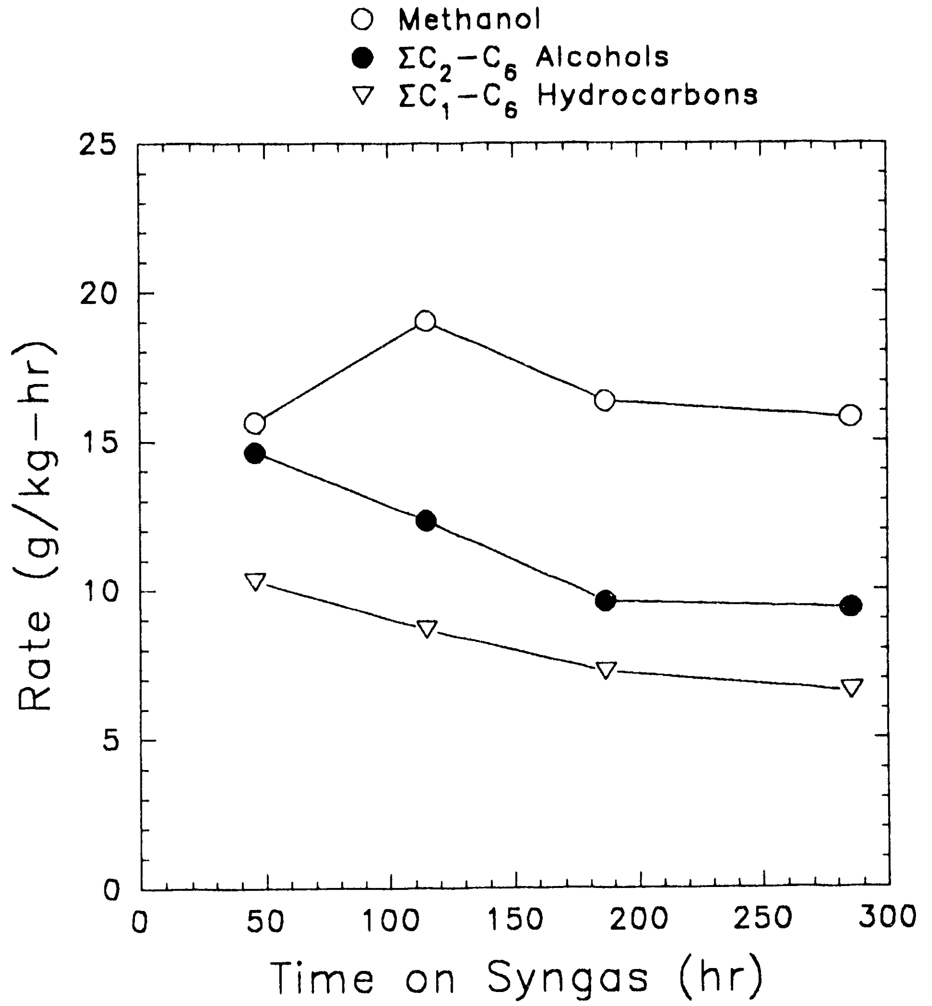
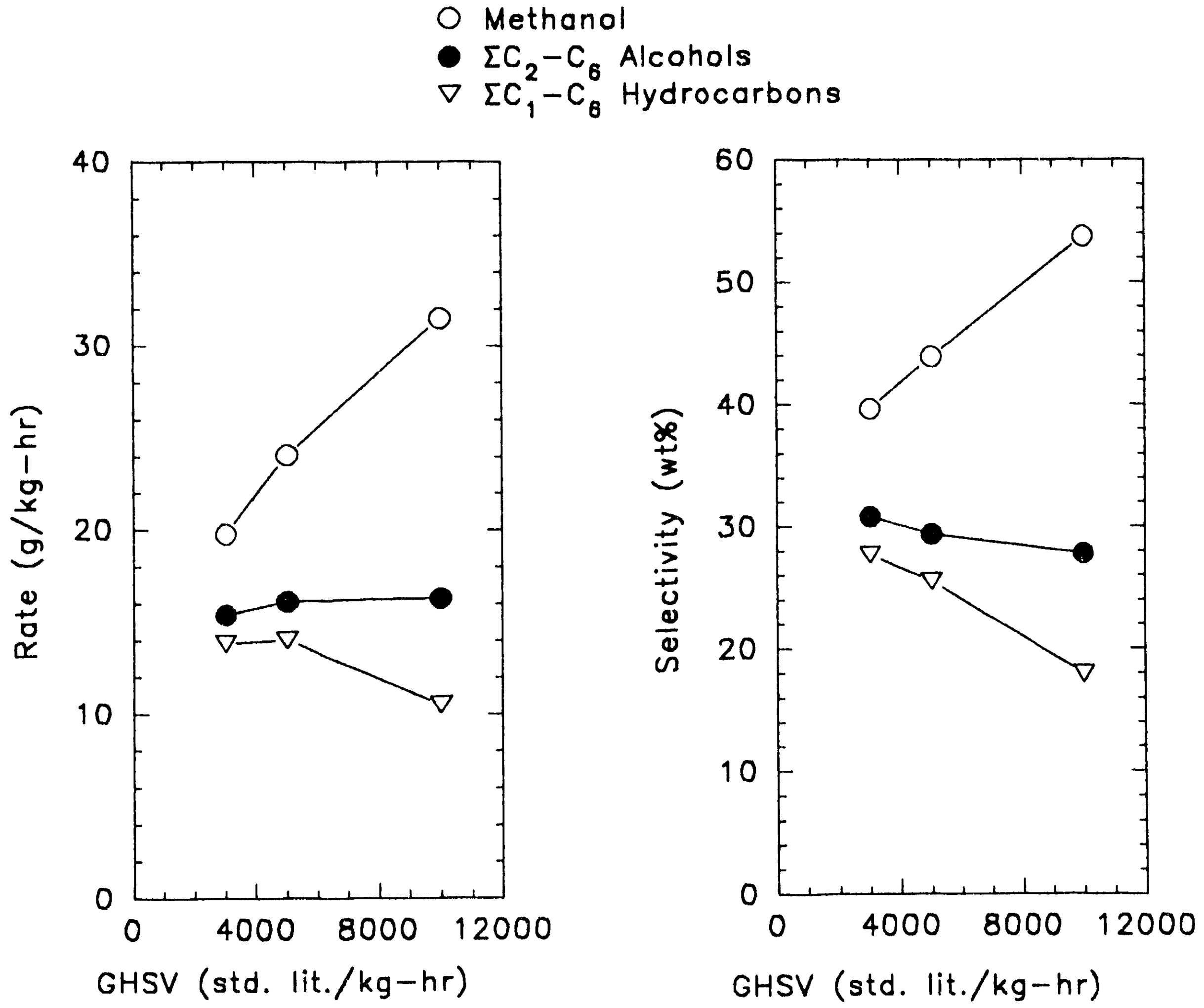


FIGURE 3-27

Effect of GHSV on Product Rates and Selectivities

Catalyst: Cu-Co

Shell Gas, 290°C, 7.0 MPa



The selectivity plot in Figure 3-27 shows that the selectivity to C_{2+}-alcohols is a weak function of GHSV, decreasing slightly with increasing GHSV. The increase in selectivity to methanol with increasing GHSV occurs at the expense of a corresponding decrease in selectivity to hydrocarbons. As can be seen, at low GHSV, the selectivity to hydrocarbons is approximately equal to the selectivity to ΣC_2-C_6 alcohols.

The alcohol product composition is in the acceptable range for direct gasoline blending. The methanol/ΣC_2-C_6 alcohols weight ratio is a strong function of GHSV, ranging from 56/44 at 3000 std. lit./kg-hr to 66/34 at 10,000 std. lit./kg-hr.

Figure 3-28 shows the alcohol product distribution obtained for this Cu-Co catalyst using the Shell feed gas. Selectivity values in Figure 3-28 are based on total organic products, including hydrocarbons and esters. Selectivity to the individual alcohols decreases with increasing molecular weight. In addition, the alcohol products are exclusively primary alcohols. In contrast to the case for the Cu/ZnO/Al_2O_3-based catalysts discussed earlier, the selectivity to linear primary alcohols is greater than the selectivity to branched primary alcohols. The high selectivity to linear alcohol products has been reported to be a characteristic of the Cu-Co based catalysts.[14]

Figure 3-29 shows the effect of GHSV on the rate and selectivity for the Texaco feed gas. The effect of GHSV on the product rates is similar to that observed for Shell gas, but the rates and relative proportions of the various products are different. Comparison with Figure 3-27 for Shell gas indicates that methanol and ΣC_2-C_6 alcohols rates are lower for Texaco gas, while the ΣC_1-C_6 hydrocarbons rate is higher for Texaco gas, across the GHSV range investigated. In fact, the selectivity to hydrocarbons for the Texaco feed gas is considerably higher than the selectivity to C_{2+}-alcohols. The overall performance of the catalyst, in terms of productivity and selectivity for alcohols, is considerably better for the Shell feed gas in comparison to the Texaco feed gas.

3.2.3.3 Effect of Temperature

Figure 3-30 shows the measured effect of temperature, between 260°C and 300°C, on the rates and selectivities for the major products. These experiments were done at a reaction pressure of 7.0 MPa using the Shell gas feed at a GHSV of 5000 std. lit./kg-hr. The production rate for all products increases with temperature. The rate of increase in methanol rate with temperature is not as great as the increase in ΣC_1-C_6 hydrocarbons rate. The result of this is that, as temperature is increased, the selectivity to methanol decreases at the expense of an increase in the selectivity to hydrocarbons. The selectivity to ΣC_2-C_6 alcohols shows little variance with temperature, remaining approximately constant at 30 wt% across the range of temperature investigated here. In summary, selectivity to total alcohols is enhanced by operation at low temperature, but this comes at the expense of decreased productivity.

3.2.3.4 Effect of Pressure

Figure 3-31 shows the effect of total pressure on the rates and selectivities for the major products. For these experiments, the pressure was varied between 5.2 MPa and 9.8 MPa at a reaction temperature of 290°C using the Shell gas feed at a GHSV of 5000 std. lit./kg-hr. The production rates of methanol, ΣC_2-C_6 alcohols, and ΣC_1-C_6 hydrocarbons increase monotonically with pressure across the range examined. The extent to which pressure influences the rate is similar for all products, resulting in little variation in selectivity as a function of pressure.

FIGURE 3-28

Alcohol Product Distribution

Catalyst: Cu-Co

Shell Gas, 290°C, 7.0 MPa, GHSV=5000 std. lit./kg-hr

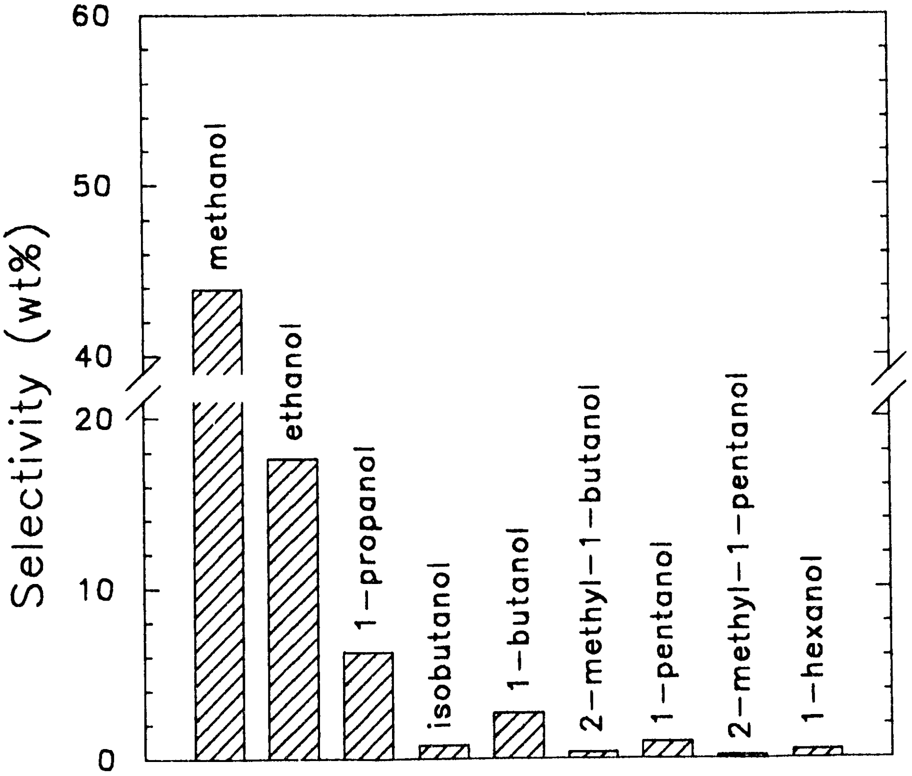


FIGURE 3-29

Effect of GHSV on Product Rates and Selectivities

Catalyst: Cu-Co

Texaco Gas, 290°C, 7.0 MPa

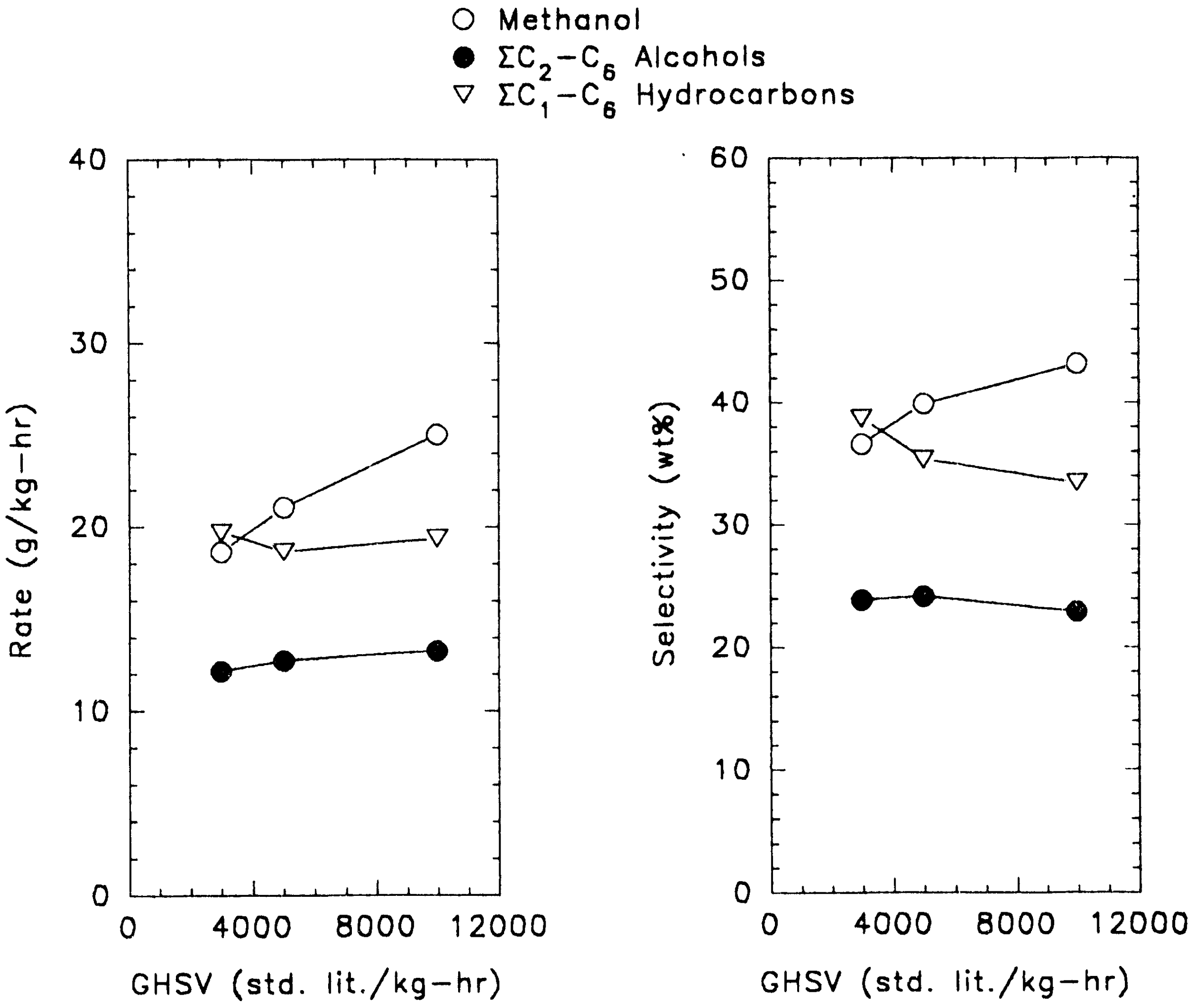


FIGURE 3-30

Effect of Temperature on Product Rates and Selectivities

Catalyst: Cu-Co

Shell Gas, 7.0 MPa, GHSV=5000 std. lit./kg-hr

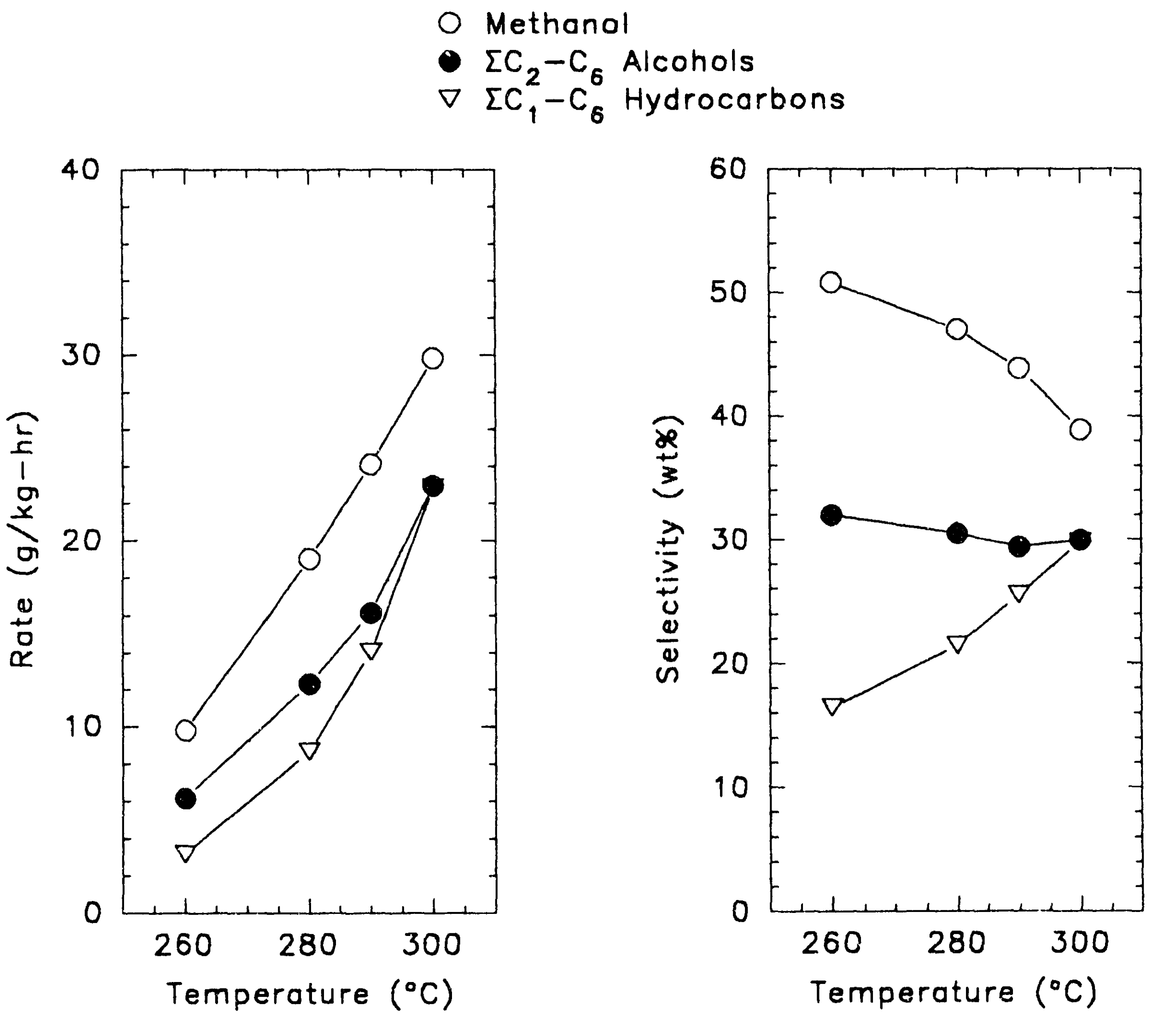
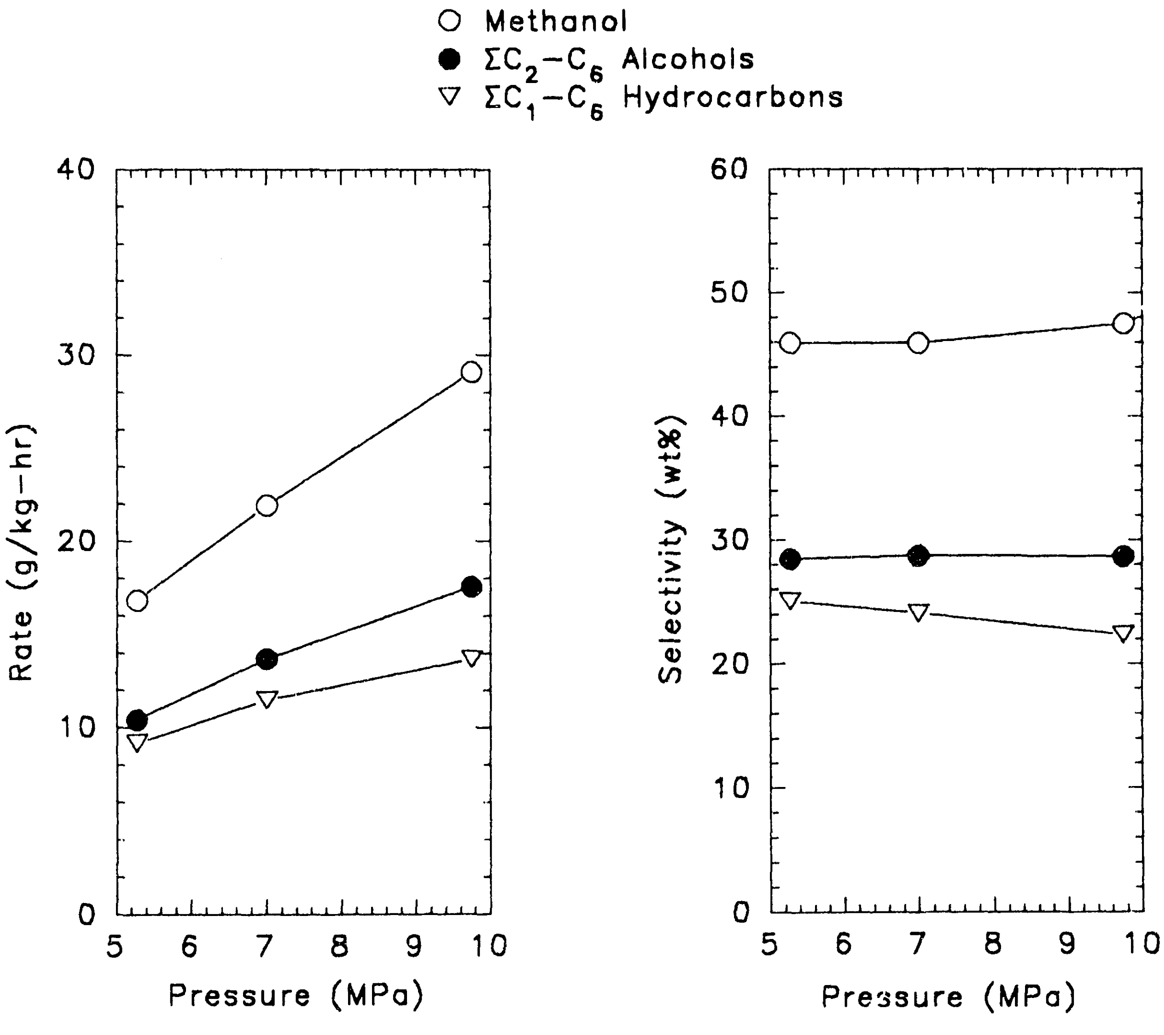


FIGURE 3-31

Effect of Pressure on Product Rates and Selectivities

Catalyst: Cu-Co

Shell Gas, 290°C, GHSV=5000 std. lit./kg-hr



3.2.4 Two-Component Catalyst Systems

The goal here was to investigate two-component catalyst systems for the conversion of syngas to mixed alcohols. Studies of the reaction mechanism for the formation of mixed alcohols indicate that higher molecular weight alcohols are formed from lower molecular weight alcohols via a sequential mechanism. The focus was to investigate the use of certain co-catalysts together with $Cu/ZnO/Al_2O_3$ in the same reactor to enhance the conversion of lower alcohols to higher alcohols. Two reaction concepts were envisioned: (1) methanol formed on the $Cu/ZnO/Al_2O_3$ component could be further reacted/homologated to higher alcohols over the co-catalyst, or (2) ethanol and/or C_2-oxygenates, formed over the co-catalyst at a greater rate than that for $Cu/ZnO/Al_2O_3$, could enter the reaction sequence to form C_{3+}-alcohols.

In this investigation, two type of catalysts were used as co-catalysts with BASF S3-86, a $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst. This catalyst was promoted with Cs in the studies discussed previously. One material, lanthanum strontium manganite ($La_{0.9}Sr_{0.1}MnO_3$), is of the class of compounds known as perovskites. This material contains cations of high basicity (La^{3+}, Sr^{2+}); basic cations are known to enhance selectivity to higher alcohols. In addition, this material contains manganese, a metal present in many catalysts developed for synthesizing mixed alcohols. The other material used as a co-catalyst was rhodium supported on La_2O_3. Rhodium on basic oxide supports, such as La_2O_3, is known to be selective for the synthesis of C_2-oxygenates, particularly ethanol and acetaldehyde, from syngas. Two Rh/La_2O_3 catalysts, differing only in Rh loading (0.5% and 5.0% by weight), were investigated. In all three cases, the co-catalyst was used together with $Cu/ZnO/Al_2O_3$ in a 50:50 mixture by weight.

Figure 3-32 shows the results obtained for 100% $Cu/ZnO/Al_2O_3$ and 50:50 mixtures of $Cu/ZnO/Al_2O_3$ with 0.5% Rh/La_2O_3, 5.0% Rh/La_2O_3, and $La_{0.9}Sr_{0.1}MnO_3$. The performance results are shown as the measured production rates for methanol and ΣC_2-C_6 alcohols versus GHSV obtained at 300°C and 7.0 MPa using Shell gas feed. Only a single GHSV was investigated in the case of the $La_{0.9}Sr_{0.1}MnO_3$ catalyst. It is important to note that the rate and GHSV are calculated based on the total weight of catalyst in the reactor, including the co-catalyst for the cases where co-catalyst was used.

For methanol synthesis, the rate is comparable for each catalyst system except the 5.0% Rh/La_2O_3 + $Cu/ZnO/Al_2O_3$ mixture. The rate for this particular system is lower than that for the other catalysts at the higher space velocities of 5000-10,000 std. lit./kg-hr. Much larger differences between the catalysts were observed for the ΣC_2-C_6 alcohols rate. None of the two-component catalyst systems performed better than the $Cu/ZnO/Al_2O_3$ operating alone with no co-catalyst. For the two Rh/La_2O_3 + $Cu/ZnO/Al_2O_3$ systems, the 0.5% Rh/La_2O_3 co-catalyst performed much better than 5.0% Rh/La_2O_3 co-catalyst. Among the two-component systems, the $La_{0.9}Sr_{0.1}MnO_3$ + $Cu/ZnO/Al_2O_3$ mixture showed the best performance in terms of ΣC_2-C_6 alcohols rate, at least at a GHSV of 5000 std. lit./kg-hr.

For the $La_{0.9}Sr_{0.1}MnO_3$ + $Cu/ZnO/Al_2O_3$ and 0.5% Rh/La_2O_3 + $Cu/ZnO/Al_2O_3$ systems, the use of the co-catalyst had only a minor effect on the distribution of alcohol products among the C_{2+}-alcohols. The most significant effect on product distribution was observed for the 5.0% Rh/La_2O_3 + $Cu/ZnO/Al_2O_3$ mixture. A comparison of the alcohol product distributions obtained for the 5.0% Rh/La_2O_3 + $Cu/ZnO/Al_2O_3$ mixture and $Cu/ZnO/Al_2O_3$ alone is shown in Figure 3-33. As shown, the selectivity to ethanol is slightly higher for the mixture, while the selectivity to products higher than ethanol is

FIGURE 3-32

Comparison of Performance of Two-Component Catalyst Systems

Shell Gas, 300°C, 7.0 MPa

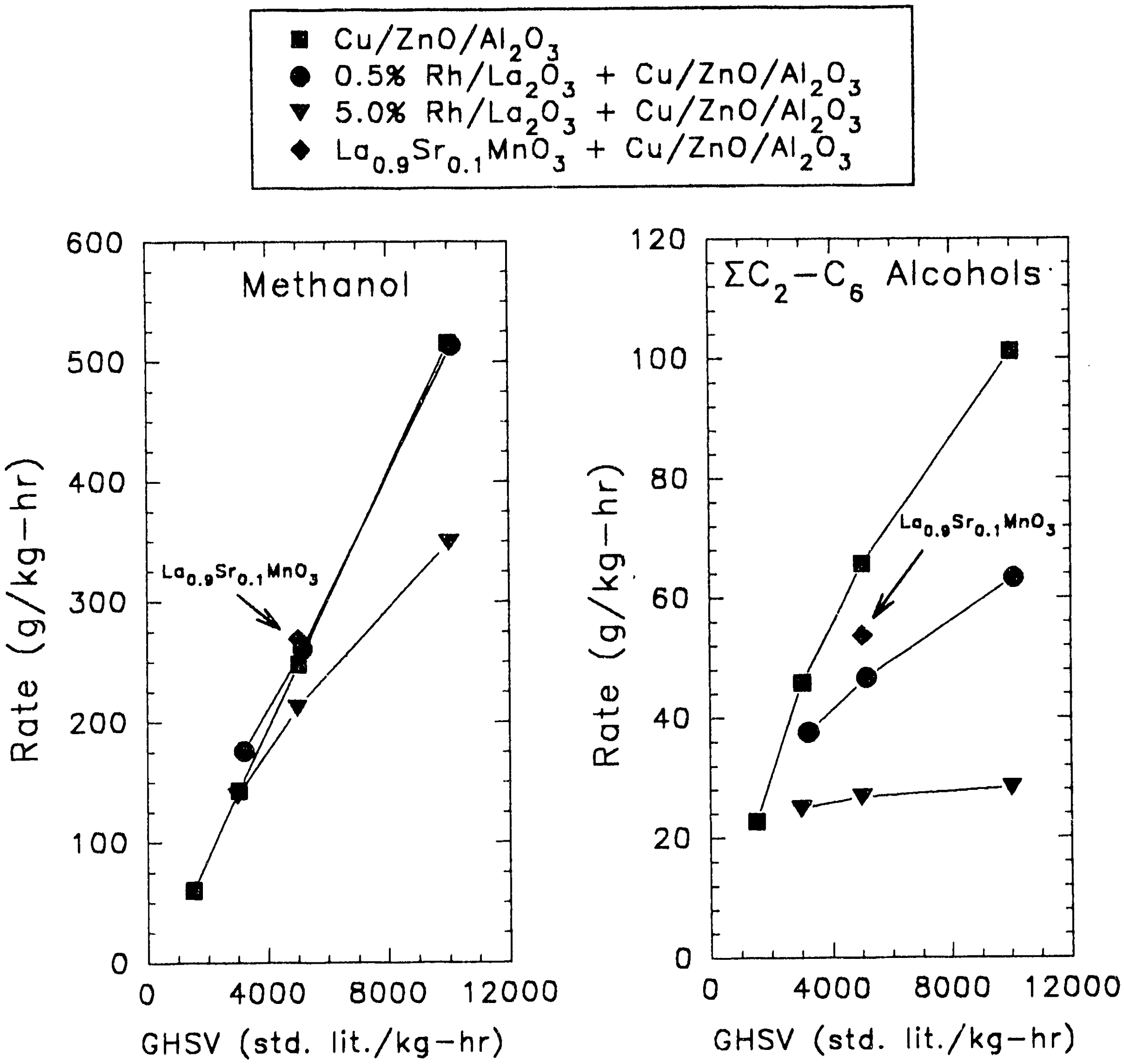
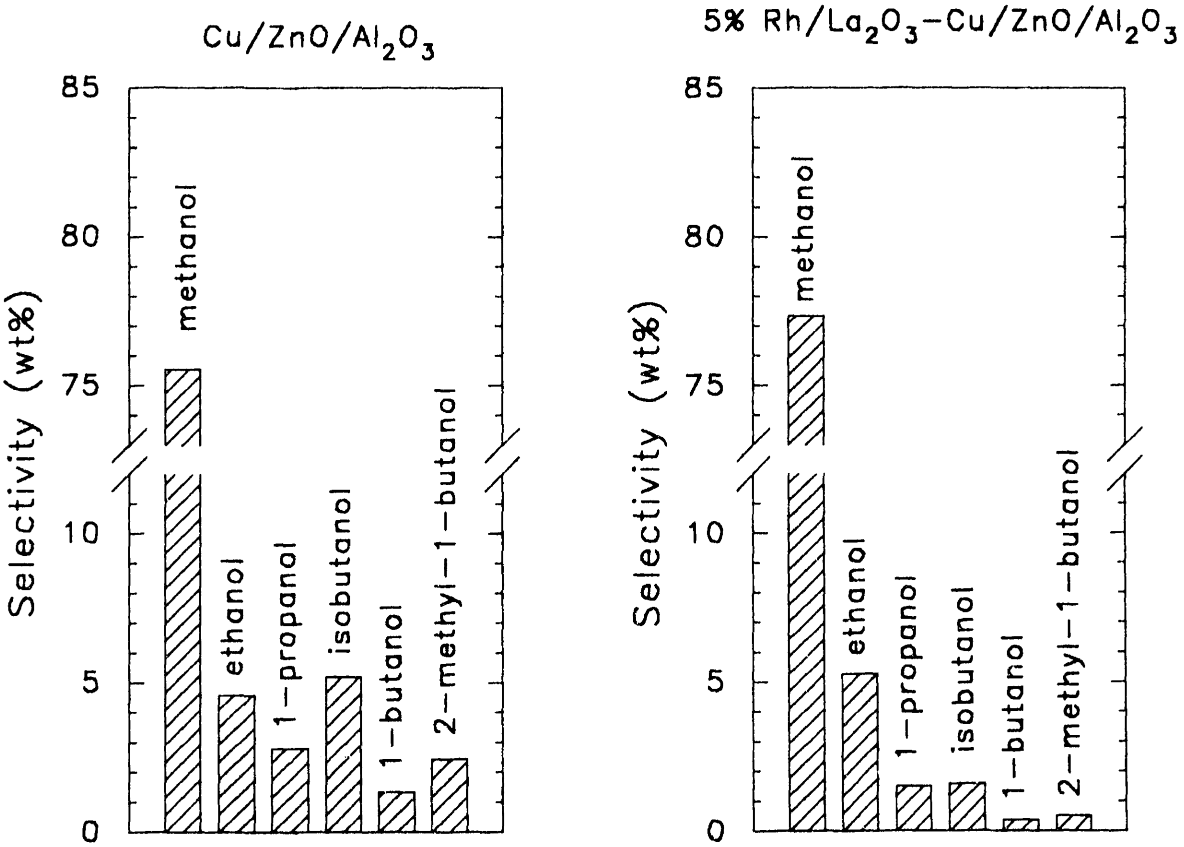


FIGURE 3-33

Comparison of Alcohols Product Distributions for $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/Al_2O_3$ + 5% Rh/La_2O_3

300°C, 7.0 MPa, GHSV=5000 std. lit./kg-hr, Shell Gas



less for the mixture. The reason for the suppression in higher products is not clear and, to gain understanding, would require further investigation.

In summary, none of the mixed catalyst systems investigated here performed better than Cu/ZnO/Al_2O_3. Obviously, further work is necessary to identify or develop viable co-catalysts.

3.2.5 Comparison of Mixed Alcohols Catalysts

In summary, several catalysts were investigated for use in a slurry reactor; these were single-component catalysts, as well as two-component systems which involved the use of a co-catalyst with Cu/ZnO/Al_2O_3. The use of the particular co-catalysts that were investigated, in physical mixtures with Cu/ZnO/Al_2O_3, apparently did not provide any performance advantage over the use of Cu/ZnO/Al_2O_3 alone. More work is needed to identify or develop suitable co-catalysts. However, it is worthwhile to compare the performance of the four single component catalysts that were investigated: (1) a Cu/ZnO/Al_2O_3 methanol synthesis catalyst, (2) a Cs-promoted Cu/ZnO/Al_2O_3 methanol synthesis catalyst, (3) Lurgi's Octamix catalyst, which is also an alkali-promoted Cu/ZnO-based material, and (4) a Cu-Co based mixed alcohols catalyst.

Comparisons of the performance of the four catalysts, at a common set of reaction conditions, are shown in Tables 3-6 and 3-7. Table 3-6 shows a comparison of the production rates of methanol, ΣC_2-C_6 alcohols, and ΣC_1-C_6 hydrocarbons at 280°C, 7.0 MPa, and 5000 std. lit./kg-hr of Shell feed gas. Table 3-7 shows the corresponding product selectivities obtained at these same reaction conditions.

TABLE 3-6

Comparison of Measured Product Rates for Cs-Cu/ZnO/Al_2O_3, Lurgi Octamix, and Cu-Co Catalysts

Reaction Conditions: Shell gas, 280°C, 7.0 MPa, GHSV=5000 std. lit./kg-hr

		Production Rate (g//kg-hr)		
Catalyst	Run No.	Methanol	ΣC_2-C_6 alcohols	ΣC_1-C_6 hydrocarbons
Cu/ZnO/Al_2O_3	11472-39	361	57.1	5.1
Lurgi Octamix	12200-31	368	31.4	3.0
Cu-Co	12071-14	16	9.6	7.3
Cs-Cu/ZnO/Al_2O_3	11168-75	357	68.5	5.7

TABLE 3-7
Comparison of Measured Product Rates for $Cs\text{-}Cu/ZnO/Al_2O_3$, Lurgi Octamix, and Cu-Co Catalysts

Reaction Conditions: Shell gas, 280°C, 7.0 MPa, GHSV=5000 std. lit./kg-hr

Catalyst	Run No.	Production Rate (g//kg-hr) Methanol	ΣC_2-C_6 alcohols	ΣC_1-C_6 hydrocarbons
$Cu/ZnO/Al_2O_3$	11472-39	83.7	13.3	1.2
Lurgi Octamix	12200-31	84.6	7.2	0.7
Cu-Co	12071-14	48.5	28.6	21.6
$Cs\text{-}Cu/ZnO/Al_2O_3$	11168-75	81.6	15.7	1.3

When producing mixed alcohols for blending into gasoline, the goal is to achieve a high selectivity for C_{2+}-alcohols, which are cosolvents for the methanol product. In addition, a high total alcohols synthesis rate is desirable, since this will increase reactor productivity. Non-selective conversion of syngas to products other than alcohols, e. g., light hydrocarbons, is undesirable.

Using the above criteria as a guide, comparisons of the four catalysts (Tables 3-6 and 3-7, and much of the other process variable studies done on these catalysts) indicate that the $Cs\text{-}Cu/ZnO/Al_2O_3$ catalysts showed the best overall performance. The ΣC_2-C_6 alcohols rate was higher for this catalyst than the others. Although the Cu-Co catalyst had the highest selectivity to C_{2+}-alcohols, the rate was significantly less than either of the other two catalysts. Moreover, the Cu-Co catalyst had the highest rate and selectivity to hydrocarbons.

The present results indicate that $Cs\text{-}Cu/ZnO/Al_2O_3$ is a viable catalyst for the slurry-phase synthesis of mixed alcohols from syngas. Further work on this catalyst, including some longer-term life tests, is necessary to determine its viability in a commercial process.

It is noteworthy that a potentially attractive characteristic of the $Cs\text{-}Cu/ZnO/Al_2O_3$ catalyst is its ability to produce a relatively high selectivity to branched-chain alcohols, particularly the "2-methyl-" isomers. Notable branched-chain product alcohols from this catalyst include isobutanol (2-methyl-1-propanol) and 2-methyl-1-butanol. These products are of particular interest because they can be dehydrated to useful olefins. The products of direct, intramolecular dehydration of isobutanol and 2-methyl-1-butanol are isobutylene and isoamylene, respectively. Isobutylene and isoamylene can be reacted with an alcohol, particularly methanol, to produce methyl tert-butyl ether (MTBE) and tert-amyl methyl ether (TAME), respectively. Both ethers are, of course, known to be outstanding oxygenated gasoline additives. Thus, alcohols produced from coal-derived syngas using $Cs\text{-}Cu/ZnO/Al_2O_3$ represent a viable, alternative source of iso-olefins for use in etherification.

3.3 Slurry-Phase Conversion of Syngas to Mixed Ethers via Mixed Alcohols

3.3.1 Product Identification

As mentioned previously, the dehydration of mixtures of alcohols is likely to yield a variety of products. The most prevalent products are expected to be mixed ethers, formed from intermolecular condensation of alcohols. In addition, olefins, which are formed from intramolecular dehydration of alcohols, are an expected side product. Ethers are the desirable products. The goal is to produce mixed ethers from product of a mixed alcohols synthesis catalyst.

A variety of ether products are expected from the condensation of a mixture of alcohols. Statistically, n(n+1)/2 different ethers can be formed from direct, intermolecular condensation of n different alcohols, assuming no rearrangement of the carbon backbone structure of the reactant alcohols. The major alcohol products from syngas conversion to mixed alcohols are C_1-C_4 primary alcohols: methanol, ethanol, 1-propanol, 1-butanol, and isobutanol (2-methyl-1-propanol). Thus, considering only these alcohol products, the number of different ethers that could be formed, by the above formula, is 5(5+1)/2=15.

Table 3-8 lists the possible ether products from condensation of C_1-C_4 primary alcohols. Also shown in the table are the structures of these ethers and their boiling points. Several of the ethers listed are not commercially available and must be synthesized for gas chromatographic identification and quantification purposes. For the purposes of the present investigation, none of the ethers were synthesized, but small samples of several of the commercially available ethers were purchased. Table 3-8 also indicates whether each ether was purchased as a pure sample for identification and quantification purposes.

TABLE 3-8
Expected Ether Products from Condensation of
Methanol, Ethanol, 1-Propanol, 1-Butanol, and Isobutanol

Ether	Structure	Boiling Point (°C)	Obtained Sample? (Y/N)
dimethyl	$CH_3\text{-}O\text{-}CH_3$	-24.9	Y
methyl ethyl	$CH_3\text{-}O\text{-}CH_2CH_3$	7.3	N
diethyl	$CH_3CH_2\text{-}O\text{-}CH_2CH_3$	34.5	Y
methyl n-propyl	$CH_3\text{-}O\text{-}CH_2CH_2CH_3$	38.9	N
methyl isobutyl	$CH_3\text{-}O\text{-}CH_2CH(CH_3)CH_3$	58	N
ethyl n-propyl	$CH_3CH_2\text{-}O\text{-}CH_2CH_2CH_3$	63.6	N
di-n-propyl	$CH_3CH_2CH_2\text{-}O\text{-}CH_2CH_2CH_3$	68.3	Y
methyl n-butyl	$CH_3\text{-}O\text{-}CH_2CH_2CH_2CH_3$	71	Y
ethyl isobutyl	$CH_3CH_2\text{-}O\text{-}CH_2CH(CH_3)CH_3$	81	Y
ethyl n-butyl	$CH_3CH_2\text{-}O\text{-}CH_2CH_2CH_2CH_3$	92.2	Y
n-propyl isobutyl	$CH_3CH_2CH_2\text{-}O\text{-}CH_2CH(CH_3)CH_3$	105	N
n-propyl n-butyl	$CH_3CH_2CH_2\text{-}O\text{-}CH_2CH_2CH_2CH_3$	117.1	N
diisobutyl	$CH_3CH(CH_3)CH_2\text{-}O\text{-}CH_2CH(CH_3)CH_3$	122	N
n-butyl isobutyl	$CH_3CH_2CH_2CH_2\text{-}O\text{-}CH_2CH(CH_3)CH_3$	N/A	N
di-n-butyl	$CH_3CH_2CH_2CH_2\text{-}O\text{-}CH_2CH_2CH_2CH_3$	142.4	N

Reaction product peak identification on the FID gas chromatograph was done in the following way. Gas chromatographic retention times were determined for all of the ethers that were obtained as pure samples. Identification of ether products for which pure samples were not available was done by considering their boiling points with respect to the other ethers, as well as by consideration of which products were expected. In addition, retention times for C_1-C_8 alcohols, C_1-C_8 hydrocarbons, and some esters were determined. Many possible products, besides ethers, could be eliminated by those determinations. Also, two studies involving dehydration of three-component alcohol mixtures of different and known composition, the results of which are presented later, assisted in the identification of gas chromatographic peaks.

Quantification of pure ether products was done by making liquid calibration mixtures of known composition and calibrating the gas chromatograph using a standard procedure. This resulted in the determination of response factors for these available ethers. Calibration for the unavailable ethers was more challenging. For these ethers, the response factors for the pure samples were used as a guide, along with the response factors for paraffins of similar structure. A correlation was made of ether response factor to the response factor of a paraffin with the same number of carbon atoms. Using this correlation, the response factors for ethers which were not available as pure samples, such as methyl ethyl ether and methyl propyl ether, could be calculated. The method used also assumed that response factors were independent of the location of the -O- linkage in the molecule or the degree of branching within the alkyl groups. So, for example, methyl n-propyl ether and diethyl ether were assumed to have the same response factor, both having four carbon atoms. Likewise, methyl isobutyl ether was assumed to have the same response factor as methyl n-butyl ether. The method used here is subject to some error; the response factors determined are probably only accurate to within 10%.

Figure 3-34 shows the correlation developed between the ether response factor and the paraffin response factor from which some ether response factors were determined. The response factor (denoted RF) is defined as the molar concentration per unit peak area. As can be seen, the ratio RF(ether)/RF(paraffin) decreases with increasing carbon number. For methyl ethyl ether, which is the only ether with three carbon atoms, the response factor was necessarily determined by interpolation. This interpolation was done by fitting the data with the curve shown in Figure 3-34.

3.3.2 Dehydration of Three-component Mixed Alcohols Streams

Two different, three-component alcohol mixtures were prepared. The composition of these mixtures is shown in Table 3-9.

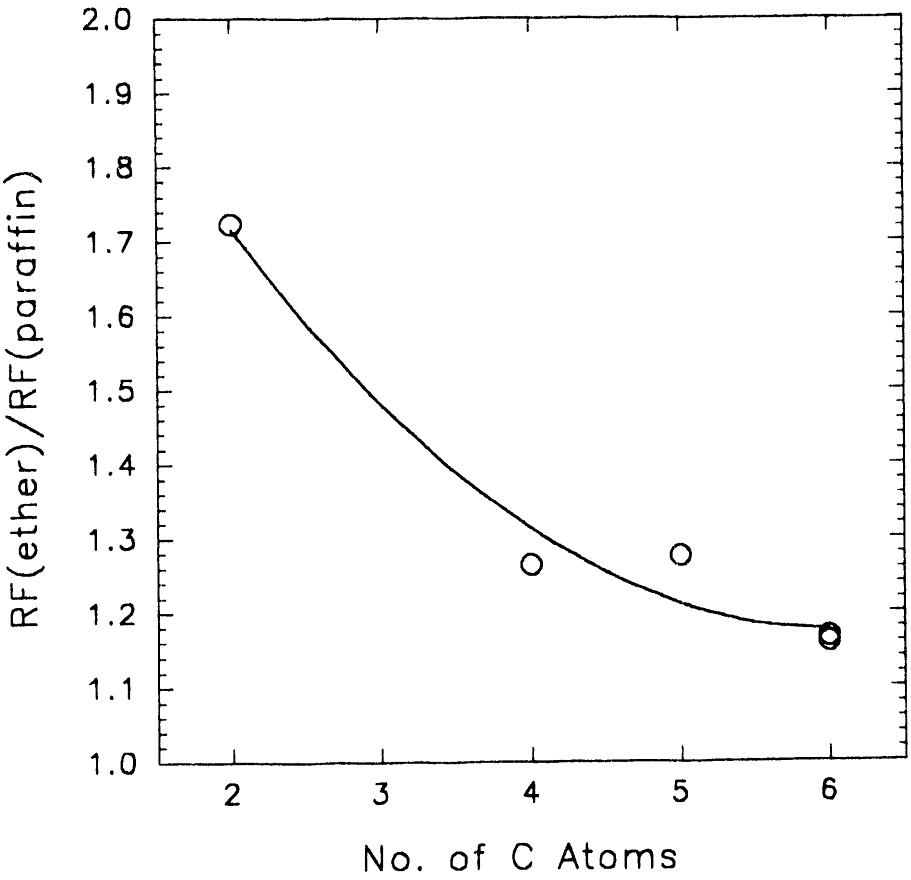
TABLE 3-9

Composition of Alcohol Mixtures Used in Alcohol Dehydration Experiments

	Concentration in Mixture (wt%/mol%)			
Mixture Number	Methanol	Ethanol	1-Propanol	Isobutanol
11168-71	64.4/73.6	25.5/20.3	10.1/6.1	--
11168-73	77.3/87.3	13.8/8.3	--	8.9/4.4

FIGURE 3-34

Correlation of FID Response Factors for Ethers and Paraffins



The proportions of methanol, ethanol, and 1-propanol in mixture 11168-71 were chosen to simulate the composition of the mixed alcohols produced over a Cu-Co based catalyst. The Cu-Co catalyst does not produce significant quantities of isobutanol, so it was not included in the mixture. The other mixture, 11168-73, includes proportions of methanol, ethanol, and isobutanol which simulate the product from an alkali-promoted $Cu/ZnO/Al_2O_3$ catalyst, such as that used in Lurgi's Octamix process. Typically, for the product from this type of catalyst, isobutanol production exceeds propanol production. For this reason, 1-propanol was omitted from this mixture. The absence of isobutanol in mixture 11168-71 and 1-propanol in mixture 11168-73 results in different product spectrums upon dehydration. This aided in identifying the ether products on the gas chromatogram for which no standard was available. Six different ethers are possible by direct condensation without C backbone rearrangement. Table 3-10 shows the expected ether products for each alcohols mixture.

TABLE 3-10
Expected Ether Products from Direct, Intermolecular Condensation of Alcohol Mixtures

Mixture Number	Expected Ether Products					
11168-71	dimethyl	methyl ethyl	methyl n-propyl	diethyl	ethyl n-propyl	di-n-propyl
11168-73	dimethyl	methyl ethyl	methyl isobutyl	diethyl	ethyl isobutyl	diiso-butyl

For the alcohol dehydration studies, these alcohol mixtures were vaporized into flowing N_2 immediately upstream of the reactor. The flow rates of N_2 and alcohol mixture were adjusted to yield 10 mol% alcohols and 90 mol% N_2 at a combined GHSV of 5000 std. lit./kg-hr. The reaction pressure for the experiments was 5.3 MPa. The catalyst, Catapal SB γ-Al_2O_3 in powder form, was combined with Drakeol 10 mineral oil, the slurry liquid. Experiments done using N_2 flow alone showed that the Drakeol 10 oil did not break down or crack at temperatures up to 300°C.

Tables 3-11 and 3-12 show results for the reaction of alcohol mixtures 11168-71 and 11168-73, respectively. These data are for reaction at 300°C. As shown in Tables 3-11 and 3-12, alcohol conversion was quite high, greater than 76% for both alcohol mixtures. Conversions of the individual alcohols were comparable, ranging from 76% to 85%. In addition, conversion shows little variation with on stream time, at least for the time scale of the experiment.

TABLE 3-11
Conversion and Selectivity for Reaction of Alcohol Mixture 11168-71

Run No: 11168-72
Reaction Conditions: 300°C, 5.3 MPa, GHSV=5000 std. lit./kg-hr
Catalyst: Catapal SB γ-Al_2O_3

Time on Stream (hr)	Methanol Conversion (%)	Ethanol Conversion (%)	1-Propanol Conversion (%)	Selectivity to Ethers (C%)	Selectivity to C_1-C_4 Hydrocarbons (C%)	Feed C Atom Recovery (%)
3.2	77	84	85	67	6.5	79
3.8	77	83	84	67	5.1	78
4.3	77	84	85	63	4.6	74

The selectivities reported in Tables 3-11 and 3-12, expressed as C%, were calculated by the following:

C% Selectivity for product(s) i = 100% x (C converted to product i)/(total feed C converted)..

The major products besides ethers were hydrocarbons. However, the GC method employed did not separate paraffins from olefins, so no distinction could be made. Presumably, the major type of hydrocarbon product formed was olefin from intramolecular dehydration of the feed alcohols. As can be seen in Tables 3-11 and 3-12, the selectivity to hydrocarbons is quite low, at least a factor of 10 lower than the selectivity to ethers for both alcohol mixtures.

TABLE 3-12
Conversion and Selectivity for Reaction of Alcohol Mixture 11168-73

Run No: 11168-74
Reaction Conditions: 300°C, 5.3 MPa, GHSV=5000 std. lit./kg-hr
Catalyst: Catapal SB γ-Al_2O_3

Time on Stream (hr)	Methanol Conversion (%)	Ethanol Conversion (%)	1-Propanol Conversion (%)	Selectivity to Ethers (C%)	Selectivity to C_1-C_4 Hydrocarbons (C%)	Feed C Atom Recovery (%)
3.9	77	80	77	74	4.4	84
4.4	76	79	77	73	4.0	83
5.0	76	80	77	72	3.8	82

Feed C recovery, the percentage of feed carbon accountable in measured products, was 74-79% for alcohol mixture 11168-71 and 82-84% for alcohol mixture 11168-73. These values were lower than expected. Other products besides ethers and hydrocarbons were detected but not quantified in the chromatograms. The total of these unknowns is not sufficient to make up for the "missing" C, but does account for a portion of it. There are two other possible reasons for the low recovery values. First, a change in the color of the $\gamma\text{-}Al_2O_3$ catalyst from white before reaction to gray after reaction indicates some carbon may have been deposited, perhaps as coke, and is not accounted for in the exit stream. Second, the feed flow rate of alcohols may have been lower than expected because of error in the syringe pump used for the injection. The extent to which each of these phenomena contributes to the low C recovery is not clear.

Tables 3-13 and 3-14 show the ether product distributions obtained for dehydration of alcohol mixtures 11168-71 and 11168-73, respectively. The product distribution is expressed in terms of the reactor exit product molar concentration for each ether normalized to the dimethyl ether product molar concentration. Thus, the values in Tables 3-13 and 3-14 are the ether product concentrations relative to the concentration of product dimethyl ether. Also shown is the calculated product distribution based simply on the probability of the various bimolecular reactions between the feed alcohols. In these calculations, the probability of formation of each product is assumed to depend on the (multiplicative) product of the molar concentration of each reactant alcohol in the feed. Thus, the probabilistic normalized ether product concentration (PNEPC) for an ether formed by condensation of alcohol (i) and alcohol (j) is calculated for each ether (ij) by:

$$PNEPC_{ij} = (y_i)(y_j)/(y_{MeOH})^2,$$

where y_i and y_j are the feed molar concentrations of reactant alcohols i and j, respectively, and y_{MeOH} is the feed molar concentration of methanol.

TABLE 3-13
Ether Product Distribution for Reaction of Alcohol Mixture 11168-71

Run No.: 11168-72
Reaction Conditions: 300°C, 5.3 MPa, GHSV=5000 std. lit./kg-hr
Catalyst: Catapal SB $\gamma\text{-}Al_2O_3$

Time on Stream (hr)	Normalized Ether Product Concentration					
	Dimethyl	Methyl Ethyl	Methyl n-Propyl	Diethyl	Ethyl n-Propyl	Di-n-Propyl
3.2	1.000	0.280	0.087	0.023	<0.011	0.005
3.8	1.000	0.292	0.088	0.029	<0.016	0.005
4.3	1.000	0.295	0.089	0.029	<0.016	0.005
Probability of biomolecular reaction based on feed concentrations of alcohols (PNEPC)	1.000	0.275	0.084	0.076	0.023	0.007

TABLE 3-14
Ether Product Distribution for Reaction of Alcohol Mixture 11168-73

Run No.: 11168-74
Reaction Conditions: 300°C, 5.3 MPa, GHSV=5000 std. lit./kg-hr
Catalyst: Catapal SB γ-Al_2O_3

Time on Stream (hr)	Normalized Ether Product Concentration					
	Dimethyl	Methyl Ethyl	Methyl Isobutyl	Diethyl	Ethyl Isobutyl	Diisobutyl
3.9	1.000	0.121	0.047	0.004	0.005	<0.001
4.4	1.000	0.121	0.045	0.004	0.005	<0.001
5.0	1.000	0.119	0.045	0.004	0.005	<0.001
Probability of biomolecular reaction based on feed concentrations of alcohols (PNEPC)	1.000	0.095	0.050	0.009	0.005	0.002

The retention times of ethyl n-propyl ether and diisobutyl ether could not be determined unequivocally, since pure component standards for these ethers were not available. So, the results shown in the tables indicate the maximum value of the concentration of ethyl n-propyl ether or diisobutyl ether based on the largest peak in the general vicinity of their expected retention time.

For both alcohol mixtures, the major product ether was dimethyl ether. This is perhaps not surprising since methanol is present in the highest concentration of both alcohol mixtures. In fact, for both alcohol mixtures, ethers with at least one methyl group attached to the -O- linkage dominate. For alcohol mixture 11168-71, the second and third most prevalent ether products are methyl ethyl ether and methyl n-propyl ether, respectively. Likewise, for alcohol mixture 11168-73, methyl ethyl ether and methyl isobutyl ether are the second and third most prevalent products. It is noteworthy that the distribution of these "methyl" ethers agrees with what would be predicted based on the simple probability of bimolecular reaction. However, the formation rate of the other ethers, those resulting from the bimolecular reaction of alcohols higher than methanol, is lower than that predicted based on simple probability. The reason for this is not clear. One possibility is that steric hindrances, caused by the bulkiness of the alcohols higher than methanol, may retard the formation of these ethers, resulting in production rates lower than those expected based on simple probability.

The results for dehydration of these simple mixtures of alcohols indicate that mixed ethers can be formed at high conversion and good selectivity over the γ-Al_2O_3 catalyst. Moreover, these favorable results can be obtained at 300°C and 5.3 MPa, a temperature and pressure which are also favorable for producing mixed alcohols from syngas. This compatibility in terms of reaction conditions suggests the possibility of combining the two reaction steps in one reactor. In this scenario, mixed alcohols produced from syngas over a mixed alcohols catalyst could be reacted in-situ over a γ-Al_2O_3 catalyst to mixed ethers. Experimental results obtained for combination of these reaction steps in a single slurry reactor, using a mixed catalyst system, are presented in the next section.

3.3.3 One-Step Conversion of Syngas to Mixed Ethers

These experiments involved the use of mixtures of two catalysts, a mixed alcohols synthesis catalyst and an alcohol dehydration catalyst, in the same autoclave reactor. The mixed alcohols catalyst was Cs-promoted $Cu/ZnO/Al_2O_3$, the same material used in the syngas to mixed alcohols studies discussed earlier. The dehydration component was Catapal SB γ-Al_2O_3, which was used in the alcohol dehydration studies discussed above. These two catalysts were slurried together in various proportions using Drakeol 10 mineral oil. The Cs-$Cu/ZnO/Al_2O_3$ component was reduced in the reactor using the same procedure as that used in the mixed alcohols synthesis studies. Peak assignment and quantification were somewhat more difficult for these studies because of the large number of products typically present in the reactor exit stream. Some minor products could not be identified.

3.3.3.1 Effect of Al_2O_3 in the Mixed Catalyst System:

Figure 3-35 shows the influence of Al_2O_3 content on the rate of synthesis of the various products. The C_{3+}-ether products consist largely of methyl ethyl, methyl n-propyl, methyl isobutyl, diethyl, and di-n-propyl ethers. In the case of the Cs-$Cu/ZnO/Al_2O_3$ catalyst alone (0% Al_2O_3 in Figure 3-35), the ether production rate is close to zero. As the Al_2O_3 fraction increases, the methanol and ΣC_2-C_6 alcohols rates decrease rapidly and monotonically. The decrease in alcohols rate is accompanied by a corresponding monotonic increase in the rate of production of dimethyl ether, at least across the range of Al_2O_3 content investigated. However, the dimethyl ether rate is expected to return to zero as the Al_2O_3 content approaches 100%, since Al_2O_3 is essentially inactive for methanol synthesis and methanol is required to produce dimethyl ether.

The influence of Al_2O_3 content on the rate of synthesis of C_{3+}-ethers is quite interesting. The C_{3+}-ethers rate passes through a sharp maximum as Al_2O_3 content is increased. The location of the maximum C_{3+}-ethers rate is at only approximately 5 wt% Al_2O_3.

The influence of the Al_2O_3 content on product selectivity is shown in Figure 3-36. The major product is dimethyl ether for Al_2O_3 content below approximately 4 wt%. Above approximately 10 wt% Al_2O_3, methanol and dimethyl ether are essentially the only products. The selectivity to C_{3+}-ethers is maximized at 5 wt% Al_2O_3. However, the maximum selectivity to C_{3+}-ethers is quite low, only 10 wt% of the total organic products.

The reason why the C_{3+}-ethers rate goes through a maximum and the dimethyl ether rate increases dramatically with increasing Al_2O_3 content is not immediately clear, but some speculation is worthwhile. The proposed reaction scheme for formation of the various products shown in Figure 3-37 provides some insight. Figure 3-37 shows that methanol, formed by syngas, can undergo subsequent reaction along two different major pathways in this mixed catalyst system. Path I consists of Al_2O_3-catalyzed dehydration of methanol to dimethyl ether. Path II represents the path along which methanol is converted to higher alcohol products. Once the higher alcohols products are formed, they can be dehydrated over Al_2O_3 to form C_{3+}-ethers. Thus, if the dehydration activity of the catalyst system is high, as in the case for high Al_2O_3 content, then Path I could plausibly dominate, thereby suppressing the production of higher alcohols. In this case, the formation of C_{3+}-ethers would also be suppressed because higher alcohols are necessary precursors. On the other hand, too little dehydration activity would cause alcohols to dominate, being formed by Path II but not reacting further to C_{3+}-ethers. Obviously, a compromise in dehydration activity is required to achieve a balance between Paths I and II. This balance occurs at a very low (5 wt%) Al_2O_3 content for the present system at the given reaction conditions.

FIGURE 3-35

Effect of Al_2O_3 Fraction on Product Rates

Catalyst Mixture: $Cs-Cu/ZnO/Al_2O_3 + Al_2O_3$

300°C, 7.0 MPa, GHSV=5000 std. lit./kg-hr, Shell gas

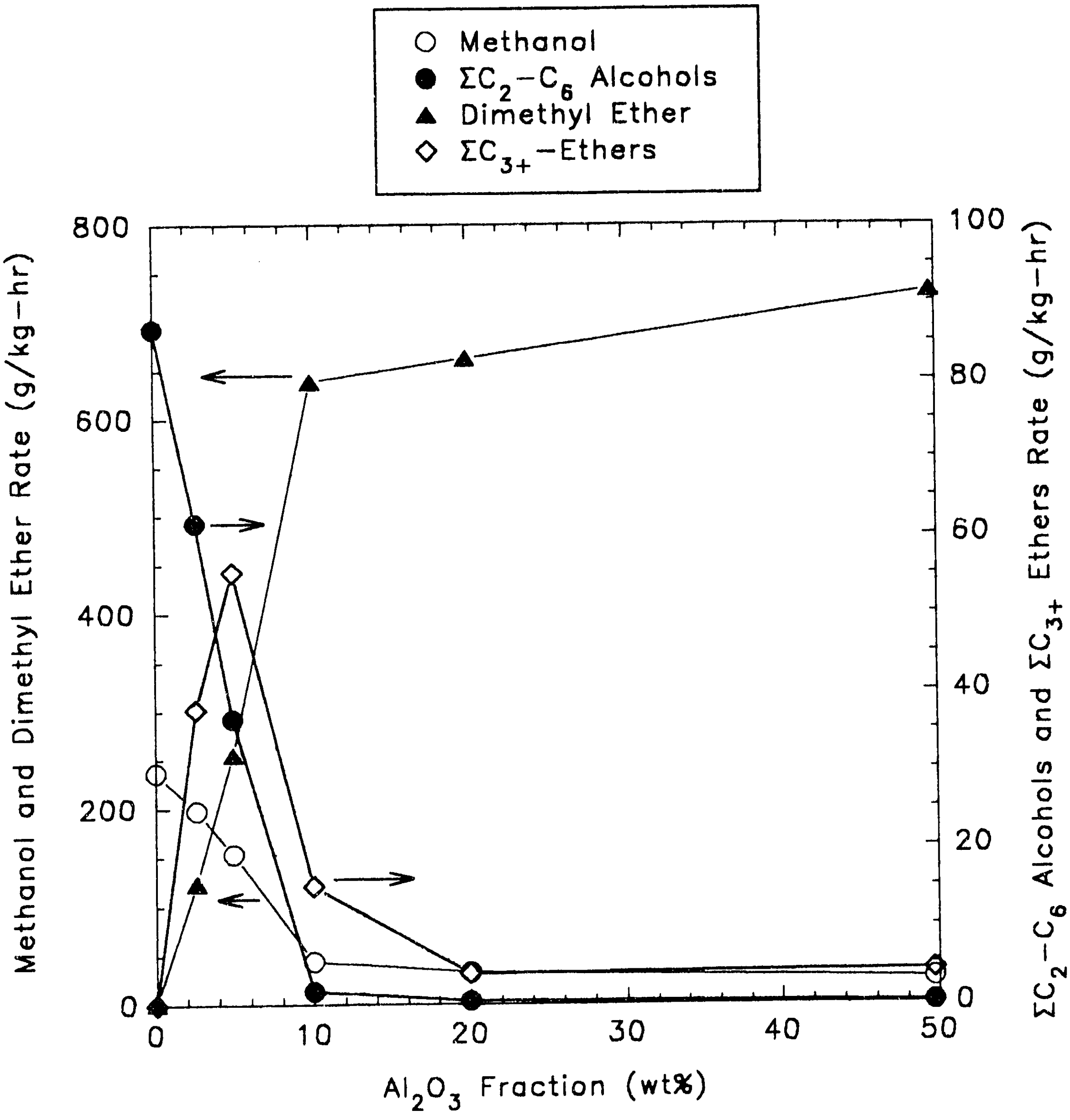


FIGURE 3-36

Effect of Al_2O_3 Fraction on Product Selectivities

Catalyst Mixture: $Cs-Cu/ZnO/Al_2O_3 + Al_2O_3$

300°C, 7.0 MPa, GHSV=5000 std. lit./kg-hr, Shell gas

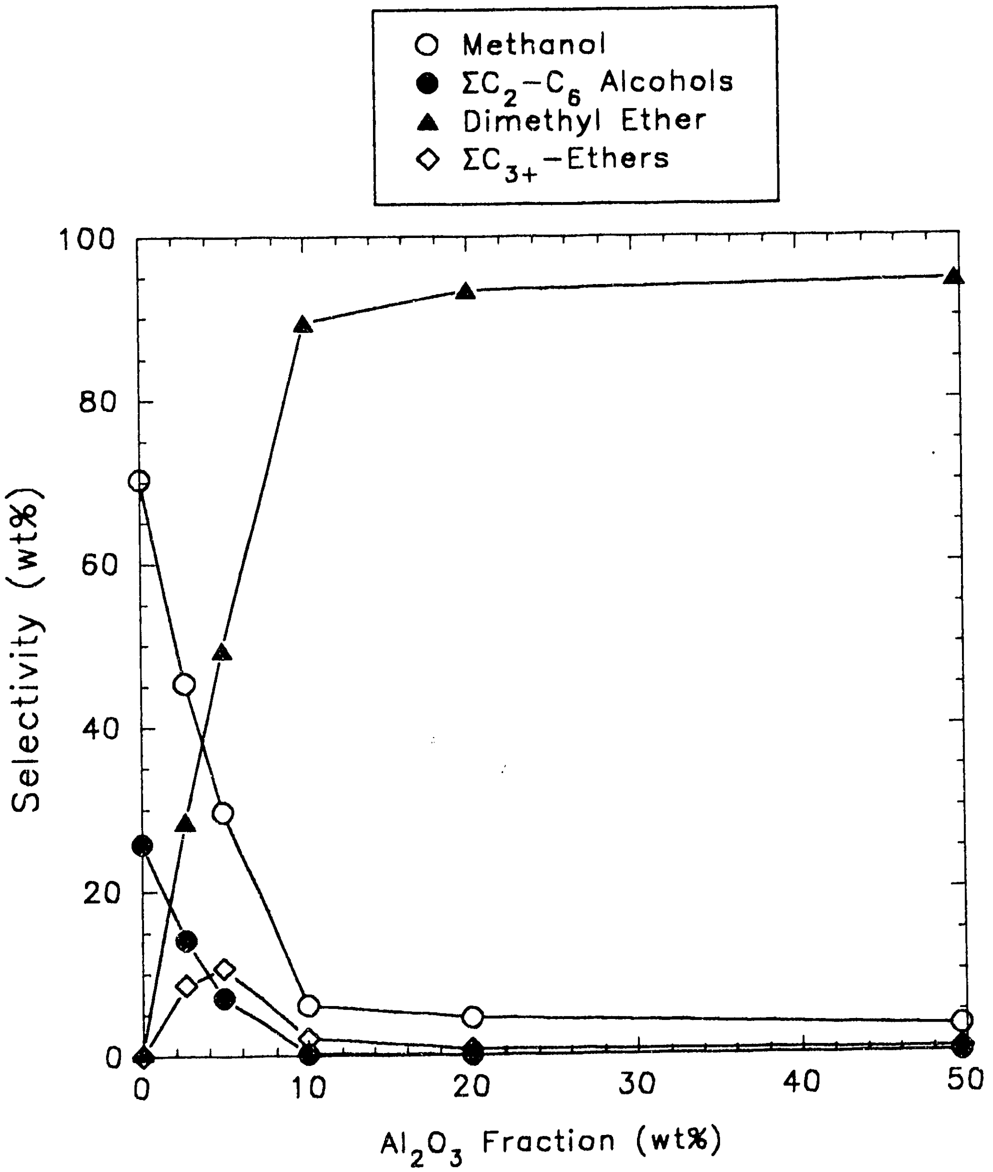
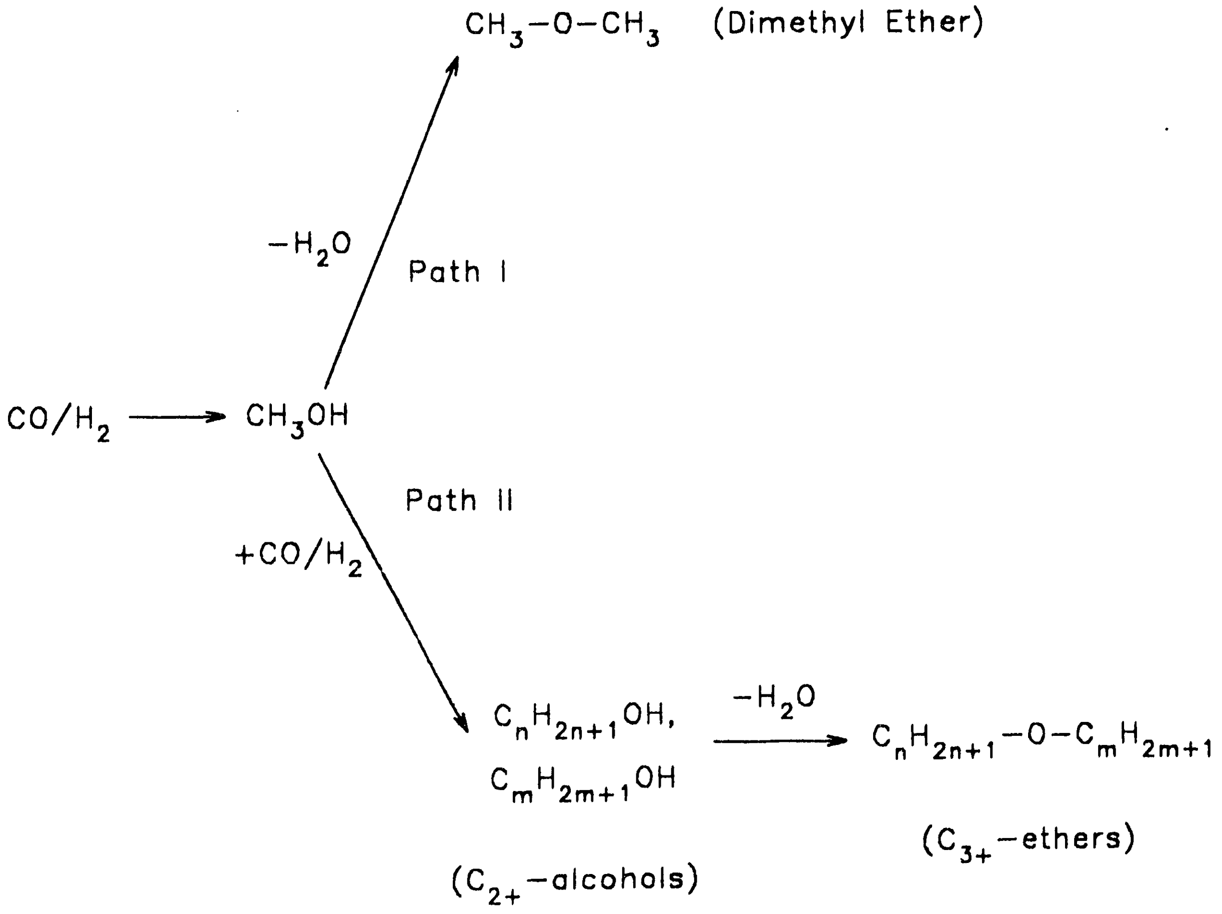


FIGURE 3-37

Proposed Reaction Scheme for Synthesis of Dimethyl Ether and C_{3+}-Ethers



3.3.3.2 Ether Product Distribution for 5% Al_2O_3 + 95% Cs-Cu/ZnO/Al_2O_3

Figure 3-38 shows the distribution of ether products obtained for the 5% Al_2O_3 mixed catalyst system at 300°C, 7.0 MPa, and a GHSV of 5000 std. lit./kg-hr of Shell gas. The distribution is expressed as the concentration of the various products normalized to the dimethyl ether concentration, the same notation used above in the discussion of mixed alcohols dehydration. Considering the distribution of alcohol products formed over Cs-Cu/ZnO/Al_2O_3 at these conditions, the ether product distribution is consistent with expectations. The major ether products have methyl groups attached to the -O- linkage; not surprising since methanol is the major alcohol product.

Also shown in Figure 3-38 is the product distribution calculated based on simple probability of bimolecular reaction, similar to the case above, only this time the calculation is based on the expected alcohol product concentrations which would be produced if the Cs-Cu/ZnO/Al_2O_3 catalyst was operating alone. Interestingly, the methyl ethyl ether and methyl n-propyl ether normalized concentrations are close to the values predicted by simple probability. By contrast, the measured methyl isobutyl ether normalized concentration is significantly less than that predicted by probability. This is perhaps reasonable in view of the expectation that less isobutanol may be formed in the mixed system since its precursor, 1-propanol, can also be reacted away to form ethers such as methyl n-propyl ether and di-n-propyl ether. Surprisingly, the diethyl ether and di-n-propyl ether measured normalized concentrations are significantly higher than that predicted by probability. The reason for the latter phenomenon is not understood and its resolution requires further investigation.

3.3.3.3 Effect of GHSV for 5 wt% Al_2O_3 + 95 wt% Cs-Cu/ZnO/Al_2O_3

The effect of GHSV on the major product rates is shown in Figure 3-39 for the 5 wt% Al_2O_3 case operating at 300°C and 7.0 MPa with the Shell gas feed. The synthesis rates for all products increase with increasing GHSV over the range of GHSV investigated. However, the degree to which GHSV affects the rate depends on the type of product. Alcohol products show a steeper rise in rate with increasing GHSV than ether products. Obviously, high selectivity to ethers is favored at low GHSV (long reactor residence time), while high selectivity to alcohols is favored at high GHSV. This phenomenon is consistent with the reaction pathways, since the formation of ethers occurs by sequential reaction of intermediate product alcohols. The CO conversion for these experiments decreases with increasing GHSV. The CO conversion ranged from 32% at 3000 std. lit./kg-hr to 18% at 10,000 std. lit./kg-hr.

3.3.3.4 Effect of On-Stream Time for Mixed Catalyst System

None of the mixed Al_2O_3 + Cs-Cu/ZnO/Al_2O_3 systems were run for more than two days, so long term activity maintenance data was not available. Table 3-15 shows the effect of on stream time, up to 50.5 hours, on the major product rates and CO conversion for the 5 wt% Al_2O_3 case. As shown, the CO conversion decreased from 26% at 25 hours to 22% at 50.5 hours, indicating a deactivation of the total catalyst system. Interestingly, the methanol and ΣC_2-C_6 alcohols rates increased significantly with time on stream. In contrast, the ether rates, including the dimethyl ether and C_{3+}-ethers, decreased substantially with time. Apparently, the dehydration component, Al_2O_3, had a faster rate of deactivation than the alcohol synthesis component, Cs-Cu/ZnO/Al_2O_3. The result is that, as the deactivation progressed, the intermediate alcohols were not consumed as rapidly to form ethers, resulting in higher alcohols production rate.

FIGURE 3-38

Measured and Predicted Ether Product Distributions

Catalyst Mixture: 95% Cs-Cu/ZnO/Al_2O_3 + 5% Al_2O_3

Run No.: 11472-51

300°C, 7.0 MPa, Shell Gas, GHSV=5000 std.lit./kg-hr

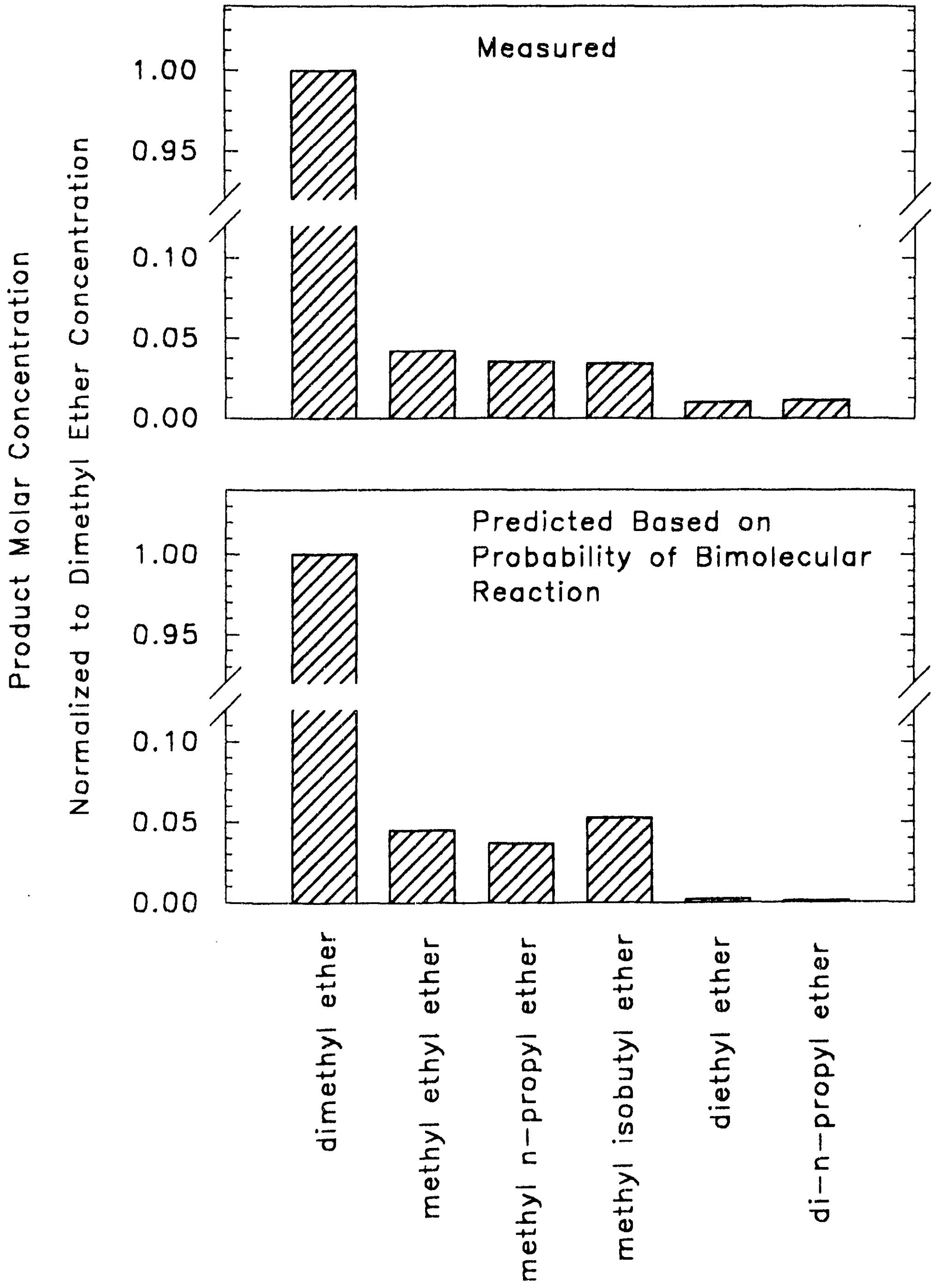


FIGURE 3-39

Effect of GHSV on Product Rates

Catalyst Mixture: 95% Cs–Cu/ZnO/Al_2O_3 + 5% Al_2O_3

Run No.: 11472-51

300°C, 7.0 MPa, Shell Gas

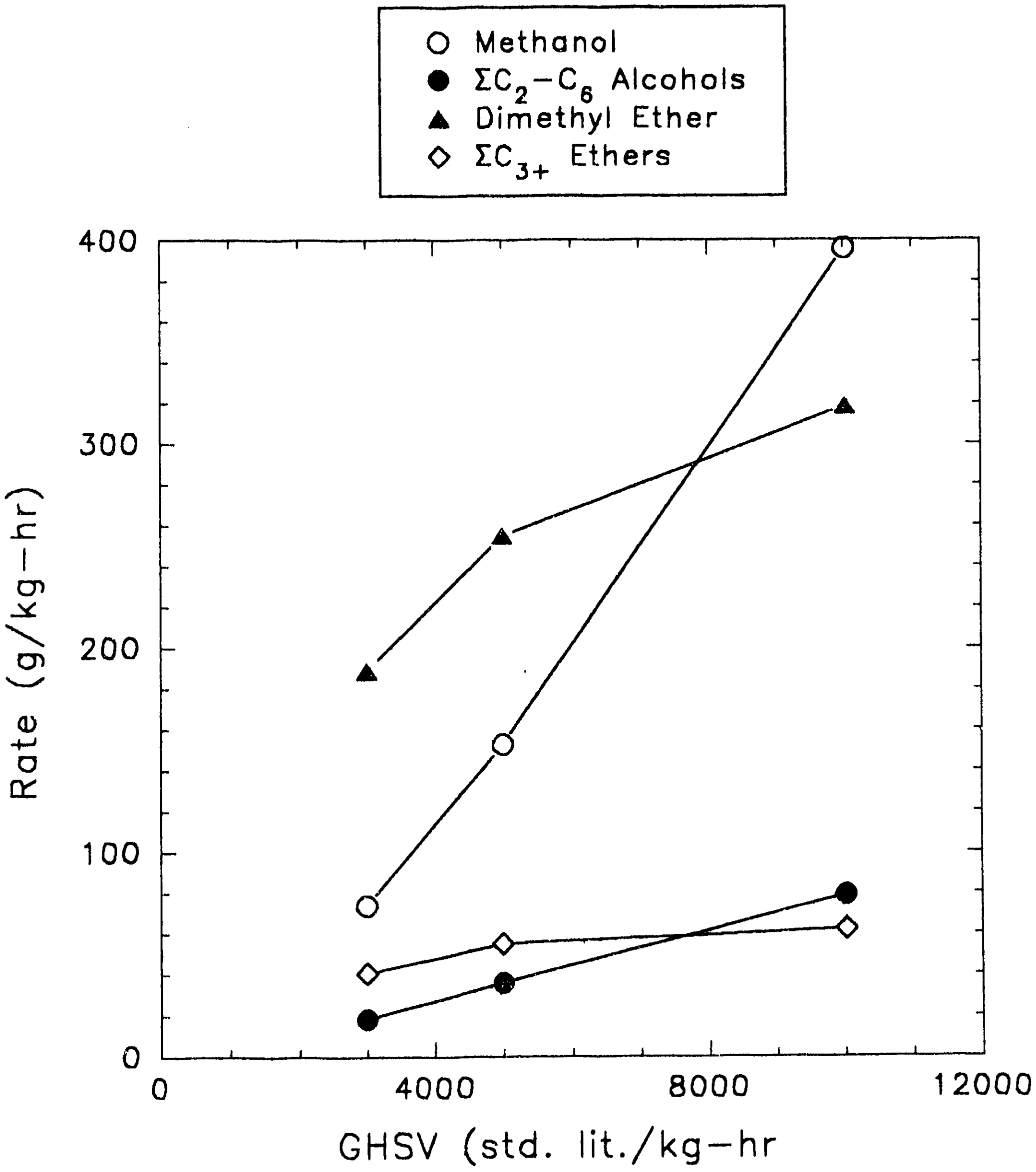


TABLE 3-15
Effect of Reaction Time on Major Product Rates

Catalyst Mixture: 5% Al_2O_3 + 95% Cs-Cu/ZnO/Al_2O_3
Reaction Conditions: 300°C, 7.0 MPa, GHSV=5000 std. lit./kg-hr, Shell gas

Time on stream (hr)	Production Rate (g/kg-hr)				CO Conversion (%)
	Methanol	ΣC_2-C_6 alcohols	Dimethyl ether	C_{3+}-ethers	
25	153	37	255	55	26
50.5	184	49	158	38	22

Several reasons could be envisioned for the deactivation of the dehydration component, but no evidence was provided to suggest a particular mechanism in the present study. Further work is necessary to investigate this phenomenon in more detail.

4.0 SUMMARY AND RECOMMENDATIONS

4.1 One-Step, Slurry-Phase Syngas Conversion to Hydrocarbons or Methanol/Hydrocarbon Mixtures

There are several key technical issues involved in the use of $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst and HZSM-5 methanol conversion catalyst in the same slurry reactor. The present study addressed, to a limited extent, two key technical hurdles: (1) identifying a slurry liquid which is stable in the presence of the acidic zeolite component but also compatible with the methanol synthesis component; and (2) establishing conditions for reaction which allow both steps in the sequence to proceed at an economically attractive rate and selectivity.

Of the slurry liquids tested, which were all of the type compatible with the methanol synthesis catalyst, decalin (decahydronaphthalene) was found to be the most stable to cracking. A correlation between stability and the inability of a liquid molecule to access the pore structure of the zeolite was identified. However, even decalin, which consists of the bulkiest molecules of the liquids investigated, cracked considerably at practical reaction temperatures. Surface silanation of the zeolite decreased, but did not eliminate, cracking of the decalin. Moreover, the product distribution during methanol conversion for the surface treated sample was very different from that for the unmodified HZSM-5. The product distribution for the surface treated sample was characterized by excessive production of methane. The high methane selectivity was probably caused by necking down of the pore openings during the silanation treatment, which resulted in the inability of molecules larger than methane to exit from the interior of the zeolite crystallites.

Despite the relatively high "background" production of hydrocarbons caused by cracking of the decalin, syngas was converted to hydrocarbons using the mixed catalyst system. However, at a reaction temperature of 250°C, a relatively high selectivity to dimethyl ether and light hydrocarbons was observed, while the selectivity to gasoline-range hydrocarbons was very low. A significantly higher reaction temperature, closer to the temperature range of 350-420°C used for methanol conversion to hydrocarbons in the gas-to-gasoline process, is probably required to achieve a higher selectivity to gasoline range hydrocarbons. In addition, GHSV must certainly play a role in the product distribution and should be investigated in more detail.

Identification of a practical slurry liquid for use with the mixed catalyst system remains a key challenge. Though decalin was the most stable of the liquids tested, its use in such a process, especially at higher temperatures than those used in the present study, would not be economical. Surface silanation was shown to decrease cracking of the decalin, but diffusion of decalin molecules into the pore structure, though highly hindered, probably will still occur. The entrance of decalin into the pore structure will be even more prevalent at higher reaction temperatures. After a thorough investigation, a commercial source has not been identified for saturated hydrocarbon liquids consisting of molecules that are bulkier than decalin.

Perhaps more detailed studies of other types of slurry liquids, besides saturated hydrocarbon types, may be worthwhile. However, these liquids would necessarily have to be compatible with the $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst. Unfortunately, one class of potential slurry liquids, silicone oils, has been shown to be incompatible with the methanol synthesis catalyst. Though not mentioned in the discussion section, one silicone oil, Syltherm, was found to break down in the presence of reduced Cu/ZnO/Al_2O_3 catalyst.

One interesting possibility for a practical slurry liquid could involve the use of hydrocarbon products of the HZSM-5 component as the slurry liquid. However, to be practical, these products must have high boiling points to minimize liquid loss from the reactor. One product worth investigating as a slurry liquid is durene, i.e., 1,2,4,5-tetramethyl benzene. This product is a solid at room temperature and boils at 193°C, close to the boiling point for decalin (185–193°C). Since this compound is aromatic, its compatibility with the methanol synthesis component is questionable, and requires investigation. Another possiblity is that the Cu/ZnO/Al_2O_3 component could be modified to produce a catalyst better able to tolerate unsaturated hydrocarbon liquids.

Surface silanation remains an area of worthwhile investigation for minimizing cracking. Only one silanation technique was used in the present study and no attempt was made to optimize it. Other silanation techniques, involving either impregnation or vapor deposition of silica precursors, may not neck down pore openings as much as the one used here, thereby yielding a potentially better product distribution for methanol conversion. Further work is required to address this speculation.

Besides the issue of slurry liquid stability, other technical issues regarding the proposed one-step process will need to be addressed. One significant issue is the requirement that the HZSM-5 component be periodically regenerated. In the current methanol-to-gasoline process operated in New Zealand, the conversion of methanol/dimethyl ether mixtures to gasoline is done in packed bed reactors. Multiple reactors are required since each reactor must be periodically brought off-line to burn off coke which has accumulated on the HZSM-5 catalyst. Presumably, the same regeneration step would be required in a one-step process. Thus, two problems arise: (1) separation of the catalyst from the slurry liquid, and (2) separation of the HZSM-5 component from the Cu/ZnO/Al_2O_3 component, since the Cu/ZnO/Al_2O_3 would probably not survive the high temperature coke burning procedure. Once separated, presumably the HZSM-5 could be regenerated in a fluidized bed. At this point, a viable means of doing the separations, particularly the separation of the HZSM-5 from the Cu/ZnO/Al_2O_3, is not apparent.

The above issues (regeneration of the HZSM-5 component and separation problems) indicate that a more practical method for overall conversion of syngas to hydrocarbons might involve the use of two separate slurry reactors in series. The first reactor would contain the Cu/ZnO/Al_2O_3 methanol synthesis component and, optionally, a dehydration component such as Al_2O_3 to convert methanol to dimethyl ether in-situ. The second slurry reactor would contain the HZSM-5 component. In this case, the requirements for a viable slurry liquid are different, since the slurry liquid in the HZSM-5 would not have to be compatible with the Cu/ZnO/Al_2O_3 catalyst. Though the reaction steps would then be separated, the use of a slurry reactor in the second reactor may still provide significant advantage in heat management.

In conclusion, further research work is necessary to address key technical issues in developing an industrially practical slurry reactor based process for converting syngas to hydrocarbons using Cu/ZnO/Al_2O_3 and HZSM-5. Further work should focus on identification of viable slurry liquids and perhaps involve zeolite catalyst surface passivation techniques.

4.2 Slurry-Phase Conversion of Syngas to Mixed Alcohols

Syngas conversion to mixed alcohols in a slurry reactor was successfully done on a laboratory scale. Several catalysts were investigated, including a Cs-promoted $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst, an alkali-promoted $Cu/ZnO/Al_2O_3$-based catalyst from Lurgi, a Cu-Co formulation, and two-component systems involving mixtures of $Cu/ZnO/Al_2O_3$ and a co-catalyst. The best performing catalyst was the Cs-promoted $Cu/ZnO/Al_2O_3$ catalyst prepared in Air Products' laboratory. This sample was prepared by a simple procedure involving impregnation of BASF S3-86 methanol synthesis catalyst with aqueous cesium formate solution, followed by drying and calcination.

For the Lurgi catalyst, the rate and selectivity to C_{2+}-alcohols was substantially lower than that measured for the Cs-promoted $Cu/ZnO/Al_2O_3$ catalyst.. Like the Cs-$Cu/ZnO/Al_2O_3$ catalyst, the Lurgi catalyst produced significant amounts of branched alcohols, specifically the "2-methyl-" isomers of primary linear alcohols. By contrast, in line with expectations, the Cu-Co catalyst produced linear alcohols, almost exclusively. The performance of the Cu-Co catalyst was characterized by higher selectivity to hydrocarbons and lower alcohol rates relative to the Cs-Cu/ZnO/Al_2O_3 catalyst. The Cu-Co catalyst did, in fact, show the highest selectivity to C_{2+}-alcohol of any of the tested catalysts. None of the two-component catalyst mixtures investigated performed as well as $Cu/ZnO/Al_2O_3$ alone. However, the use of two-component catalyst systems is believed to be a fruitful area for further research.

The effect of various process variables on the performance of the Cs-promoted $Cu/ZnO/Al_2O_3$ catalyst was investigated in detail. Determinations were made of the effects of temperature, GHSV, syngas composition, and co-feeding methanol and ethanol with the syngas. The results show that selectivity to C_{2+}-alcohols is favored at low GHSV, high temperature, and low H_2/CO. In addition, methanol and ethanol addition to the feed increased the rate of synthesis to higher alcohol products, thus demonstrating the desirability of recycling those products to the reactor feed to enhance the product slate.

It is noteworthy that the methanol/C_{2+}-alcohols product distribution obtained for once-through operation at industrially practical reaction conditions, using a feed syngas typical of the product of a coal gasifier, was in the range suitable for blending into gasoline.

Preparation of the Cs-promoted catalyst should be optimized to attempt to improve its performance even further. Variables such as cesium loading, cesium precursor composition, and $Cu/ZnO/Al_2O_3$ substrate type should have an impact on the ultimate performance. In addition, longer term activity maintenance studies should be done to better ascertain the significance of catalyst deactivation.

As mentioned previously, a potentially attractive characteristic of the Cs-$Cu/ZnO/Al_2O_3$ catalyst is its ability to produce a relatively high selectivity to branched-chain alcohols, particularly the "2-methyl-" isomers. Notable branched-chain product alcohols from this catalyst include isobutanol (2-methyl-1-propanol) and 2-methyl-1-butanol. These products are of particular interest because they can be dehydrated to useful iso-olefins, such as isobutylene and isoamylene. Isobutylene and isoamylene can be reacted with an alcohol, particularly methanol, to produce methyl tert-butyl ether (MTBE) and tert-amyl methyl ether (TAME), respectively. Both ethers are, of course, known to be outstanding oxygenated gasoline additives. Thus, alcohols produced from coal-derived syngas using Cs-Cu/ZnO/Al_2O_3, besides representing a viable gasoline additive in their own right, may be an alternative source of iso-olefins for use in etherification.

4.3 Slurry-Phase Conversion of Syngas to Mixed Ethers via Mixed Alcohols

The present work has shown that mixed alcohols can be dehydrated selectively to mixtures of ethers using an Al_2O_3 catalyst in a slurry reactor. Selectivity to olefins, the major side products, at practical reaction conditions was an order of magnitude lower than the selectivity to ethers. The measured ether product distribution was generally consistent with that expected based on simple statistical probability of bimolecular reaction. However, the results indicate that the formation of some ethers, particularly those with both alkyl groups larger than methyl, was somewhat suppressed relative to probabilistic predictions. Thus, dehydration of two mixtures of alcohols, both of which contained mostly methanol, produced mostly ethers with at least one methyl group attached to the -O- linkage.

One-step, slurry-phase syngas conversion to mixed ethers using a mixed catalyst system of Cs-Cu/ZnO/Al_2O_3 plus Al_2O_3 was also successfully done. In this system, mixed alcohols formed in-situ over the Cs-Cu/ZnO/Al_2O_3 catalyst were dehydrated to mixed ethers. However, significant quantities of C_{3+} ethers, i.e. those larger than dimethyl ether, were formed only for a certain range of Al_2O_3 catalyst fraction in the reactor. For the reaction conditions used in the present study, the rate and selectivity to C_{3+} ethers was maximized for a catalyst mixture consisting of 95 wt% Cs-Cu/ZnO/Al_2O_3 and 5 wt% Al_2O_3. For catalyst mixtures with lower Al_2O_3 fraction the product mix shifts toward alcohols, while higher Al_2O_3 fraction yields almost exclusively dimethyl ether. It is not surprising that the ether product distribution for the optimum catalyst mixture showed a slight deviation from that predicted based on simple probability of bimolecular reaction of the major product alcohols of the Cs-Cu/ZnO/Al_2O_3 catalyst component. For example, the selectivity to methyl isobutyl ether was slightly less than that predicted based on bimolecular reaction probability. This phenomenon is thought to be a result of the sequential nature of the reaction mechanism by which the higher alcohols, such as isobutanol, are formed.

For the one-step synthesis, short term activity maintenance results indicate a rapid deactivation of the dehydration catalyst component. However, longer term studies are necessary to determine the significance and cause of the deactivation. In addition, mixed catalyst systems involving the use of other mixed alcohols synthesis components and other dehydration components should be investigated.

Another key issue that needs to be addressed is the viability of using the ether products from dehydration of mixed primary alcohols as fuels or fuel additives. For example, the characteristics with respect to their use in gasoline must be investigated. Some important criteria for a gasoline additive are the blending octane number and blending Reid vapor pressure (RVP). Octane testing and RVP determinations of various ethers representative of the product of mixed alcohols dehydration is the subject of ongoing work. The potential use of these product ethers in diesel fuel must also be assessed.

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