Areas for further work towards the commercialization of the LPMEOH process should include the reactor hydrodynamics, especially at high slurry concentrations, as well as mass transfer limitations and it's effects on reactor performance.

2.4 New Developments

The majority of work on improving methanol synthesis processes has been in the area of catalysis. Alkali hydroxides have been found to significantly improve the activity of Cu/ZnO catalysts for methanol production. The greatest activity increase is for cesium, and in decreasing order:

$$Cs > Rb > K > Na > Li$$

Furthermore, an optimum amount of promoter exists for any given set of operating conditions.

Several directions have been identified for future activity in catalyst research. One of these has been the development of selective and stable homogeneous catalysts. Methanol has been produced from a 1:1 H_2:CO mixture in dioxane at 182 C (360 F) and 30 MPa (4350 psia), using $Co_2(CO)_8$ catalyst. There has also been an interest in catalysts using noble metals, such as Ru-CO and Ru-Rh catalysts. Union Carbide has performed some work on methanol synthesis using $Ru_3(CO)_{12}$. It is known that Cu/ZnO catalysts promote both the CO hydrogenation as well as the water-gas shift reactions. Understanding the bi-functional nature of Cu/ZnO catalyst and it's combination with alkali promoters will remain a high priority.

3.0 HIGHER ALCOHOLS FROM SYNTHESIS GAS

3.1 Ethanol

There are presently several commercial as well as developing processes for the production of ethanol from synthesis gas. A well understood and highly selective procedure for ethanol production is the multi-step process, where methanol is first synthesized, and CO and H_2 are then added to give ethanol:

$CO + 2H_2$ -----> CH_3OH

$CH_3OH + CO + 2H_2$ -----> $CH_3CH_2OH + H_2O$

Another path is the insertion of CO into the methanol molecule using a ruthenium-iodine (Ru-I) or iridium-iodine (Ir-I) catalyst and hydrogenating the resulting acetic acid to ethanol. This is the case with the Ensol process (Srivastava, 1990):

$CO + 2H_2$ -----> CH_3OH

$CH_3OH + CO$ -----> CH_3COOH

$CH_3COOH + 2H_2$ -----> $CH_3CH_2OH + H_2O$

Alternatively, instead of acetic acid, one could hydrogenate the methyl acetate. This is the route used by the Davy-McKee process (Srivastava, 1990):

$CO + 2H_2$ -----> CH_3OH

$2CH_3OH + CO$ -----> $CH_3CO_2CH_3 + H_2O$

$CH_3CO_2CH_3 + 2H_2$ -----> $CH_3CH_2OH + CH_3OH$

A much studied process, but not yet commercial, is the reductive carbonylation (homologation) of methanol to ethanol and acetaldehyde (Srivastava, 1990):

$$CH_3OH + 2H_2 + CO \text{----}> CH_3CH_2OH + H_20$$

The reaction is catalyzed by $Co_2(CO)_8/RuCl_3/I_2$ system. Significant rate enhancement is associated with the iodine promoter, and ruthenium has been found to be the best co-catalyst for the reaction (Srivastava, 1990).

3.2 Mixed Alcohols

The term mixed alcohols or higher alcohols is commonly used to refer to the range of C_2 to C_6 alcohols. The use of mixed alcohols in gasoline blends improves the miscibility characteristics of the oxygenate, as compared with using only methanol.

The present technology for the production of higher alcohols is based on several categories of higher alcohol synthesis catalysts (Kiennemann et al., 1991). A brief summary of these is given below:

- Modified Fischer-Tropsch catalysts which are based on cobalt or iron: these have productivities between 0.1 to 0.15 gm/gm of cat.-hr and selectivities of 70 to 80% for C_2+ higher alcohol content.

- Methanol synthesis catalysts modified by the addition of alkali metals: these are typically alkalanized ZnO/Cr_2O_3 catalysts which operate at high pressures and temperatures (26 MPa and 350-400 C), or low pressure copper-based catalysts which have high productivities (0.45 gm/gm of cat.-hr) but suffer from selectivity drawbacks due to the formation of ketones, esters, etc.

- Other catalysts such as supported rhodium or molybdenum: the Rh-based catalyst are known to be very selective towards the C_2 oxygenates; the Mo-based catalysts produce C_1-C_6 alcohols, but have the drawback of requiring

H_2S in the feed gas to maintain their activity, and also produce significant amounts of CO_2 during reaction.

The two reactions of importance in the synthesis of higher alcohols, similar to methanol synthesis, are the hydrogenation of CO according to:

$$nCO + 2nH_2 = C_nH_{2n+1}OH + (n-1)H_2O$$

where the resulting product is the C_n aliphatic alcohol, and the water-gas shift reaction which proceeds according to:

$$CO + H_2O = CO_2 + H_2$$

Light hydrocarbons are produced from side reactions according to:

$$2nH_2 + nCO \text{-----}> C_nH_{2n} + nH_2O \text{ and,}$$

$$(2n+1)H_2 + nCO \text{-----}> C_nH_{2n+2} + nH_2O$$

Thermodynamically, hydrocarbon formation is favored. However, the catalyst transforms the process into a kinetically controlled one, favoring the production of alcohols.

The product distribution is a direct function of the catalyst used to carry out the synthesis. Linear and branched higher alcohols are produced over alkali-modified methanol synthesis catalysts. The alkali-promoted Group VIII metals produce mainly linear alcohols. Newly developed alkali-doped MoS_2 catalysts also produce mainly linear alcohols.

3.2.1 Emerging Commercial and Semi-Commercial Processes

There are several commercially available processes for the synthesis of higher alcohols. These are discussed below, with particular emphasis on the catalysts and operating conditions (Srivastava, 1990).

- IFP Process

Reports and patents published by IFP (Institut Francais du Petrole) indicate the use of copper and cobalt oxides, alkali metal salts, and oxides of either chromium, iron, vanadium, or manganese, as catalyst components for the synthesis of higher alcohols. A selectivity to alcohols of 70% has been reported. IFP has emphasized the long life expectancy and improved stability of their catalyst. The IFP technology has been undergoing development at a 6000 bbl/year pilot plant at Chiba, Japan. The performance and operating ranges for the IFP catalyst are listed in Table 3.1 (Srivastava, 1990).

Studies have been conducted by the IFP to determine the effect of composition in the CuO/CoO/Cr_2O_3 system. Methanol seems to be the predominant product in Cu-rich and high Cr:Cu atomic ratios. Co-rich regions increase the methanation rate. Cu-Co catalysts have the tendency to methanate at temperatures above 290 C (554 F).

A simplified block diagram of the IFP process is shown in Figure 3.1. A two-stage reactor scheme with intermediate quench is employed in the synthesis. In the IFP configuration a recycle of methanol or ethanol is used. The recycle increases the conversion to longer chain alcohols such as n- butanol. Per-pass conversions of 12 to 18% have been reported. The product composition is 80-85% methanol, with the higher alcohols accounting for the remainder. The crude alcohol stream contains up to 35% water. Water removal is achieved through extractive distillation, with diethylene glycol (DEG) being used as the solvent. An optimized separation scheme removes the C_1-C_3 alcohols in the first step, and separates the higher alcohols/water from DEG in the second step. The alcohol/water mixture is then phase separated.

TABLE 3.1

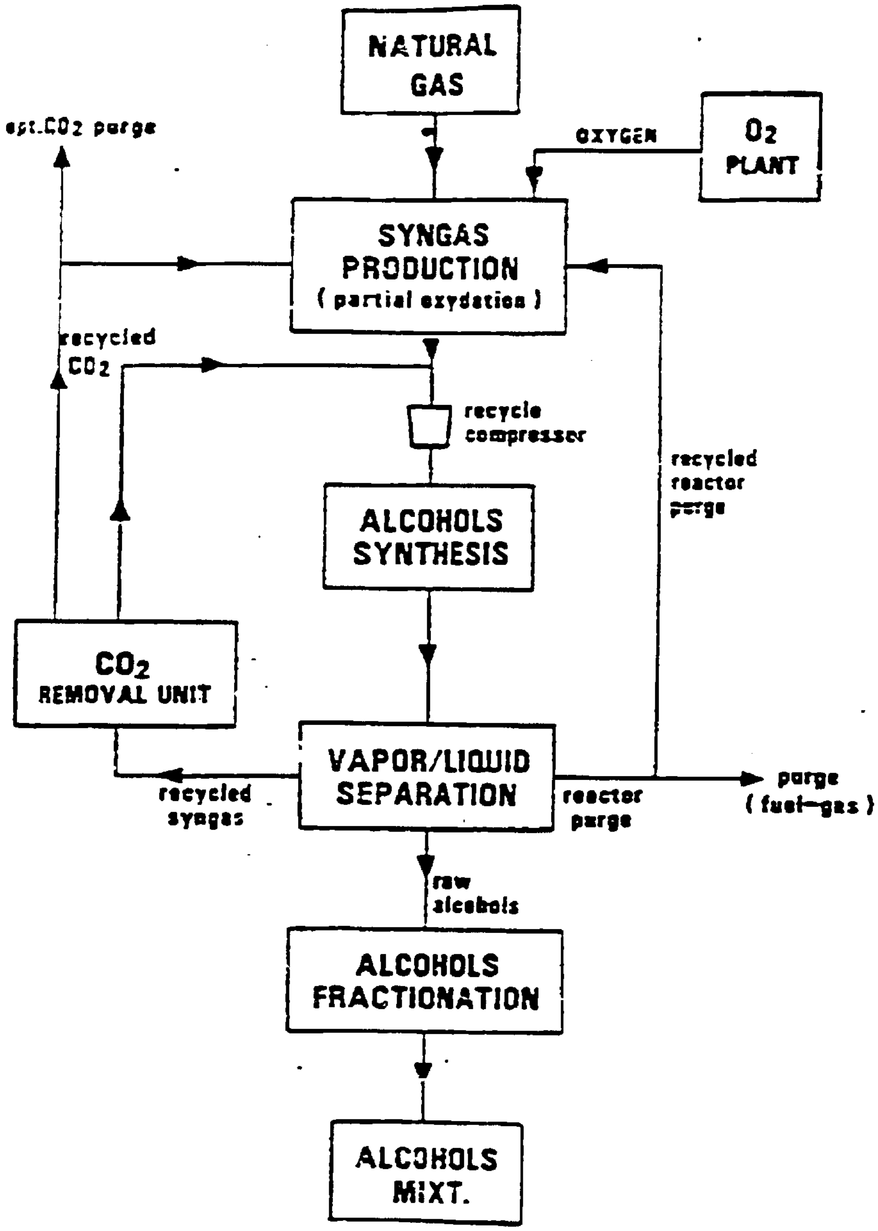
Basic Operating Characteristics of Higher Alcohol Synthesis Technologies

[Srivastava, 1990]

Process	1	2	3				4	5	
Main Characteristics	SEHT (MAS) Process	IFP (Substifuel) Process	Dow HAS Process	UCC HAS	LU[a] HAS	Dow HAS	Lurgi OCTAMIX Process	LU[a] HAS Process	LU[a] HAS
Main Constituents of Catalysts	K/Zn/Cr	K/Cu/Co/Al	K/Co/MoS_2	Cs/MoS_2	Cs/MoS_2	K/MoS_2	Alkali/Cu/Zn/Cr Promoters	Cs/Cu/ZnO	Cs/Cu/ZnO/Cr_2O_3
Catalyst Stability (life), h	8,000	-2,000	>8,000	N.A.	>200	N.A.	8,000	>1,200[b]	>750[b]
Operating Temp., °C	350-420	260-320	306	300	295	255	285-300	300	300
Operating Pres., MPa	10-18	6-10	10.3	2.75	8.2	10.3	6-9	9.1	9.1
Syngas Space Velocity, 100 h^{-1}	3.0-8.0	3.0-6.0	3.8	12.0	7.8	3.2	3.0-6.0	3.265	3.255
Syngas Feed H_2/CO Ratio	2-3	1-2	1[c]	1	0.96	1.02[c]	0.5-1.0	0.7	0.7
Syngas CO_2 Content, vol%	1.0-6.0	2.5-3.5	0.0	0.0	0.0	0.0	1.0	0.0	0.0
Performance Characteristics									
Thermal Efficiency, %	56	---	---	---	---	---	60	---	---
CO Conversion Per Pass[d], %	14	12-15	16	4.8	9.1	12.3	13-30	22	25.5
Liquid Product Selectivity, %	90	70-75	88	80	77	85	95	>96	>96
C_2+OH Selectivity, %	20-30	25-50	51.6	32.8	37.3	32.2	20-30	31.3	26.5
Alcohol Space Time Yield, kg/l cat/hr[e] or kg/kg cat/hr[f]	0.21[e]	0.1-0.15[e]	0.23-0.30[f]	0.256[f]	0.32[f]	0.19-0.32[f]	0.46[e]	0.373[f]	0.46[f]

[a] Lehigh University
[b] Deactivation data in text are in Ref. 23
[c] Contained 50 ppm H_2S
[d] CO conversion exclusive of CO_2
[e] STY in kg oxygenate product per hour per l catalyst
[f] STY in kg oxygenate product per hour per kg catalyst

FIGURE 3.1
Simplified Block Diagram of the IFP Process
[Srivastava, 1990]



- SEHT Process

The SEHT (Snamprogetti/ Enichem/ Haldor Topsoe) process for the production of higher alcohols has been demonstrated at a 40 ton/day unit at Pisticci, Italy. The MAS (Metanolo et Alcoli Superiori) product has been distributed and marketed as a gasoline blending agent in Western Europe.

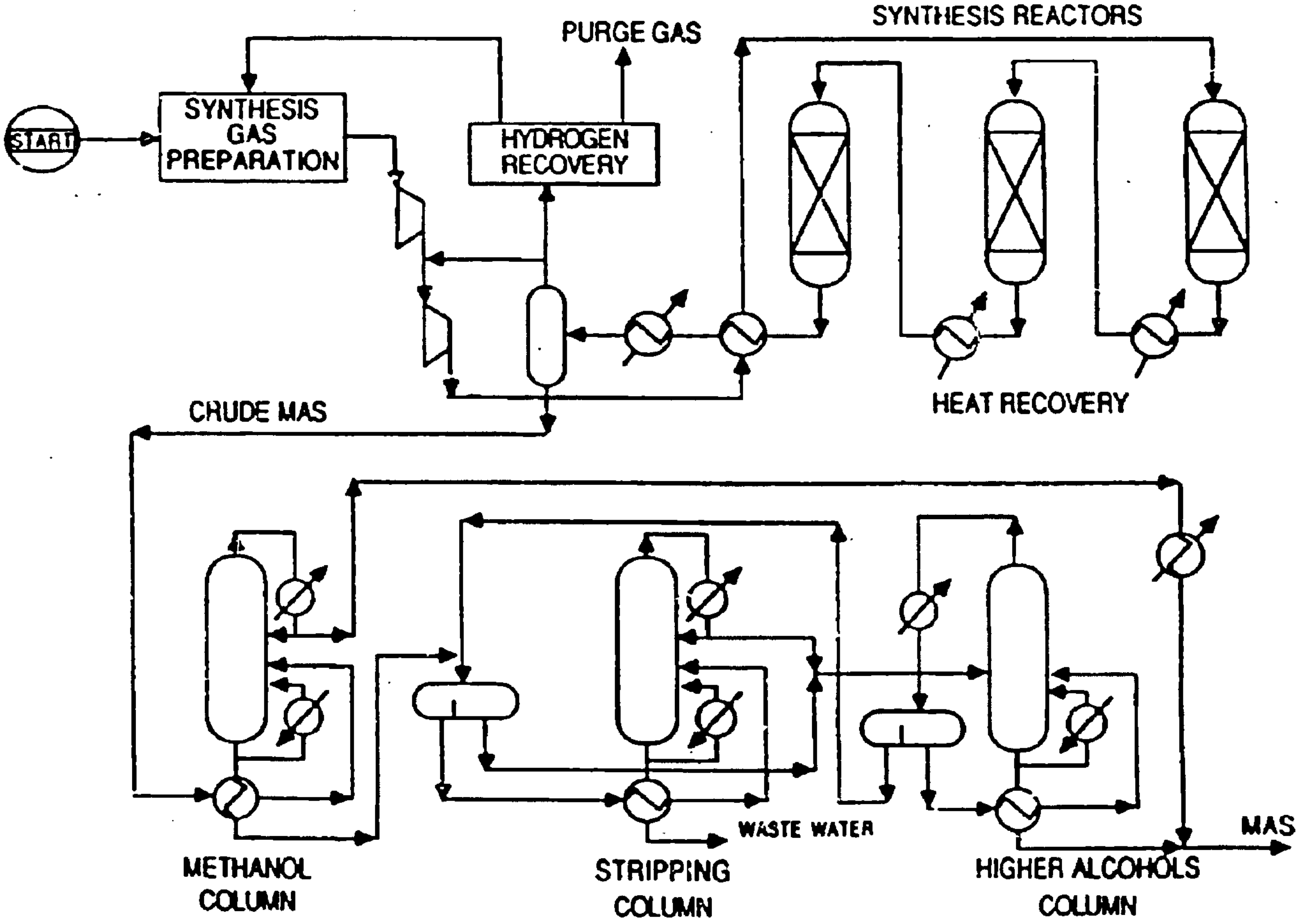
A simplified process flow sketch is shown in Figure 3.2. Snamprogetti has not disclosed any specific operating pressures or temperatures for the process, but H_2/CO ratios approaching the 2/1 stoichiometric value has been reported. Published literature and patents do disclose the use of Zn/Cr catalysts for the process. Significant quantities of isobutanol, and low yields of linear alcohols are observed in the product composition. Such distribution along with the H_2/CO ratio for the SEHT catalyst, are typical of alkali-modified high-pressure methanol synthesis catalysts with operating pressures of 15-25 MPa (2175-3625 psia) and a temperature range of 310-420 C (590-788 F). Recent versions of the SEHT process indicate that the catalyst requires the presence of CO_2 in the reactor feed gas. The performance and operating ranges for the SEHT catalyst are listed in Table 3.1.

To be effective in keeping methanol miscibility in gasoline in the presence of water, it is important to keep the water level in the MAS product to a minimum. Snamprogetti achieves water levels of less than 1000 ppm in the product stream. In the SEHT process scheme the water content of the crude alcohol is reduced by feeding the product stream to a low temperature shift reactor, followed by the removal of CO_2. A recent version of the process without the CO-shift and CO_2 removal has been described by Snamprogetti. Elimination of the CO-shift and CO_2 removal steps results in a simpler process, but requires an azeotropic distillation step.

FIGURE 3.2

Simplified Flow Diagram of the SEHT Process

[Srivastava, 1990]



- Lurgi "Octamix" Process

This process is claimed to be an extension of Lurgi's low-pressure methanol technology (Srivastava, 1990). The catalyst used is Cu/ZnO modified by the addition of alkali salts and hydroxides which improve the selectivity towards higher alcohols. Operating conditions with this alkali-modified Cu/ZnO catalyst are less severe than with the Zn/Cr catalysts. Operating temperatures are in the range of 270-300 C (518-572 F), with the pressure range of 5-10 MPa (725-1450 psia). The performance and operating ranges for the Octamix catalyst are listed in Table 3.1.

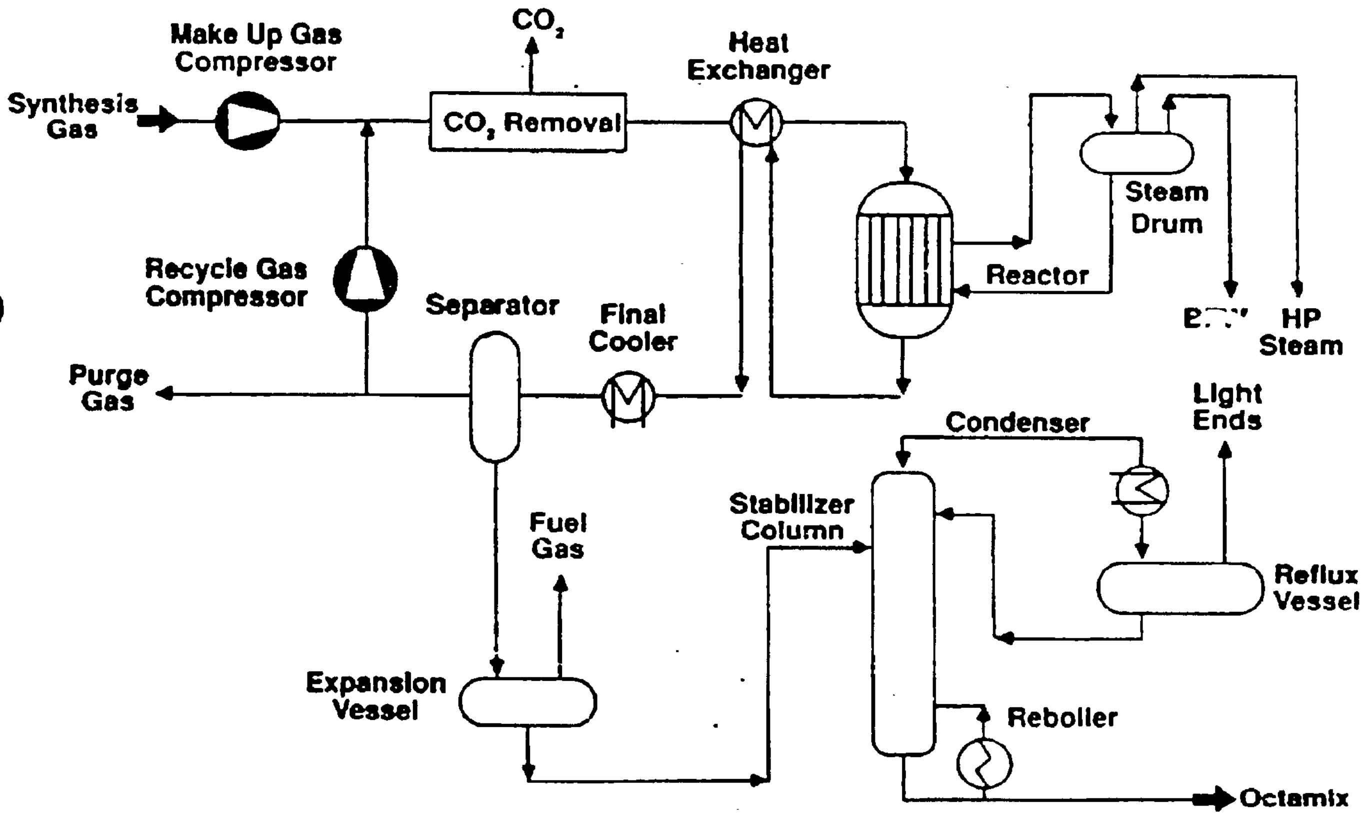
It is known that potassium is useful in converting methanol synthesis to higher alcohol synthesis catalysts. This is however, at the expense of some loss in activity. Lurgi's catalyst has the advantage of not requiring substantial potassium addition for higher alcohols production. High pressures also increase the conversion, but at the expense of decreased higher alcohols yield. The quantity of methanol in the product ranges between 55 to 88% depending on the feed gas composition. The high quantity of C_6+ alcohols produced with the Lurgi catalyst at low H_2/CO ratio may indicate the use of undisclosed metals or promoters. The Cu/ZnO acts simultaneously as an alcohol synthesis, in addition to a shift catalyst, enabling the consumption of the water produced by the reaction. The decreased amount of water simplifies the product purification.

A simplified flow diagram for the Lurgi process is shown in Figure 3.3. The process employs a tubular reactor for the synthesis. The reactor is cooled by boiling water on the shell side. The concentration of CO_2 is reduced to levels of 1% allowing the conversion of water to H_2 and CO_2, which as mentioned, simplifies the purification step. The AMISOL process, using a mixture of methanol-amine is used to remove CO_2 from the feed gas. A H_2/CO

FIGURE 3.3

Simplified Flow Diagram of the Lurgi Process

[Srivastava, 1990]



ratio of 0.5:1.0 is desirable for the feed gas. The process is demonstrated at a 10 ton/day pilot plant in Germany. At this scale, catalyst life of four (4) years has been observed.

- Dow Chemical/ Union Carbide (Dow/UCC) Process

A modified Fischer-Tropsch catalyst, MoS_2, is used by Dow/UCC in their process for the production of higher alcohols (Srivastava, 1990). The catalyst is highly selective and has operating conditions similar to the low-pressure methanol synthesis catalysts. Operating conditions for the process are pressures in the range of 7-21 MPa (1000-3000 psia) and temperatures of 250-300 C (482-572 F). The H_2/CO ratio in the feed gas is typically around 1.2:1.0. The performance and operating ranges for this type of catalyst are listed in Table 3.1. The product consists of mainly straight-chain alcohols on the C_1-C_5 range. Selectivities of 85% with CO per-pass conversion in the range of 20-25% are typical. Molybdenum-based catalysts exhibit good water-gas shift activity. This simplifies the removal of water from the product.

The wide range of feasible operating conditions along with the high CO-shift activity of the catalyst, makes a wide range of design possible. A novel water separation method, using molecular sieves, has been selected by Dow/UCC to remove water from the alcohol product. This is only possible though, if the water content is less than 20 wt%. Pilot-scale work in both fixed-bed and fluidized-bed reactors have been carried out by Dow. The process has demonstrated several problems including catalyst deactivation and low conversion rates. It is also observed that with the Dow/UCC catalyst, the rate of the undesireable methanation reaction tends to increase as conversion and selectivity to higher alcohols increases.

3.2.2 New Developments: Catalysts

As with methanol, research activity in the area of higher alcohols production has concentrated on development of improved catalyst systems. Studies have been conducted to determine the effects of catalyst composition as well as operating conditions, for the conversion of synthesis gas to methanol and higher alcohols (Stiles et al., 1991).

The most efficient methanol synthesis catalyst, composed of copper oxide, zinc oxide, and aluminum oxide, has been modified by addition of various elements. The results of such composition changes and variations in operating conditions, on the higher alcohols production have been reported (Stiles et al., 1991). A summary of these results is given in Tables 3.2a and 3.2b.

Manganese is known to be an effective catalyst for the synthesis of higher alcohols, but it requires extremely high operating pressures and produces large quantities of methane. Addition of Mn to the methanol synthesis catalyst with a composition of 2 atoms of Cu: 2 atoms of Mn: 2 atoms of Zn, with aluminum oxide comprising 20 wt% of total oxides, results in the increase of higher alcohols fraction approaching 20%. This is obtained with a temperature range of 375-400 C (707-752 F) and a pressure range of 8-17 MPa (1200-2500 psia). The total alcohols production increases significantly in going from the lower to the upper end of the pressure range.

Magnesium carbonate has been found to be an excellent catalyst stabilizer, allowing high temperature operation with little thermal deactivation of the catalyst. Silica as a component replacing alumina, creates a strong dehydration tendency. The dehydration reaction of two methanol molecules results in the formation of dimethyl ether (DME). In the presence of silica and at 400-425 C (752-797 F) a very substantial increase in DME is observed.

TABLE 3.2a
Effects of Added Ingredients[a]
[Stiles et al., 1991]

Added Ingredient	Quantity, %	effect on Productivity	effect on Methanation	HA ratio[b]	Shift in HA Components	Remarks
Ca	5	none	none	none	little change	
Sr	5	none	none	little	more $C_{3}2$-C_4	
Be	5	increase	increase	increase	more C_3-C_4	
Ce	5	none	increase	increase	no change	
La	5	decrease	little	little	no change	
Nd	5	none	little	slight increase	no change	
mixed La	5	none	slight increase	slight increase	little change	
SiO_2	5	none	increase	decrease	more C_2's and C_3's	increased DME
TiO_2	5	none	increase	decrease	more aldehyde	some increased DME and aldehyde
ZrO_2	5	increase	increase	increase	more aldehyde	

[a] All are added as nitrate salts except SiO_2 and TiO_2, which are derived from colloidal silicia (colloidal SiO_2, derived from Ludox, a Du Point product and trademark) and Tyzor (Tyzor, the source of the TiO_2, is a lactic acid ester of TiO_2 which hydrolyzes to Ti(OH), in water). Effects of each of the above can be moderated (tailored) by alkali carbonate catalyst preparation conditions, and changes in other ingredients. HA = higher alcohols

[b] HA = Higher Alcohols

TABLE 3.2b
Additional Factors Affecting the Fraction of Higher Alcohols and their Distribution
[Stiles et al., 1991]

	HA[a] Fraction	Alcohol Distribution	Productivity	Methanation
Substituting Cr for Al	Increases	None	None	Increase
Increasing P	Decreases	Variable	Increase	Decreases
Increasing SV	Decreases	Moves to lighter alcohols	Increases	Decreases
Increasing T	Increases	Increases heavier alcohols	Increases to max/then decreases	Increases
Addition of Co	Increases	Largely BtOH	Increases	Sharp increase
As an ingredient Cu	Decreases	No effect	Sharply increases	Increases at high T
Mn	Increases	Shift to C_3+	Decreases	Increases
Zn	Slight increase	None	Increases (with Cu)	No significant change

[a] HA = higher alcohols

For the production of methanol with a higher alcohols fraction in the 20-30% range, the optimal pressure is in the range of 17-24 MPa (2500-3500 psia). Both productivity and efficiency are benefited by high pressure. For the synthesis of methanol operating temperatures in the 220-320 C (428-608 F) range are favorable, and for higher alcohols temperatures above 375 C (707 F). The tendency for methanation also increases with increasing temperature. For higher alcohols synthesis, temperatures in the range of 375-440 C (707-824 F) are favored when operating in the 17-31 MPa (2500-4500 psia) pressure range.

The effect of feed gas composition on the synthesis of higher alcohols has also been examined. Although CO_2 has beneficial effects for methanol synthesis, it is harmful to the higher alcohol ratio and methanation. High concentrations of CO_2, suppresses the overall productivity of the catalyst system. On the laboratory scale the optimum CO/H_2 ratio in the feed gas has been determined to be 40% CO and 60% H_2, but in commercial operation the CO content is held below 12% to control the high exotherms.

The laboratory work on higher alcohols synthesis has also produced some guidelines on the materials of construction to be used. To reduce methanation problems, it has been suggested (Stiles et al., 1991) that the synthesis reactor and all other hot surfaces exposed to the process, should be fabricated from copper, brass, copper bronze, or galvanized iron.

4.0 ETHERS FROM SYNTHESIS GAS

4.1 MTBE and ETBE

Among the oxygenates, methyl tertiary butyl ether (MTBE) is one of the most promising fuel additives, due to several useful properties. These include a low vapor pressure, ease of blending without phase separation, and high octane performance value. The major feedstocks for the production of MTBE are isobutylene and methanol. A comparable oxygenate to MTBE, ethyl tertiary butyl ether (ETBE), may become more attractive as methanol prices go up. Ethanol is used instead of methanol in producing ETBE.

The reaction of methanol with isobutylene, to produce MTBE, proceeds according to the following reaction:

$$(CH_3)_2\text{-}C=CH_2 + CH_3OH \text{ -----> } CH_3\text{-}O\text{-}C\text{-}(CH_3)_3 \qquad H = -37214 \text{ kJ/kg.mole}$$

The reaction is catalyzed by strongly acidic cation-exchange resins such as commercially available Dowex 50W and Amberlite IR-100. A temperature range of 65-93 C (150-200 F) and pressures of 0.7-1.0 MPa (100-150 psia) are common. Conversions of 94-96% isobutylene per pass, and selectivities as high as 98% can be achieved.

The reaction kinetics for the production of ETBE are very similar to that for MTBE. The blending properties and production yields are more favorable for ETBE, but these benefits have so far been offset by the higher cost of the ethanol feedstock.

Production of methanol, ethanol, and higher alcohols from synthesis gas has already been discussed in previous sections of this report. The isobutylene necessary for the ether production, though, has conventionally been derived from petroleum. It would be of great interest to produce both MTBE and ETBE wholly from coal-derived synthesis gas. The dehydration reaction of isobutanol would yield isobutylene. The alcohol synthesis and dehydration reactions are:

$$4CO + 8H_2 \text{-----}> (CH_3)_2\text{-}CHCH_2OH + 3H_2O$$

$$(CH_3)_2\text{-}CHCH_2OH \text{-----}> (CH_3)_2\text{-}C=CH_2 + H_2O$$

This would eliminate the need for petroleum-based isobutylene. Good selectivities of isobutanol can be obtained using $Cu/ZnO/Al_2O_3$ catalyst promoted with cesium. Temperatures in excess of 300 C (572 F) and pressures in the range of 10-13 MPa (1450-1900 psia) are typical for the alcohol synthesis. It should be noted that Air Products has scheduled isobutanol production runs, in their slurry reactor at the LaPorte facility, for the early part of 1992.

The alcohol synthesis, dehydration, and ether synthesis, are the steps required in an indirect procedure for producing ethers. Since methanol and isobutanol mixtures can be produced from synthesis gas, a more direct route would be the direct coupling of alcohols to ethers. Recent work has shown that on superacid resins the following reaction can occur:

$$CH_3OH + R\text{-}OH \text{-----}> CH_3O\text{-}R + H_2O$$

Production of ethers from higher alcohols over various resins has been investigated (Klier et al., 1991). Amberlyst-15 and Nafion H have been among the resins to be tested in a temperature range of 90-157 C (194-315 F) and pressures of 0.1-7.5 MPa (15-1100 psia). Isobutanol can be coupled with methanol over Nafion-H resin according to:

$$(CH_3)_2\text{-}CH\text{-}CH_2OH + CH_3OH \text{----}> (CH_3)_2\text{-}CH\text{-}CH_2\text{-}O\text{-}CH_3$$

The product of this reaction is methyl isobutyl ether (MIBE) instead of MTBE. The direct route to ethers has several drawbacks associated with it. First, neither the octane-enhancing value nor the long-term stability of MIBE has been established. Furthermore, the operating conditions for the alcohol coupling are more severe than those for the methanol-olefin coupling, and the selectivities are lower.

4.2 Dimethyl Ether (DME)

The production of dimethyl ether (DME) or mixtures of DME and methanol has been of interest for several reasons. It can be used for peak shaving applications in power generation facilities. Mobil's Methanol-To-Gasoline (MTG) process uses DME/methanol mixture as an important feedstock. DME is also used as feedstock for the production of acetic anhydride. Recently it has been proposed that DME could also be an effective building block for the synthesis of mixed ethers, such as MTBE (Underwood et al.,1991). Production of DME from synthesis gas can be achieved in several ways.

In the conventional process for the conversion of synthesis gas to DME, three steps are required (Srivastava, 1990). Coal-derived synthesis gas is usually too rich in CO to be used directly for DME synthesis. Therefore the first step is to adjust the composition of the feed gas via the water-gas shift reaction:

$$CO + H_2O = CO_2 + H_2$$

Once the H_2 to CO ratio is adjusted, the gas is reacted over catalyst to produce methanol:

$$CO + 2H_2 \text{-----}> CH_3OH$$

In the final step DME is formed as the result of methanol dehydration:

$$2CH_3OH \text{-----}> CH_3\text{-}O\text{-}CH_3 + H_2O$$

All three reactions are equilibrium limited and exothermic. The exothermic heat of reaction could result in loss of productivity, as both the shift, as well as the methanol synthesis catalysts are subject to severe deactivation if overheated. To avoid thermodynamic limitations and excessive catalyst deactivation, caused by high temperatures, conventional gas-phase reactors must be run at low per-pass conversion. Commercially, DME is produced using multiple reactors in series with high recycle rates.

Rather than the conventional multi-step route, direct DME synthesis has been investigated and in 1983 Shell was awarded a patent for their work in this area (Srivastava, 1990). A Cu/ZnO catalyst supported on gamma alumina has been used. The methanol synthesis is believed to occur on the Cu/ZnO component, with the dehydration of methanol occuring on the alumina component. At 6 MPa (870 psia) and a temperature range of 292-300 C (558-572 F), typical selectivities of 97% DME, 1.5% methanol, and 1.5% hydrocarbons, are observed.

Prior work in the area of DME production has focused on improving the catalysts used in the multi-step synthesis. Single-step processes in the gas-phase, such as the one patented by Shell, may not be commercially feasible. One reason is the fact that the catalyst has been observed to require frequent regeneration. The limitation on the per-pass conversion due to heat dissipation requirements of the gas-phase process is the other factor.

4.3 New Developments: Slurry Reactors

Recent work by Air Products and Chemicals, Inc. has focused on the single-step synthesis of DME and methanol mixtures using a slurry-based process (Lewnard et al., 1990, Bhatt et al., 1991). Combining the three reversible reactions: shift, methanol synthesis, and dehydration, in a single step, drives each thermodynamically by removing its inhibiting product as reactant in the subsequent reaction. The single-step synthesis has the advantage of higher conversions of CO to DME and methanol. But this increase can only be realized at low temperatures, since higher temperatures inhibit the overall conversion. The use of a slurry reactor provides the necessary control on temperature. The slurry