5.3.2 Higher Alcohols

5.3.2.1 Introduction and Historic Notes

Mixtures of methanol with higher alcohols (mainly C_2-C_6) can be used pure or as an additive to gasoline as transportation fuels (94-100). In the United States, however, the Clean Air Act prohibits selling new unleaded fuels, or fuel additives in unleaded fuels, unless specifically waived by EPA. Four EPA waivers were granted between 1979 and 1985, and a new waiver for the Lurgi OCTAMIX alcohol product is reported to have been granted in February 1988 (101). The EPA waivers granted for methanol/higher alcohol blends are summarized in Table 5-4. An alcohol blend acceptable under the DuPont waiver is listed in Table 5-5.

In addition, the use of 10 percent ethanol in gasoline is covered by a 1978 waiver and MTBE (methyl tertiary-butyl ether) by a 1979 waiver based on a request by ARCO to allow MTBE and TBA (tertiary-butyl alcohol). The DuPont and Lurgi waivers allow a wider range of alcohols than ethanol, TBA, and the ethers MTBE and TAME (tertiary-amyl methyl ether), and cover alcohol mixtures that can be directly synthesized from synthesis gas (SG). However, certain EPA restrictions, particularly the volatility specifications (evaporative index, EI), have imposed economic penalties on alcohol blends and have impeded their acceptance by refiners and blenders. It is not known at this time whether the February 1988 Lurgi waiver relaxes the EI specifications.

The technical advantages of using the alcohol (C_1-C_6) blends with gasoline are the following:

- improvement of octane number to fill the gap left by banning the use of lead-containing antiknock agents,
- improved hydrocarbon solubility compared to pure methanol-gasoline blends,
- improved water tolerance compared to pure methanol-gasoline blends,

Table 5-4. EPA Waivers Granted For Methanol/Cosolvent Alcohol Blends

Applicant	Blend	Date Granted
SUN	MeOH/TBA (0-5.5%)	6/14/79
(Anafuel Unlimited) American Methyl	"Petrocoal" Up to 12% MeOH Up to 6% C_4OH's Max. 15% MeOH Proprietary Corrosion Inhibitor	9/28/81
ARCO	"Oxinol" 4.8% MeOH 4.8% TBA 3.5% Max. O_2	11/7/81
DuPont	Up to 5% MeOH 3.7% Max. O_2 Must Meet Evaporative Index	1/14/85
Lurgi	"Octamix" Blending Specifications and Evaporative Index Requirements not yet Published by EPA	2/1/88

Table 5-5. **Acceptable Methanol/Cosolvent Alcohol Blend Under the DuPont Waiver**

	2 parts Methanol	+ 1 part Cosolvent Alcohol	= 2:1 Methanol/ Cosolvent Alcohol Blend	
Composition, Wt. %				
Methanol	100%	0-5.0	68.33 Max	
C_2-C_4 OH		90.0 Min	30.00 Min	
C_{5+} OH		0-5.0	1.67	
Ketones		0-2.0	0.67	1.67 Max
Esters		0-2.0	0.67	
Ethers		0-2.0	0.67	
Aldehydes		0-2.0	0.67	

- improved driveability, and
- good control of volatility.

Fuels containing higher-alcohol blends have been in use in West Germany (ca. 3-5 mol percent) for automobile transportation.

Other potential uses of higher alcohols include: fuel for combined cycle peak electric power generation, manufacture of olefins (ethylene from ethanol, propene from propanol, iso-butene from isobutanol), substitution for propane in LPG applications, alkylation and solubilization of coal, and transportation medium for coal in slurry pipelines.

As pointed out above, higher alcohols can be produced directly from SG by catalytic processes. The early processes for higher-alcohol synthesis (HAS) were practiced in Germany. BASF reported as early as 1913 cobalt- or osmium-catalyzed synthesis of a mixture of alcohols, aldehydes, ketones, acids, and other oxygenated compounds as well as hydrocarbons at 10-20 MPa and 300-400°C. In 1923-24 the Fischer-Tropsch "Synthol" process for alcohol mixtures was developed. Later, higher alcohols were found to be coproducts of methanol synthesis over ZnO/Cr_2O_3 catalysts (BASF, 1920's), alkalized ZnO/Cr_2O_3 catalysts (Natta, 1928), and alkalized copper-based catalysts (Natta, 1958). Toward the end of World War II, I.G. Farben and Ruhrchemie in Germany developed the "Synol" process that was based on low-temperature (<200°C) medium-pressure (20 atm) Fischer-Tropsch synthesis utilizing iron catalysts. The process incorporated several reactor stages with intermediate CO_2 removal and gas recycle (<u>100</u>). In 1984 the Dow Corporation announced a new process for higher alcohols based on alkalized MoS_2 catalysts (<u>103</u>) and Union Carbide filed patent applications the same year (<u>104</u>).

5.3.2.2 Present Technology

Currently, a large number of plants for alcohols other than methanol or for methanol/higher-alcohol mixtures are completed, under construction, engineered or planned, with a total annual capacity of over 2.6 billion kg (37). Some of these plants entail processes for fermentation ethanol, and others for specialty alcohols such as the plasticizer and solvent 2-ethylhexanol. But the overall build-up of large capacities for fuel alcohols by catalyzed processes is evident.

This section focuses on HAS from coal-derived SG, i.e., on indirect liquefaction of coal to C_1-C_4 alcohols. The technology for HAS has been demonstrated on both bench- and pilot-plant scale, and a large plant with the capacity of 15,000 tons/yr was operated for six years. The processes are based on (1) modified high-pressure methanol technology utilizing alkalized zinc oxide-chromia catalysts, (2) combined methanol-Fischer-Tropsch technology utilizing copper-cobalt-oxide catalysts, (3) modified low-pressure methanol catalytic technology utilizing alkalized copper oxide catalysts, and (4) the Dow-Union Carbide technology utilizing alkalized molybdenum sulfide catalysts.

Recently proven processes for HAS from SG that have been demonstrated either on industrial scale, on pilot-plant scale, or by extensive experimentation on bench scale are reviewed here in some detail, and they include (1) the SEHT (MAS) process, (2) the IFP (Substifuel) process, (3) the Dow HAS process, (4) the Lurgi OCTAMIX process, and (5) the Lehigh University (LU) HAS process. The basic operating characteristics for these five HAS processes are summarized in Table 5-6. For this table the entries for the MAS, IFP and OCTAMIX processes were taken from Reference 101 and cited literature, those for the Dow HAS process from patent literature and Lehigh University's DOE reports, and those for the LU HAS process from Reference 105.

A. The SEHT (MAS) Process

The technology for higher alcohols based on alkali-promoted ZnO/Cr_2O_3 methanol synthesis catalysts that had been used since the1920's for the high-pressure methanol synthesis was further developed by Snamprogetti, Enichem, and Haldor Topsoe A/S (SEHT) and used the acronym MAS from the Italian for "Metanolo piu Alcoli Superiori" (methanol plus

Table 5-6. Comparative Operating Characteristics for Various Alcohol Processes

Process	1	2	3 MoS$_2$-based HAS				4	5	
Main Characteristics	SEHT (MAS) Process	IFP (Substifuel) Process	Dow HAS Process	UCC HAS	LU HAS	Dow HAS	Lurgi OCTAMIX Process	LU[a] HAS Process	LU[a] HAS
Main Constituents of Catalyst	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$_2$O$_3$
Catalyst Stability (life), h	8,000	~2,000	>8,000	n.a.	>200	n.a.	8,000	>1,200[b]	>750[b]
Operating Temperature, °C	350-420	260-320	306	300	295	255	285-300	300	300
Operating Pressure, MPa	10-18	6-10	10.3	2.75	8.2	10.3	6-9	9.1	9.1
Syngas Space Velocity, 1000 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	36.5
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 and in reference 114.
[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

higher alcohols). The SEHT MAS process built on the expertise of Snamprogetti in catalysis of SG reactions; Haldor Topse's expertise in the development of new processes and catalysts, and manufacture of industrial catalysts; and Enichem's know-how in product evaluation gained through marketing of oxygenated compounds.

After catalyst and process development and preliminary economic evaluation, the SEHT group decided to forgo building a pilot plant and instead opted for an industrial prototype plant. This plan was accomplished by modifying a high-pressure methanol plant, closed in 1963, at Pisticci in Southern Italy. The Pisticci plant was operated at 15,000 tons per year of MAS between August 1982 and 1987 (101) but is now closed. The plant consists of three sections -- a unit for the preparation of SG starting from natural gas, a synthesis unit for the production of crude MAS, and a distillation unit. The flow diagram of the MAS process is shown in Figure 5-16. The MAS process operates at 9-18 MPa, 330-430°C, and gas hourly space velocity (GHSV) of 3000-15,000 with H_2/CO ratios of 0.5-3. The catalyst, principally $K/ZnO/Cr_2O_3$, is covered by Italian (106) and U.S. (107) patents. A life test up to 8000 hours has shown good performance and no deactivation for 6000 hours (108), although the initial activity of the catalyst in the plant was some 40 percent lower than the initial activity in the laboratory. Operating characteristics are listed in Table 5-6, Column 1.

The typical composition and properties of MAS are given in Table 5-7. The crude MAS product contains some 20 percent water because it is operated at high temperatures and a significant portion of CO_2 that iseither the product, a reactant, or a recycled gas is converted to water by the reverse water gas shift reaction. Although the MAS process could be operated to obtain ratios of methanol to higher alcohols from 60/40 to 80/20, the target choice 70/30 has been considered a good compromise between economic factors and performance. The main advantages of the MAS product for gasoline blending were considered to be as follows (108):

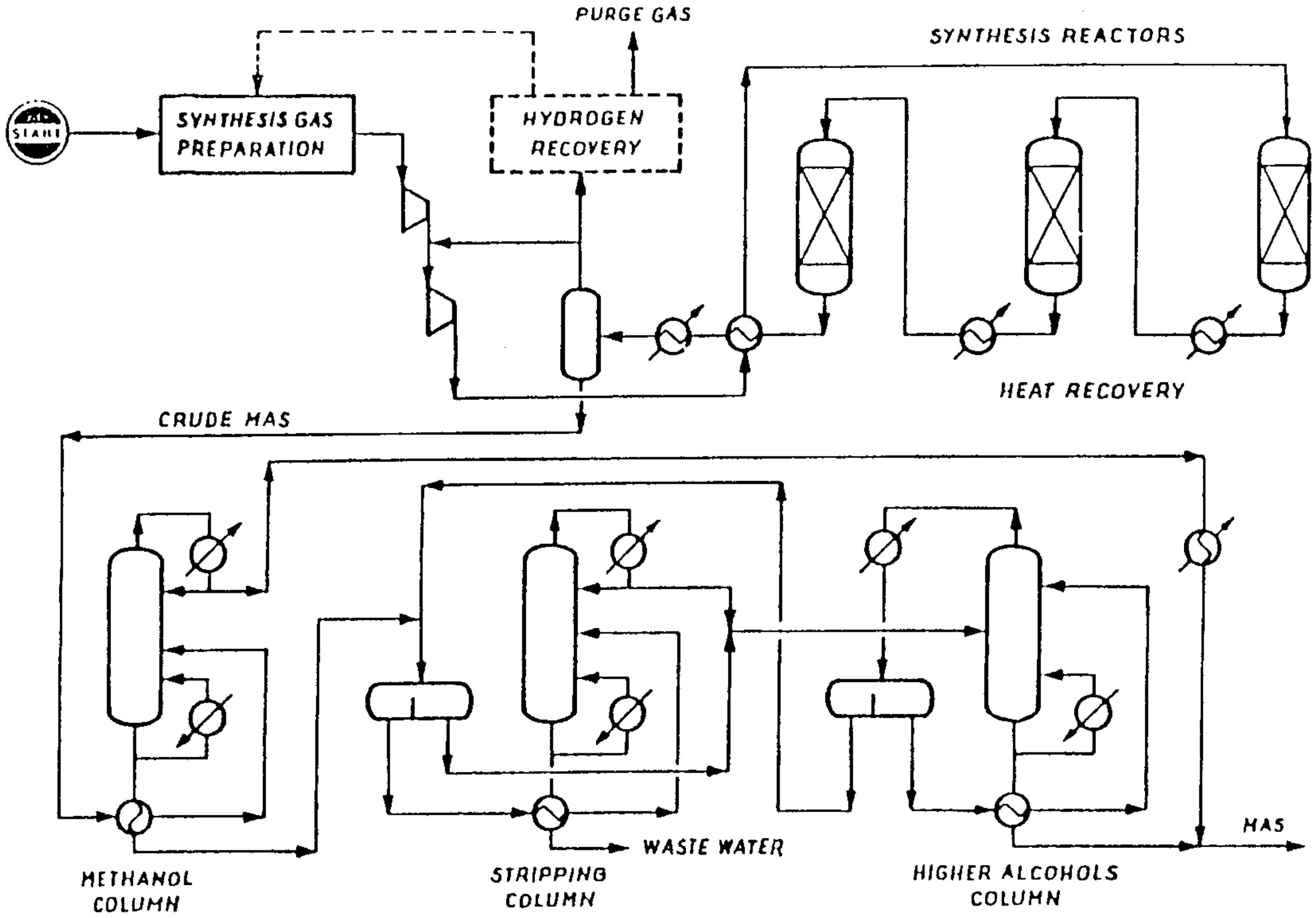


Figure 5-16. Flow Diagram of MAS Process

Table 5-7. Typical Composition and Properties of MAS

Typical Composition	Weight Percent Min	Weight Percent Max
Alcohol C_1	68.0	72.0
Alcohol C_2	2.0	3.0
Alcohols C_3	3.0	5.0
Alcohols C_4	10.0	15.0
Alcohols C_5+	7.0	12.0
Ketones and Aldehydes		2.0
Esters		0.1
Acidity (as acetic acid)		0.007
Water		0.1
Ash		0.001
Copper		0.1 ppm
Appearance Clear and free of suspended matter		

Typical Properties		
Density at 20 °C	kg/l	0.804
R.V.P	bar	0.230
Evap. at 70-100-150 °C	% vol.	61-85-95
Lower Heat Value	kcal/kg	5870
Oxygen content	wt. %	41
Octane "blending"		
- research method		120-135
- motor method		93-106
- $\frac{\text{research + motor}}{2}$		106-121

- Low tendency to phase separation in the presence of water,
- a strong reduction of volatilitiy due to methanol addition,
- high octane blending characteristics,
- good fuel properties,
- reduction of exhaust emissions,
- good compatibility with the materials normally employed in the automobile fuel system,
- excellent driveability,
- no influence on fuel consumption.

MAS-gasoline blends containing 5 percent MAS were distributed in one hundred AGIP PETROLI and IP filling stations under the name "SUPER E".

B. The IFP (Substifuel) Process

The IFP (Institut Francais du Petrol) higher-alcohol synthesis technology utilizes alkalized copper-cobalt-oxide catalysts covered by IFP patents (109-112). In the case of (alkalized) ternary Cu-Co-Cr-oxides, the diagram in Figure 5-17 shows which compositions of these catalysts promote methanol synthesis, hydrocarbon synthesis and higher alcohol synthesis. The copper-chromia component being a methanol synthesis catalyst and the cobalt component a Fischer-Tropsch hydrocarbon synthesis catalyst, the IFP Cu-Co-Cr oxide catalyst can be viewed as a combination of C_1 oxygenate and C_n ($n = 1$) hydrocarbon-forming functions. This is reflected in the proposed mechanism discussed in Section 5.3.2.5.

A demonstration plant with capacity of 7000 bbl/yr (670 tons/yr) utilizing the IFP Substifuel technology and process design has been built by Idemitsu Kosan at its research facilities in Chiba, Japan. The first demonstration was carried out from December 1984 to March 1985 under the Japanese government-sponsored RAPAD (Research Association for Petroleum Alternative Development), and a report on this operation was presented in 1986 (114). The source of syngas was natural gas. The block diagram of the IFP/Idemitsu Kosan process is shown in Figure 5-18.

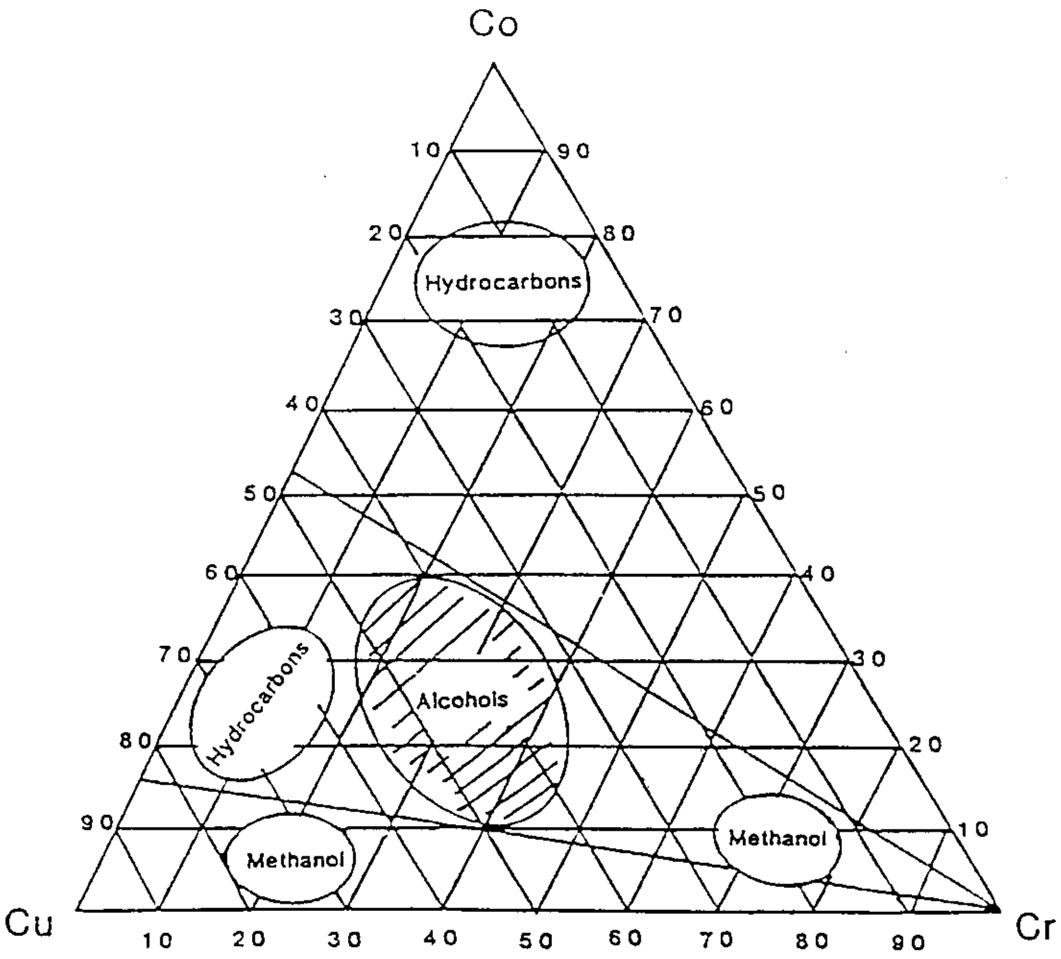
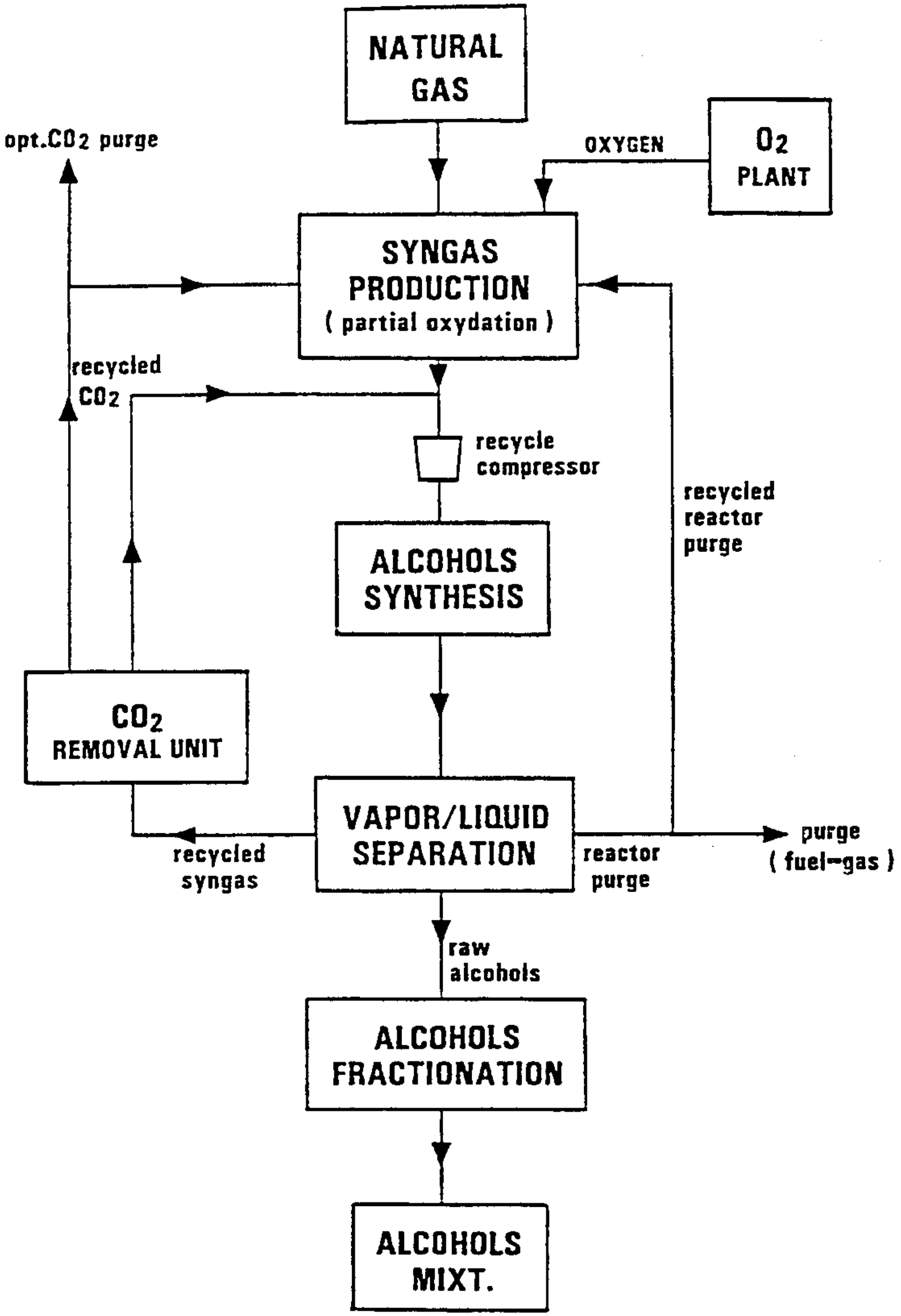


Figure 5-17. Influence of Composition on the Selectivity of IFP-1 Catalysts

Figure 5-18. Block Diagram of the Integrated Natural Gas to Alcohols Complex



In this process the separation section serves to remove water from the crude alcohol product (2.5-5 weight percent) to less than 0.2 percent, and includes azeotropic distillation with water entrainment. The reactor section is shown in Figure 5-19. Two reactors equipped with multiquenched bed systems to achieve good heat transfer are used in series with intermediate cooling, yielding high CO conversion after CO_2 removal and recycle.

The IFP process operates at 6-10 MPa, 260-320°C, and GHSV 3000-6000 with H_2/CO ratios of 1.0-2.0. Catalyst life has been reported suffering from deactivation caused by coke deposition, separation of Co from the originally homogeneously distributed Co and Cu phases, loss of cobalt as carbonyl, and formation of surface carbides (113). The performance and the composition of four IFP catalysts are presented in Table 5-8. It is presumed that the IFP/Idemitsu Kosan plant uses the second-generation IFP catalyst (catalyst 2 in Table 5-8). Some of the data in this table are at variation with those for the IFP process in Table 5-6, Column 2, which are documented in the MITRE report (101), partly based on an IFP report (114). The typical composition of the IFP fractionated higher-alcohol product is listed in Table 5-9, and their octane blending values in Table 5-10.

The gasoline compatibility of the IFP/Idemitsu Kosan alcohol product was found comparable to that of the methanol/TBA mixtures that are the ARCO gasoline additives. Provided that most of the butane is removed from the gasoline pool before blending, the alcohol-gasoline blends can be used as high-octane lead-free gasoline during summer time in many countries (114). An extensive evaluation program with a series of tests on a fleet of cars under the RAPAD program has been announced (114). Economic analysis of the IFP/Idemitsu Kosan process has also been performed, and the production cost of the alcohol product is represented in Figure 5-20.

Figure 5-19. Reactor Section of IFP/Idemitsu Kosan Process

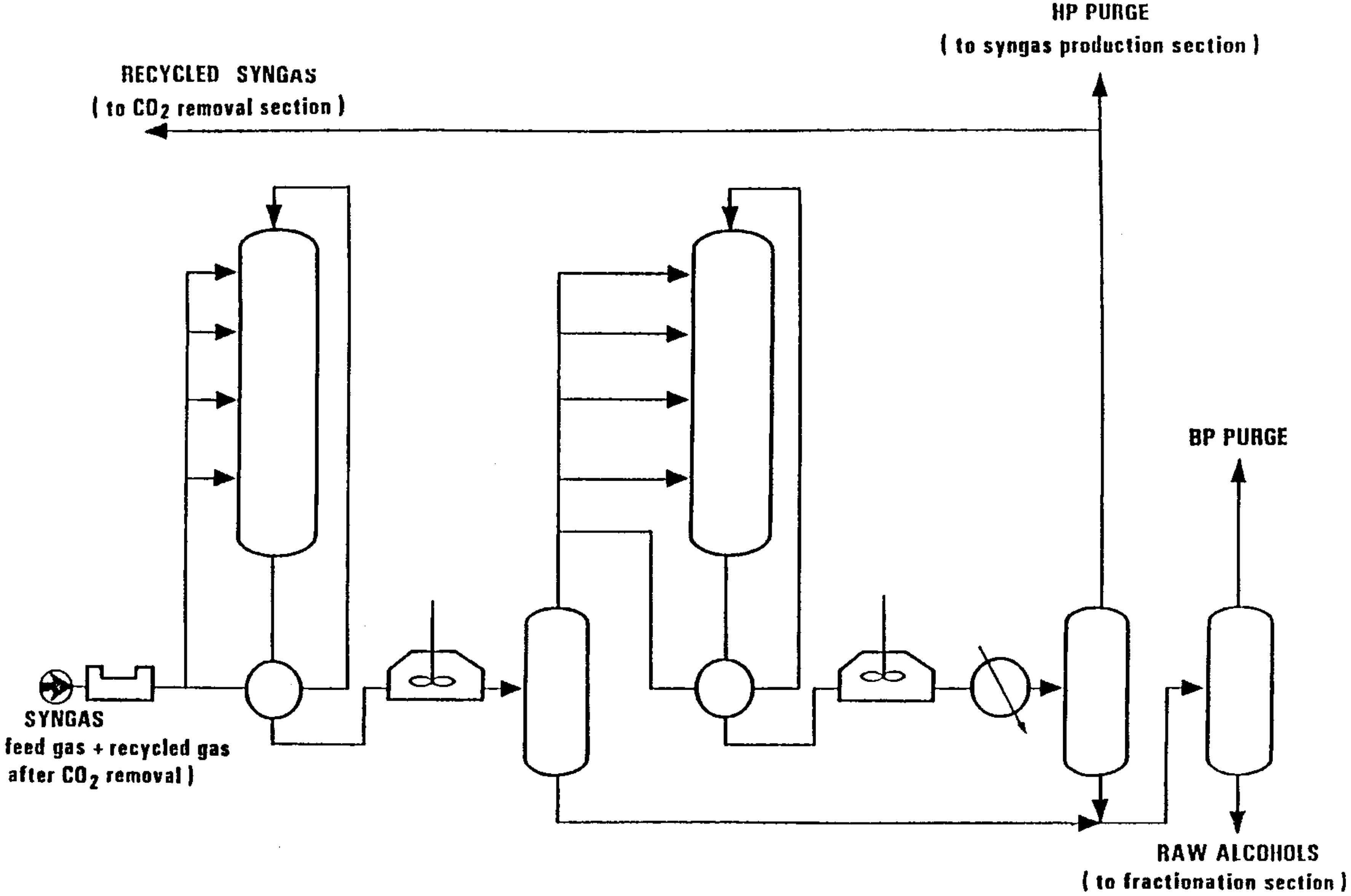


Table 5-8. Performance and Composition of IFP Catalysts

Cat.	Composition Atomic ratio	MeOH%	C_2+OH%	S_a[A]	Yield(C_1-C_4OH)[B]
1[C]	$CuCoM_{0.8}A_{0.09}$ M = Cr, Fe, V, or Mn A = alkali U.S. Pat. 4122110	20-26	74-80	90-95	0.27-(1.29)0.92
2[C]	$CuCo(M_1+M_2)_{0.8}A_{0.09-0.1}M_3$ M_1 = Cr, Mn, Fe, or V M_2 = rare earth M_3 = noble metals (0.005-0.5 wt%) A = alkali U.S. Pat. 4291126	20-24	76-80	ca. 95	0.27-0.40
3[D]	Cu/Co/Al/A/(M_1)(M_2)(M_3)(Zn)(Cr) M_1 = Mn, V, Fe, Re M_2 = Sc, Yb, Th, Zr, or rare earth M_3 = noble metals (0.02-0.8 wt%) A = alkali G.B. Pat. 2118061	28-61	39-72	62-70	0.11-0.15
4	Cu/Co/Zn(B)/Al(C)/A/(M) A = alkali or alkaline-earth B = Cd or Mn^{2+} C = Cr, Mn^{3+}, or Ti M = group VIII metals (Rh, Ru, Pd, Os, Ir, or Pt) G.B. Pat. 2158730	-----	20-77[E]	50-77[E]	0.06-0.09[E]

[A] S_a is the selectivity towards all alcohols.
[B] The yield is in g (ROH) hr^{-1} $gcat^{-1}$.
[C] The stability is unknown.
[D] The longest time was 8000 hr.
[E] Data after 1000 hr on stream.

Table 5-9. Composition of Fractionated Alcohols from Demonstration Unit

Composition of Fractionated Product
(fractionated C_1 - C_6 alcohols)

	Wt %		
Methanol	63.5	C_2	69.5
C_2+ Alcohols	35.8	C_3	17
Alcohols	99.3	C_4	6.5
C_5+ Hydrocarbons	0.2	C_5	3
Esters	0.3	C_6	4
Other Oxygenates	0.2		100
	100.0 (water content 0.16%)		

Table 5-10. Motor-Fuel Properties of Fractionated Alcohols from Demonstration Unit

Typical blending values*
of fractionated C_1 - C_6 alcohols

Alcohols	C_1	C_2	fract. C_1 - C_6 alcohols	nC_3	iC_3	nC_4	tC_4	nC_6
R.O.N								
add. 5% Vol.	134	135	120.8	117	122	94	108	56
add. 10% Vol.	132	132	120.8	118	120	96	110	56
M.O.N.								
add. 5% vol.	98	100	97.4	92	96	80	94	41
add. 10% vol.	100	104	98.4	90	96	78	93	46

* Fractionated C_1 - C_6 alcohols: T.O.B.V. with D gasoline sample.
Individual alcohols: Hinkamp, J., Oil and Gas Journal, 1983.

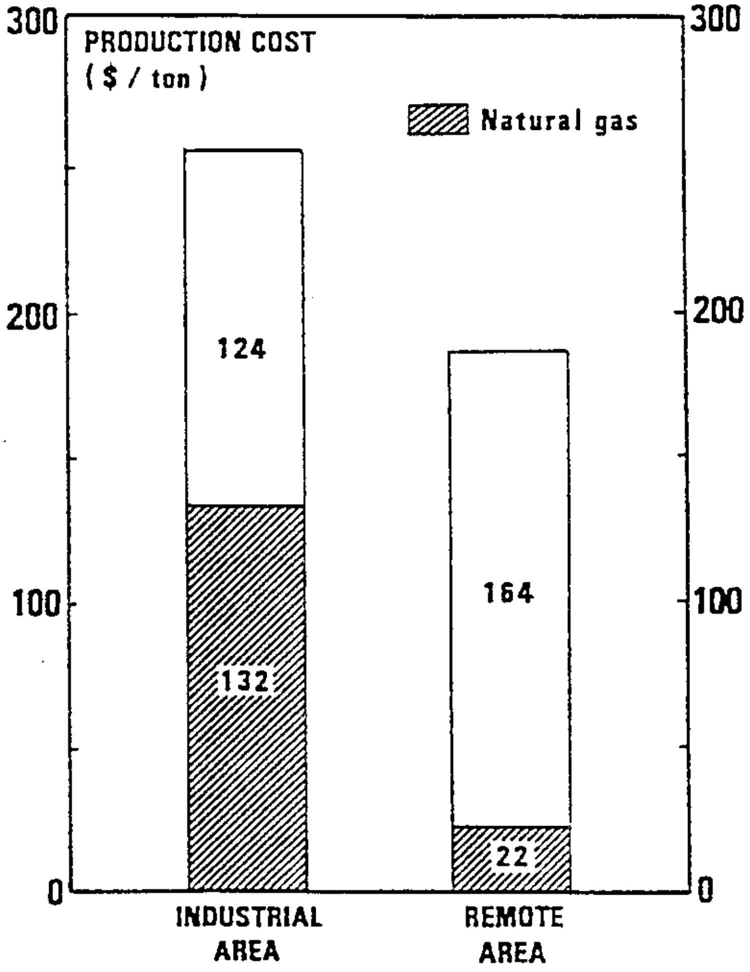


Figure 5-20. Breakdown of Production Cost of C_1-C_6 Alcohols

C. The Dow HAS Process

The Dow technology utilizes alkali/MoS_2 and alkali/Co/MoS_2 catalysts to steer the synthesis to C_1-C_4 alcohols with methanol/ethanol mixtures in various proportions being the dominant product. The process was announced in 1984 (103) after the Dow 0.2-0.225 tons/day (equivalent to 82 tons/yr if continuously operated) pilot plant in Midland, Michigan, operated since 1979 for Fischer-Tropsch synthesis of hydrocarbons was switched to alcohol production in 1982. The Dow alcohol synthesis pilot plant project was concluded in 1984. Patents covering alkali/MoS_2 catalysts were filed by the Dow (103) and Union Carbide (104) Corporations, and additional work was performed at Lehigh University that not only verified the Dow patents, but added specific information on the efficiency of different alkali promoters, catalyst preparation and improvements, and the mechanism of chain growth (90, 115). Research into the alkali/TX_2 catalysts (T, transition metal; X, chalcogenide) for alcohols continues under DOE sponsorship at Union Carbide Corporation (UCC) (116) and Lehigh University (117).

The Dow/UCC process has been demonstrated to operate at 7-20 MPa, 280-310°C, and GHSV 5000-7000 with H_2/CO ratios of 0.9-1.2 with space time yields of 170-400 g alcohol product per kg catalyst per hour. For typical operating characteristics and yields, see Table 5-6. A year-long life test at Dow revealed an extraordinary stability. The catalyst is highly tolerant to sulfur in the feed gas unlike any of the copper-based or Fischer-Tropsch catalysts. A very marked promotion effect of H_2S on increased ethanol yields via methanol homologation over the alkali/MoS_2 (but not alkali/Co/MoS_2) catalysts has been reported (118). The alkali components promote the highest rates of alcohol synthesis at an optimum concentration, as exemplified in Figure 5-21.

Because of the very short chain length n for the C_n $(n \geq 2)$ alcohols, the alcohol product can be recycled to the extinction of methanol (103,118), and C_2+ alcohol fuel rich in ethanol can be obtained. It is probable that the Dow process utilizing coal-derived synthesis gas can economically compete with fermentation ethanol, although the

Figure 5-21a. Effect of Cs Content of the MoS_2 Catalysts on the Product Yield

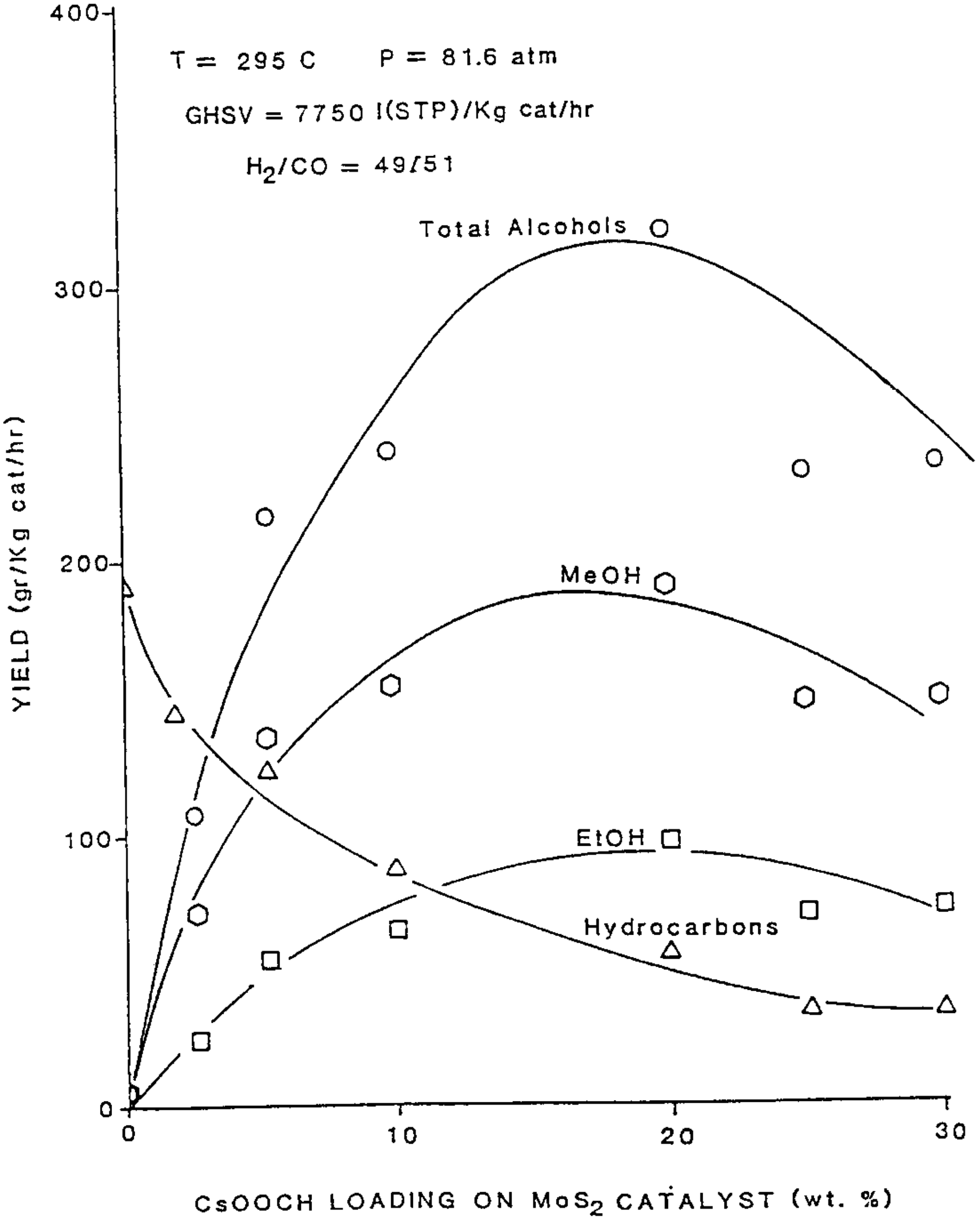
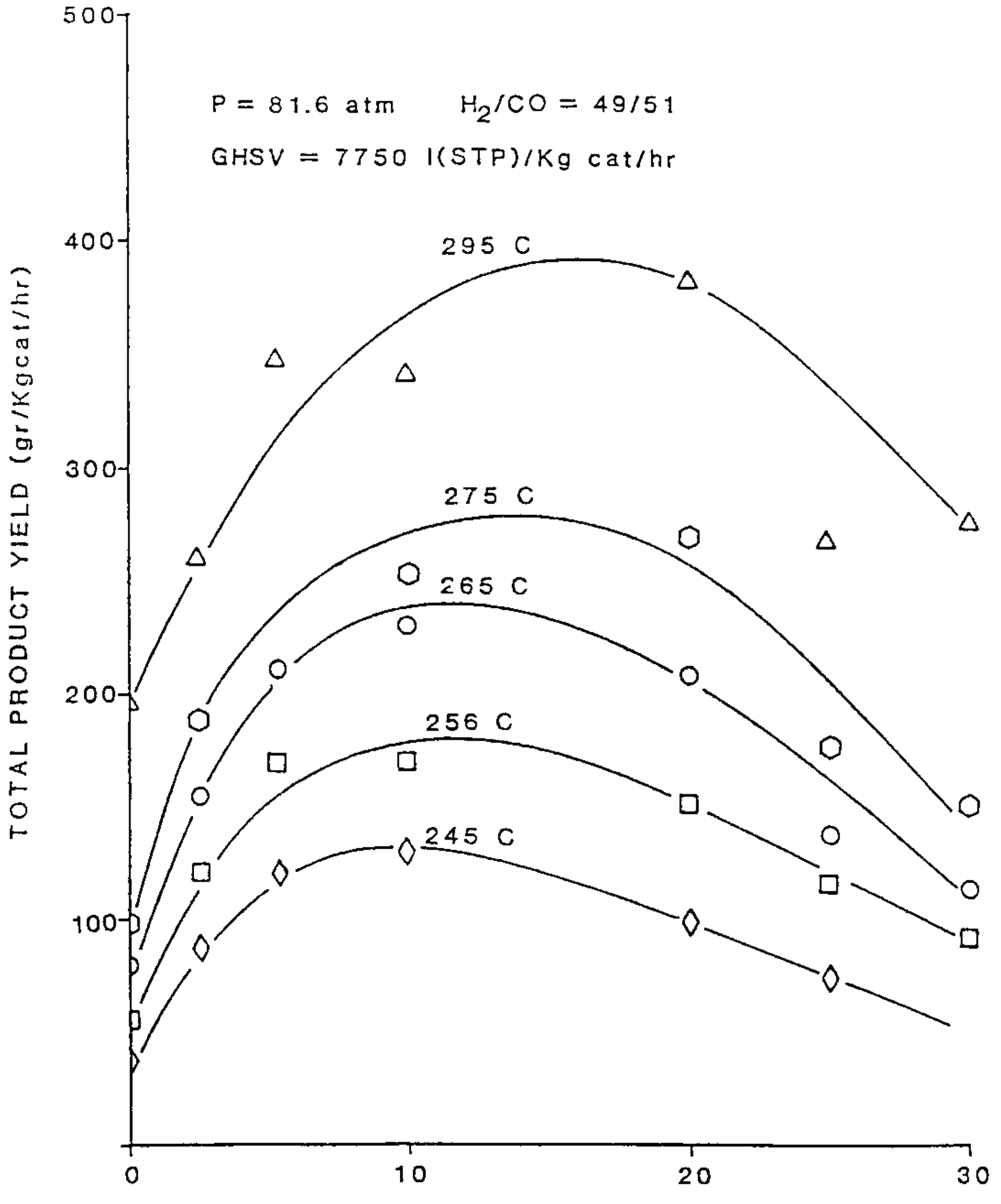


Figure 5-21b. **Effect of Cs Content of the MoS_2 Catalysts on the Total Product Yield as a Function of Temperature**



side-product hydrocarbon makes still appears too high (cf. Table 5-6, Column 4).

D. The Lurgi OCTAMIX Process

In contrast to the SEHT (MAS) Process that utilizes alkali-modified high-pressure methanol synthesis catalysts, the Lurgi OCTAMIX Process utilizes copper-based low-pressure methanol synthesis catalysts. The Lurgi catalysts are engineered (1) to reach a long service life of the copper catalyst under the higher-alcohol synthesis conditions that are more severe (higher temperatures, lower H_2/CO ratios) than methanol synthesis conditions, (2) to adjust the water gas equilibrium in such a way that the water which inevitably occurs in higher-alcohol synthesis is used up for the conversion of CO to CO_2 and hydrogen, and (3) to achieve satisfactory space time yield for the higher-alcohol mix (119).

The flow sheet for the Lurgi process is shown in Figure 5-22. The OCTAMIX process operates at 6-9 MPa, 285-300°C, and GHSV 3000-6000 with H_2/CO ratios of 0.5-1 and 1 percent CO_2. The catalyst stability over 8000 hours has been reported (101) based on the operation of a 3,650-tons/year pilot plant in Frankfurt, Germany. A 73,000-tons/year plant is planned adjacent to a refinery, possibly also combined with ammonia synthesis. Operating characteristics and space time yields are listed in Table 5-6 Column 4, and the typical composition of the OCTAMIX fuel in Table 5-11.

The properties of OCTAMIX as gasoline blends were established for three types of gasolines of different origins -- a cat cracker type, a reformate gasoline, and a mix containing a significant portion of petrochemical products. The density and the blending density of OCTAMIX are presented in Table 5-12, showing that the density of the gasoline plus oxygenate fuel mix is only about 0.5-0.7 percent higher than of the gasoline above. The boiling behavior and the Reid vapor pressure of OCTAMIX are superior to those of methanol/gasoline mixtures, and are comparable with those of the methanol/TBA blend (OXINOL), a property that is also applicable to the SEHT (MAS) product. The tolerance of various

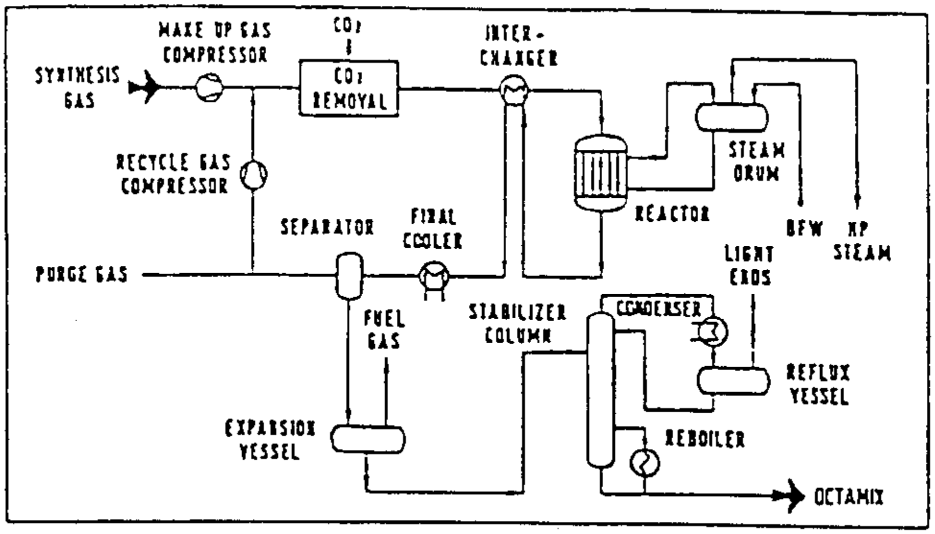


Figure 5-22. Flowsheet for the OCTAMIX Synthesis

Table 5-11. OCTAMIX Compositions

Compositions in Wt %

		OCTAMIX 40A			OCTAMIX 40B			OCTAMIX 50	
	Total	Alcohols	Esters Ketones	Total	Alcohols	Esters Ketones	Total	Alcohols	Esters Ketones
C_1 - Oxygenate	59.7	59.7	-	59.6	59.6	-	49.8	49.8	-
C_2 - Oxygenate	7.4	7.4	-	15.1	15.1	-	9.3	9.3	-
C_3 - Oxygenate	3.7	3.7	-	6.0	6.0	-	4.7	4.7	-
C_4 - Oxygenate	8.3	8.2	0.1	6.6	6.6	-	10.3	10.2	0.1
C_5 - Oxygenate	5.1	3.6	1.5	3.8	3.2	0.6	6.4	4.5	1.9
C_6 - Oxygenate	7.7	3.3	4.4	4.1	2.8	1.3	9.6	4.1	5.5
C_7 - Oxygenate	4.9	3.0	1.9	3.1	1.8	1.3	6.1	3.7	2.4
C_8 - Oxygenate	2.8	0.5	2.3	1.2	0.3	0.9	3.4	0.6	2.8
Hydrocarbons	0.1	-	-	0.1	-	-	0.1	-	-
Water	0.3	-	-	0.4	-	-	0.3	-	-
	100.0	89.4	10.2	100.0	95.4	4.1	100.0	86.9	12.7
H_2/CO Syngas		1.0			1.0			0.95	
P reaction, bar		70.0			70.0			100.0	
T reaction, °C		270.0			270.0			275.0	
Recycle C_1+ Light Ends		-			0.3			-	

Table 5-12. Blending Densities of OCTAMIX

Density at 15°C

	Pure Component	Blending Density
OCTAMIX 40 A	0.8078	0.8253
OCTAMIX 40 B	0.8055	0.8242
METHANOL 60% } HA 40% }	0.793	0.8087

gasoline/alcohol blends to water was investigated, with the result that the high-olefin gasolines such as the cat cracker gasoline are much less tolerant to water than the reformate type with its low olefin and high aromatics content. The materials compatibility of the OCTAMIX/gasoline blends poses no problem, as at least in Europe it has been common practice for some years to use methanol-resistant plastics in all new cars (119).

E. The Lehigh University HAS

Lehigh University (LU) engaged in higher-alcohol synthesis (HAS) on copper-based catalysts since 1982 (105-120). Although research has not been done on a pilot-plant scale, the data obtained are believed to be directly applicable for scale-up. The selection of the alkali component of the copper-based low-pressure methanol catalysts has been addressed systematically. The catalysts have been optimized, and activity and selectivity tests conducted in a wide range of conditions. An engineering model based on mechanistic input has been developed, and long-term tests performed in which the deactivation of the catalysts by carbonyls, the retention of the alkali component, and the physical changes have been established for continuous periods of operation up to 1250 hours.

The tubular stainless steel reactor of 1.9 cm diameter was provided with an outer brass sleeve to minimize longitudinal exotherms. Both the reactor and the inlet SG lines were alternatively equipped with a variety of purification devices and materials such as guard beds, charcoal traps, zeolite traps, copper lining, brass fittings, and aluminum containers. The engineering model was developed for both the differential and integral operation of the reactor, which can be viewed as an element of the Lurgi multi-tubular reactor. In the mechanistic studies that provided the basis for the engineering model, additional liquids--primarily methanol and other alcohols -- were injected into the SG at variable rates by a liquid metering pump. The schematic of this experimental system is shown in Figure 5-23.

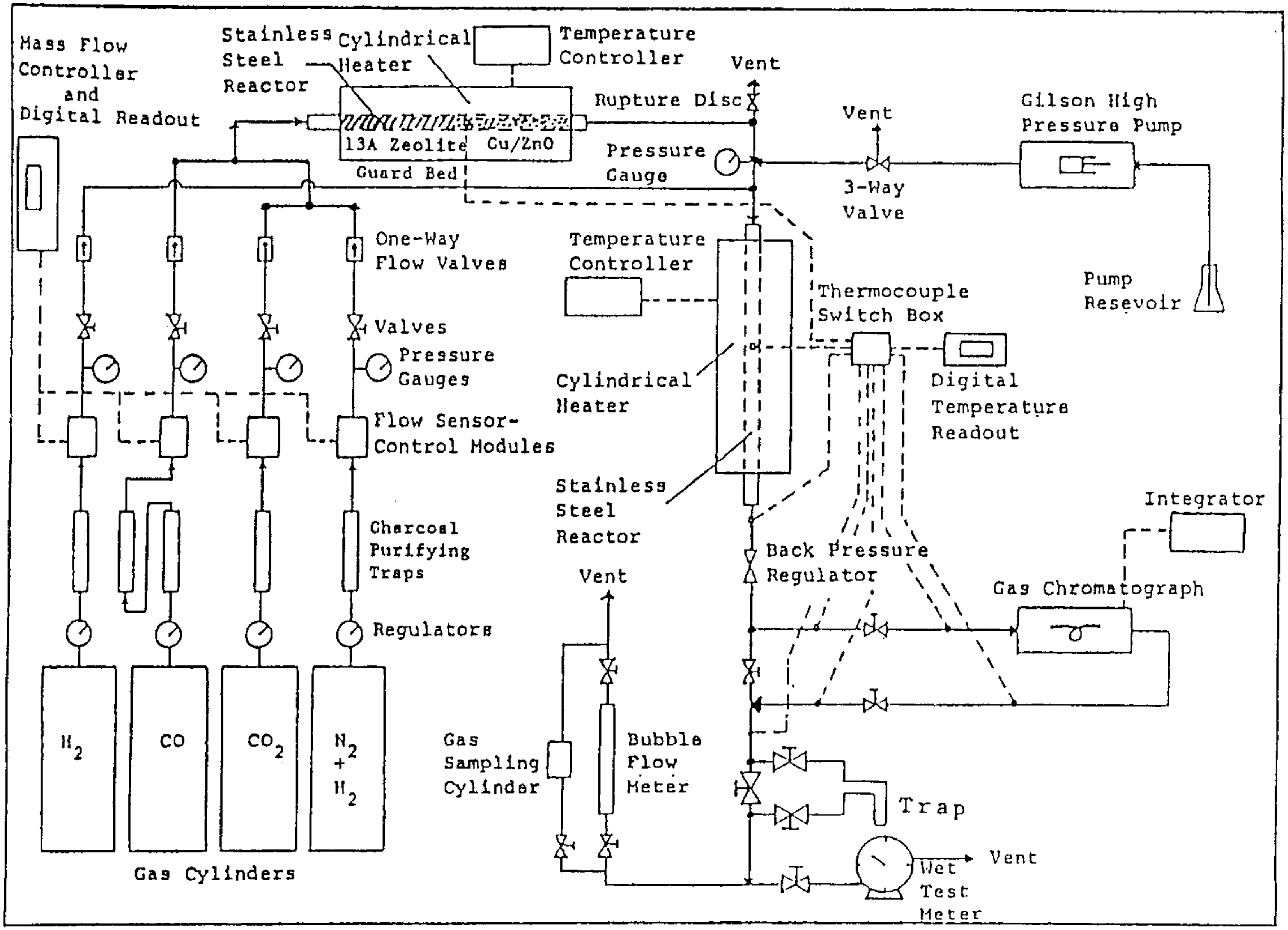


Figure 5-23. Schematic of the Catalytic Testing System

The heavy alkali-doped copper-based catalysts are also excellent water gas shift catalysts (73), and the LU HAS system produced a low water content similarly as the Lurgi OCTAMIX process. The LU HAS was run at 7.6-9.1 MPa, 260-325°C, and GHSV 3000-10,000 with H_2/CO ratios of 0.45-0.7. The synthesis gas contained no CO_2 in the feed, but CO_2 was a product of HAS. The operating characteristics and the space time yields are listed in Table 5-6, Column 5. A more detailed account of initial activities and selectivities for various Cs/Cu/ZnO, $Cs/Cu/ZnO/Al_2O_3$, and $Cs/Cu/ZnO/Cr_2O_3$ catalysts is given in Table 5-13. The effect of the different cesium promoter loading of the binary Cu/ZnO catalyst on the selectivity for higher (C_2+) oxygenate synthesis shown in Table 5-15 demonstrates that (1) the alkali dopant enhances both the total yield and particularly dramatically the selectivity to C_2+ oxygenates, and (2) there is an optimum concentration of the alkali promoter (0.34 percent Cs for the binary Cu/ZnO catalyst) for the maximum yield of alcohols and maximum selectivity for C_2+ oxygenates.

It is also apparent from Table 5-14 that among the supported $Cs/Cu/ZnO/M_2O_3$ (M = Al, Cr) the Al_2O_3-supported catalyst gives high yield of alcohols but poor selectivity to C_2+ oxygenates. The Cr_2O_3-supported catalyst gives both high yields and high selectivities for C_2+ oxygenates. Therefore, Cr_2O_3 is a support of choice, at least with the class of hydrotalcite-based precursors employed in the LU work. Under the methanol synthesis conditions (250°C, 7.6 MPa, $H_2/CO = 2.33$, GHSV = 10,000), the 3-percent $Cs/Cu/ZnO/Cr_2O_3$ catalyst gave a space time yield of 1.05 kg of methanol/kg catalyst/hour with 98 percent selectivity, the only side products being ethanol (1.3 percent) and methyl formate (0.6 percent) (105). These are the highest STY's and selectivities reported for methanol synthesis from CO_2-free synthesis gas.

A kinetic model was developed for the LU HAS based on the chain growth mechanism described in Section 5.3.2.6. The chain growth reactions are schematically shown in Figure 5-24 where 1, b_1, and a_o are kinetic constants for linear growth (1) and beta-addition (b_1), $C_n + C_1$

Table 5-13. **Operating Characteristics for Cs-doped Copper-Based Catalytic Processes Obtained at Lehigh University**

Syngas Content of CO_2 was zero. Initial Activities.

Main Characteristics			LU HAS	Catalyst No.		
Main Constituents of Catalyst	Cu/ZnO	0.34 percent Cs/Cu/ZnO	2.5% Cs/Cu/ZnO/ Al_2O_3	0.4% Cs/Cu/ZnO	0.25% Cs/Cu/ZnO	3% Cs/Cu/ZnO/ Cr_2O_3
Operating Temperature, °C	310	310	310	300	300	300
Operating Pressure, MPa	7.6	7.6	7.6	9.1	9.1	9.1
Syngas Space Velocity, 1000 h^{-1}						
Syngas Feed (H_2/CO) Ratio	0.45/1	0.45/1	0.45/1	0.7/1	0.7/1	0.7/1
Performance Characteristics						
Thermal Efficiency, %	~60	~60	~60	~60	~60	~60
CO Conversion Per Pass, %						
Liquid Product Selectivity, %	94.7	97.4	97.0	~96.0	n.a.	n.a.
(C_2+OH) Selectivity, %	30	58	5.6	26-27	25-30	~35
Alcohol Productivity, kg/kg cat/h	0.314	0.440	0.542	0.373-0.436	0.439	0.458

A detailed typical composition of the LU HAS product is given in Table 5-14.

Table 5-14. Comparison of Product Compositions

Comparison of the product compositions obtained from H_2/CO = 0.45 synthesis gas at 310°C, 7.6 MPa, and GHSV = 3260 l(STP)/kg cat/hr over binary Cu/ZnO and 0.34 mol% Cs/Cu/ZnO catalysts.

Product Type	Product	Yield, g/kg cat/hr	
		Undoped Cu/Zno	0.34 mol% Cs/Cu/ZnO
Hydrocarbons Water & CO_2	Methane	3.4	7.6
	Ethane	11.3	4.7
	Propane	2.1	1.1
	Water	1.3	1.7
	CO_2	367.0	403.0
Linear Primary and Secondary Alcohols	Methanol	204.0	157.0
	Ethanol	22.6	17.0
	1-Propanol	10.1	38.1
	1-Butanol	3.4	8.2
	2-Butanol	0.7	1.8
	1-Pentanol	0.9	4.7
	2-Pentanol & 3-Pentanol	0.8	3.0
	1-Hexanol	2.0	5.5
Branched Primary and Secondary Alcohols	2-Methyl-1-Propanol	20.7	48.6
	2-Methyl-1-Butanol	8.6	15.5
	3-Methyl-2-Butanol	1.7	1.7
	2-Methyl-1-Pentanol	5.1	12.4
	2-Methyl-3-Pentanol	2.0	4.1
Aldehydes	Propanol	-	1.6
	2-Methylpropanol	0.7	1.9
Ketones	2-Butanone	0.7	2.1
	3-Pentanone	-	2.3
	2-Methyl-3-Pentanone	3.0	5.4
Methyl Esters	Methyl Formate	3.6	2.4
	Methyl Acetate	10.5	9.9
	Methyl Propanoate	4.6	14.0
	Methyl Butanoate	1.0	2.7
	Methyl Isobutanoate	4.1	13.7
	Methyl Pentanoate	1.2	1.6
	Propyl Acetate	2.0	1.4

Table 5-15. Effect of Cesium Loading of Catalyst on Selectivity

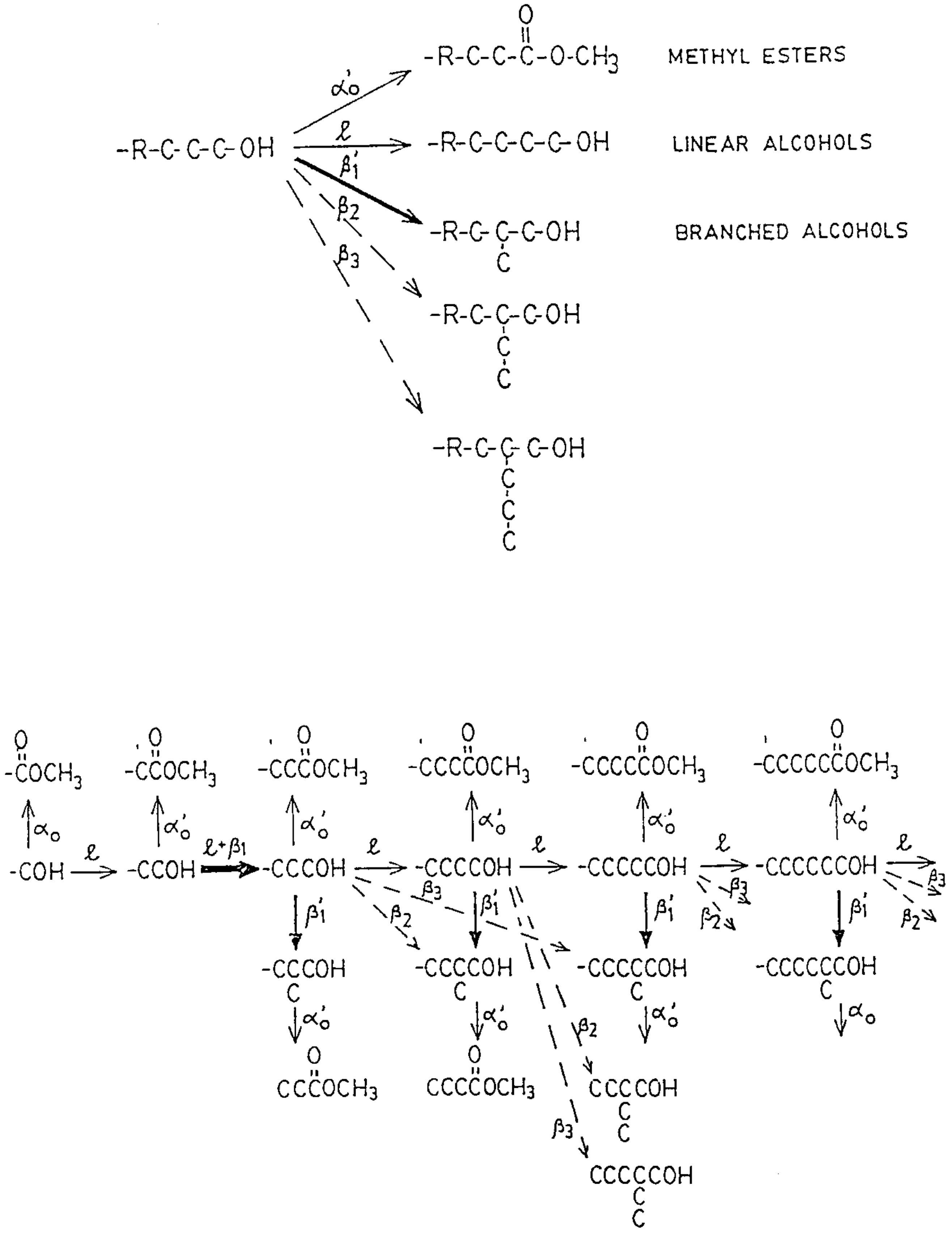
Effect of Cesium Loading of the Binary Cu/ZnO catalyst on the Selectivity (S) for Higher-Oxygenate Synthesis, where S is defined as

$$\frac{>C_1 \text{ Oxygenates}}{\text{Methanol} + (>C_1 \text{ Oxygenates})} \times 100$$

in wt%.

Catalyst	Product Yield, g/kg cat/hr		S, Wt.%
	Methanol	$>C_1$ Oxygenates	
Undoped Cu/ZnO	204	110	35.0
0.25 mol% Cs/Cu/ZnO	181	165	47.7
0.34 mol% Cs/Cu/ZnO	157	220	58.4
0.43 mol% Cs/Cu/ZnO	162	137	45.8
1.5 mol% Cs/Cu/ZnO	213	42.8	16.7

Figure 5-24. Chain Growth Reactions



-> C_n+1 and a_o that for methyl ester formation from C_n chains; b_n are kinetic constants for minor paths in which a C_m ($m = 2,3$) intermediate is added to a C_n ($n \geq 2$) growing chain. The model for the integral reactor is schematically represented in Figure 5-25 where k stands for the set of kinetic parameters 1, b_1, etc., and C_j/C_1 are the ratios of the concentration of products of chain length j to that of methanol. An example comparing the observed and predicted product yields with an optimized set of the parameters k for one set of HAS conditions is shown in Figure 5-26. An overall correlation of calculated and observed HAS product yields over the Cs/Cu/ZnO and Cs/Cu/ZnO/Cr_2O_3 catalysts with variable Cs concentrations is shown in Figure 5-27, demonstrating that the model is successful for large numbers of catalysts.

The catalyst life data were also reported for the LU HAS (<u>105</u>). All the Cu-based catalysts rapidly deactivated in stainless steel units, primarily due to iron carbonyl poisoning. However, deactivation rates as low as 1.8 percent/100 hours in terms of loss of CO conversion activity were achieved in copper-lined reactors, pipes and fittings utilizing a well-purified SG under the severe HAS conditions of 300°C, 9.1 MPa, and $H_2/CO/CO_2 = 0.7/1.0/0.0$. There was a larger loss of selectivity to C_2+ alcohols (but not to total alcohols) during the life tests, most of which could still be traced to residual iron deposits that give rise to the growth of hydrocarbon residues on the catalyst surface. A minor deactivation was due to physical deactivation of the catalyst by sintering. The alkali promoter, Cs, was not lost or redistributed in the reactor bed in tests up to 1250 hours.

Comparison of the LU HAS product (Table 5-14) with the Lurgi OCTAMIX product (Table 5-11) shows a similar composition in that methanol and 2-methyl-1-propanol (iso-butanol) are the dominant alcohols. It is therefore expected that the February 1988 EPA waiver will apply equally to the (refined) LU HAS and the OCTAMIX blends, and the characteristics of these two products will be similar. The differences between LU HAS and the Lurgi OCTAMIX processes are in the catalyst formulation and

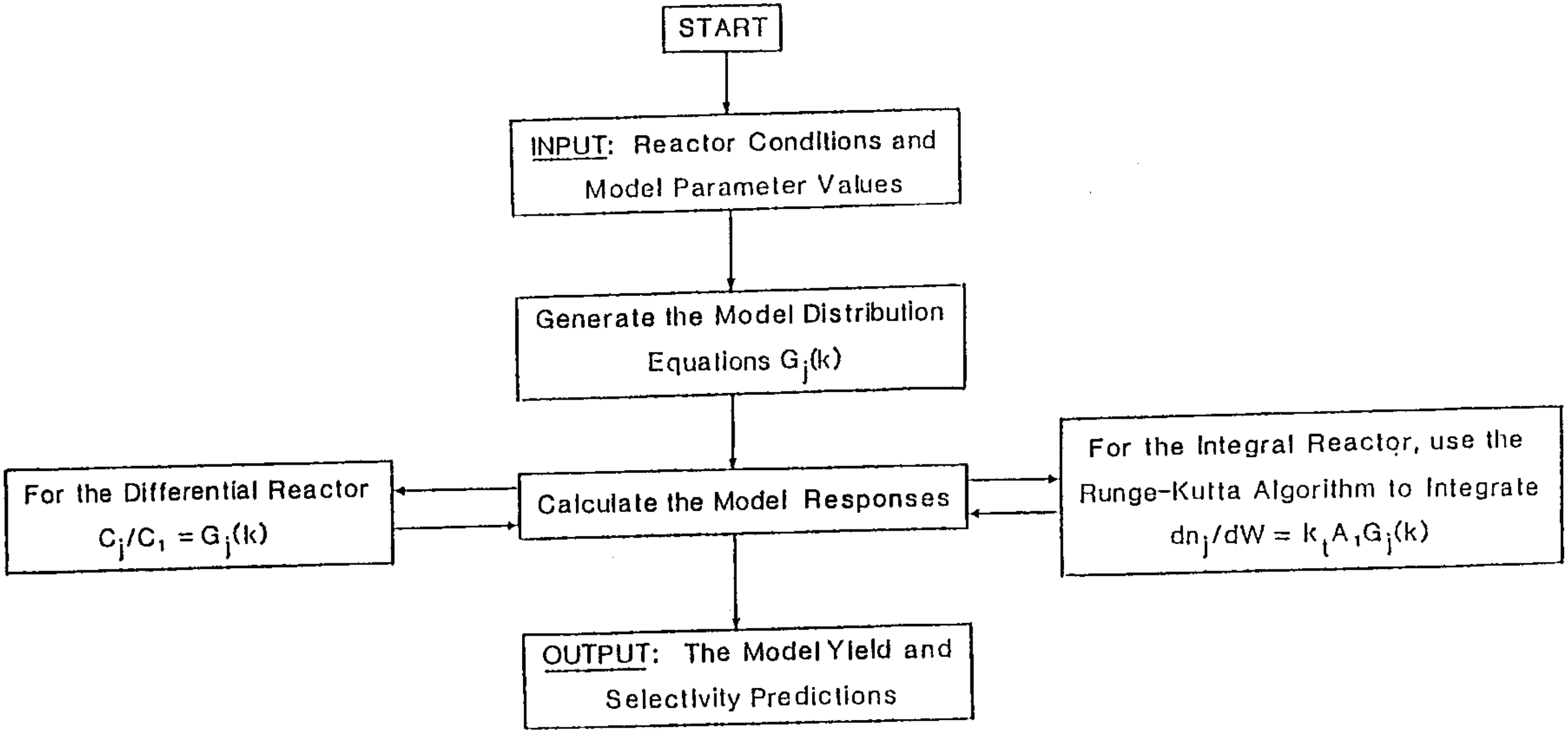


Figure 5-25. Integral, Isothermal, Plug-Flow, Fixed-Bed Kinetic Model

Figure 5-26. **Measured and Predicted Product Yields**

Measured product yields*for a 0.4 mol% CsOOCH promoted Cu/ZnO catalyst at 583K, 9.1 MPa, H_2/CO = 0.45, and GHSV = 3265 ℓ(STP)/kg cat/hr compared with the predicted oxygenate yields based upon a reaction network to be presented in the next section of this report. The estimated kinetic parameters are $\ell = 0.254$, $\beta_1 = 3.299$, $\beta_2 = 0.121$, $\beta_3 = 0.152$, and $\alpha_o' = 0.221$.

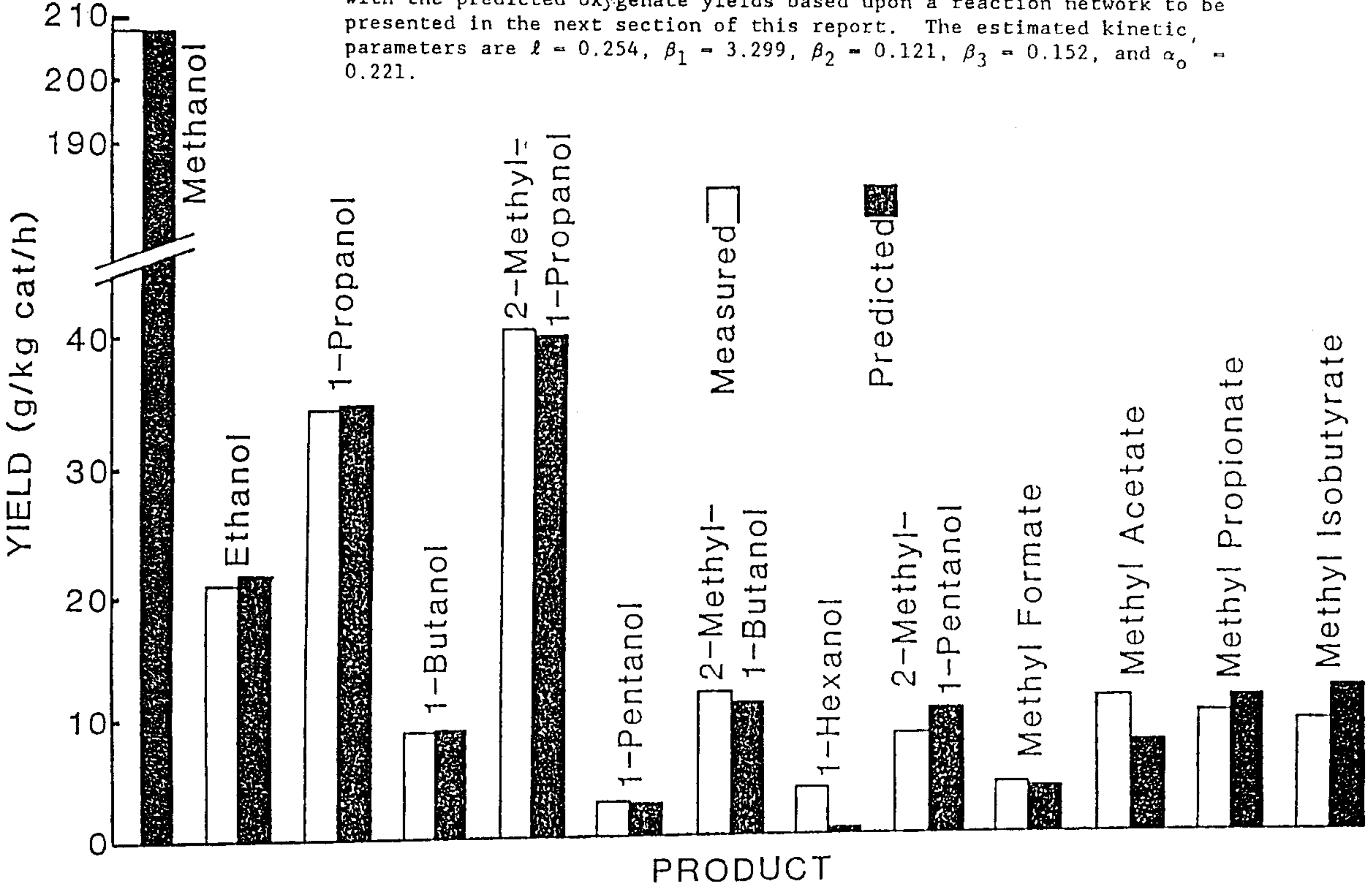
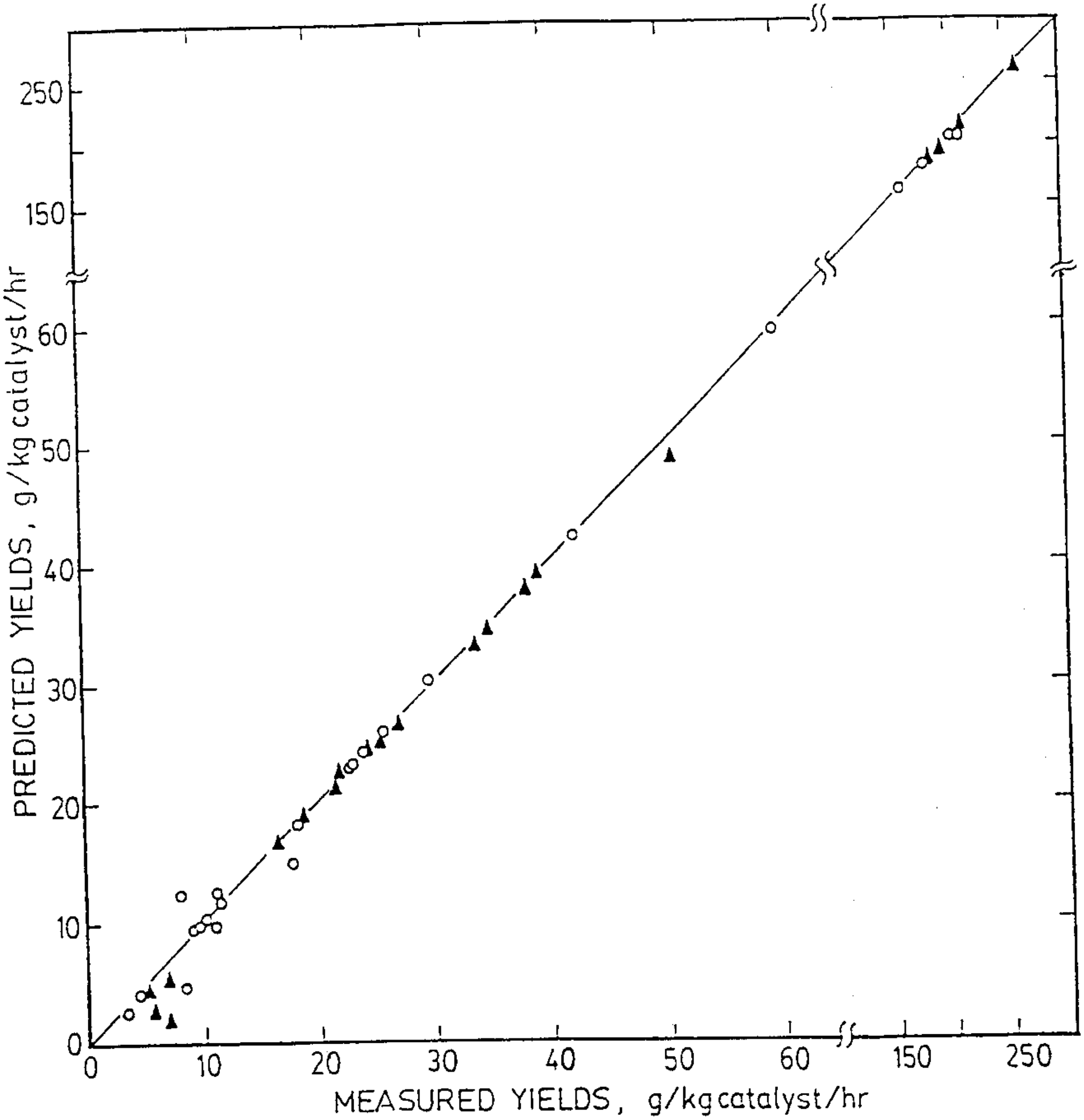


Figure 5-27. Comparison of Measured and Predicted Yields



Comparison of the measured* and predicted yields of the individual oxygenate components for the Cs/Cu/ZnO (o) and Cs/Cu/ZnO/Cr_2O_3 (▲) catalysts, with Cs concentrations in the range 0-1.5 mol% and 0-5 mol%, respectively. The predicted oxygenate yields are based on the kinetic model.
The yields were measured at 583K, 7.6 MPa, $H_2/CO = 0.45$ and GHSV = 3265 L(STP)/kg catalyst/hr and 5330 L(STP)/kg catalyst/hr for the Cs/Cu/ZnO and Cs/Cu/ZnO/Cr_2O_3, respectively.

possibly composition, as well as in selectivities under given conditions to C_2+ oxygenates.

5.3.2.3 General Remarks on Higher-Alcohol Technology and Its Economics

The most recent evaluation of the HAS technology and its economics by MITRE Corporation (101) arrived at the following conclusions:

- The 1988 price of methanol is $0.72/gal, of OCTAMIX estimated at $0.89-0.90/gal (approximately 25 percent higher than methanol) and of MTBE $1.01/gal (approximately 40 percent higher than methanol).
- There is a market for 46 million barrels per year of oxygenated octane-enhancing fuel-blending compounds; currently this market is split about 50:50 between ethanol and MTBE, with MTBE rising.
- The use of MTBE is projected to reach a limit because of a limited capacity for the source isobutene, which is mostly obtained from petroleum, and a higher production cost due to a two-stage process less efficient than the direct synthesis of higher alcohols.
- Isobutanol (2-methyl-1-propanol) is a better cosolvent than ethanol, and acceptable blending characteristics are obtained with isobutanol/methanol mixtures but not with pure methanol.

The final version of the MITRE report (101) will be published sometime in Fall 1988, and therefore the above statements are tentative as of the writing of the present report.

5.3.2.4 Chemistry and Mechanisms of Higher-Alcohol Synthesis

The mechanisms of methanol synthesis were discussed in Section 5.3.1. Although chemical mechanisms, particularly those of catalyzed reactions, are often difficult to resolve, much progress has been made in the understanding of C_2+ oxygenate syntheses. The various early hypotheses as well as current views are summarized herein, and the contrasting catalytic functions that result in the synthesis of ethanol-rich or isobutanol-rich C_2+ oxygenates are emphasized.

The first step in higher-alcohol synthesis over metal oxide catalysts involves the formation of a carbon-carbon bond. The first hypothesis of a mechanism for this process was advanced by Fischer (121) who suggested that higher alcohols are formed from methanol and carbon monoxide, as depicted by Equations [1] and [18-20].

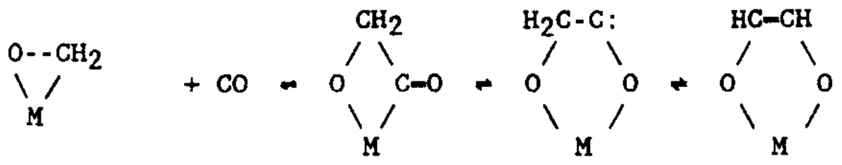
$$CO + 2H_2 \rightarrow CH_3OH \qquad [1]$$

$$CH_3OH + CO \rightarrow CH_3COOH \qquad [18]$$

$$CH_3COOH + H_2 \rightarrow CH_3CHO + H_2O \qquad [19]$$

$$CH_3CHO + H_2 \rightarrow CH_3CH_2OH \qquad [20]$$

This reaction sequence would involve CO insertion into the OH bond of methanol to form the C-C bond, followed by sequential hydrogenation. A similar homologation of methanol by CO/H_2 has been proposed by Natta et al. (99) and Vedage et al. (70). More recently, it has been proposed (122) that the homologation of methanol by CO proceeds via a symmetric intermediate, as shown by Equation [21].



[21]

In contrast, Frolich and Cryder (123) and Morgan (124) concluded that the synthesis of higher alcohols occurs predominantly by condensation of lower alcohols. Using the Frolich and Cryder proposal that the controlling reaction in the synthesis of higher alcohols was the condensation of two methanol molecules to produce ethanol via dehydration and elimination of water (Equation [22]), Graves (125) was

$$2CH_3OH \rightarrow CH_3CH_2OH + H_2O \qquad [22]$$

able to qualitatively predict the presence or absence of certain higher alcohols when simple rules for addition were involved. Because of the observations of Brown and Galloway (126) that appreciable yields of dimethylether were formed during methanol synthesis over ZnO/Cr_2O_3 catalysts, a two-step dehydration mechanism involving dimethyl ether as an intermediate (Equations [23] and [24]) was considered, but this was discounted because the "information was insufficient to warrant any definite conclusion" (97).

$$2CH_3OH \rightleftharpoons (CH_3)_2O + H_2O \quad [23]$$

$$(CH_3)_2O \rightleftharpoons CH_3CH_2OH \quad [24]$$

An aldehyde condensation mechanism [25]

$$2HCHO \rightarrow CH_2OH \cdot CHO \xrightarrow{H_2} CH_3CHO + H_2O \quad [25]$$

has been invoked by Fox et al. (127) for non-catalytic alcohol synthesis over alkali acetylides, where the formaldehyde molecules are derived from methanol. The latter mechanism is reminiscent of the first steps of homogeneous base-catalyzed formose chemistry (128).

The proposed mechanisms for C-C bond formation that yield C_2-C_5 alcohols can be classified as

- CO insertion into a methyl-metal bond or into the C-O bond of methoxide,
- CO homologation of methanol via a symmetric intermediate, and
- Coupling of aldehydic or alcoholic species.

These three mechanistic pathways were recently distinquished by ^{13}C-NMR analysis of the products formed when small amounts of $^{13}CH_3OH$ or $CH_3{}^{13}CH_2OH$ were injected into the H_2/CO synthesis gas feed over Cu/ZnO and Cs/Cu/ZnO catalysts (129) and over Cs/MoS_2 and $K/CoS/MoS_2$ catalysts (90). The results of these ^{13}C-labeling studies will be summarized, and it will be shown that higher alcohols are formed over the alkali/MoS_2 catalysts by a different mechanism than the way they are formed over the Cs/Cu/ZnO catalysts.

Over the alkali-promoted copper-based catalysts, the C_2+ oxygenates are favored by low H_2/CO (1.0-0.5) ratios and high temperatures (>550°K (277°C)) (70, 105). The main products aside from methanol are ethanol, 1- propanol, and 2-methyl-1-propanol, and the alkali dopants enhance the rates of the chain growth. Over the alkali/MoS_2 catalysts C_2+ oxygenate synthesis has been demonstrated (90, 103, 104) at $H_2/CO = 1$ and temperatures of 523-603°K (250-330°C) to yield mainly C_2+ linear alcohols, and the presence of cobalt in the catalyst has been found to greatly enhance the methanol homologation C_1->C_2 (103, 118). Thus, there is a tendency for the alkali/Cu/ZnO catalysts to produce branched alcohols and for the alkali/MoS_2 catalysts to produce linear alcohols, and it will become clear that this is a reflection of the different dominant mechanisms for C-C bond formation that are occurring over these catalysts.

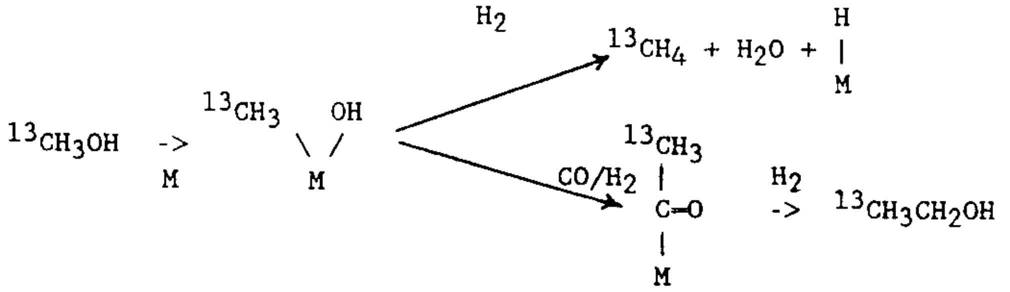
A. C_1->C_2

Injection of $^{13}CH_3OH$ yields C-2 labeling of ethanol over the Cs/MoS_2 and alkali/Co/MoS_2 catalysts (90), as represented by Equation [26].

$$^{13}CH_3OH + {}^{12}CO/H_2 \xrightarrow[\text{alkali/(Co)/MoS}_2]{} {}^{13}CH_3{}^{12}CH_2OH \qquad [26]$$

This outcome [26] indicates a CO insertion into the CH_3-O bond for linear alcohol growth over the MoS_2 catalysts. This path is enhanced by the presence of cobalt and accounts for the dominance of linear alcohols over alkali/MoS_2 catalysts.

Further support for the CO insertion mechanism over these catalysts is provided by the observation that methane produced as a side-product was also labeled by the ^{13}C. This side-reaction can be represented by Equation [27].



[27]

Injection of $^{13}CH_3OH$ into the $^{12}CO/H_2$ synthesis gas stream yields doubly labeled ethanol over the Cu/ZnO and Cs/Cu/ZnO catalysts (129)

$$^{13}CH_3OH + CO/H_2 \xrightarrow[(Cs)/Cu/ZnO]{} {}^{13}CH_3{}^{13}CH_2OH\ (+\ CO/H_2) \qquad [28]$$

This was interpreted as the C_1->C_2 step occurring by coupling of two C_1 aldehydic species by a mechanism similar to that proposed by Fox et al. (127). This outcome [28] rules out any ^{12}CO insertion mechanism such as several previously proposed (70,99,121,122) and is opposite to that [26] observed over the alkali/MoS_2 catalysts.

B. C_2->C_3

Injection of $CH_3{}^{13}CH_2OH$ over the Cu-based catalysts or growth of $^{13}CH_3{}^{12}CH_2OH$ over the alkali/MoS_2 catalysts yields different isotopic 1-propanols over the two types of catalysts.

Over alkali/MoS_2 and alkali/Co/MoS_2 catalysts, the C_2->C_3 step occurs by the same type of linear growth via CO insertion as in the C_1->C_2 step, as evidenced by the isotope reaction

$$^{13}CH_3CH_2OH + {}^{12}CO/H_2 \xrightarrow[\text{alkali/(Co)/MoS}_2]{} {}^{13}CH_3CH_2{}^{12}CH_2OH \qquad [29]$$

Over Cs/Cu/ZnO catalysts at high temperatures, path [30] occurs selectively (<u>129</u>)

$$CH_3{}^{13}CH_2OH + CO/H_2 \xrightarrow[Cs/Cu/ZnO]{} {}^{13}CH_3CH_2CH_2OH \qquad [30]$$

Result [30] is consistent with aldol-type β-addition with oxygen retention reversal, as shown in reaction sequence [31].

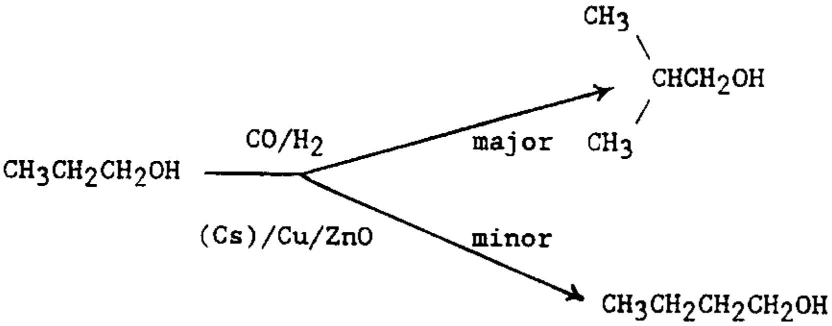
$$\begin{array}{l}
CH_3{}^{13}CH_2OH \underset{H_2}{\overset{-H_2}{\rightleftharpoons}} CH_3{}^{13}CHO \underset{H^{\ominus}}{\overset{-H^{\ominus}}{\rightleftharpoons}} {}^{\ominus}CH_2{}^{13}CHO \quad \text{(enolate or carbanion)} \\
{}^{\ominus}CH_2{}^{13}CHO + H_2CO \underset{\beta\text{-addition}}{\;->\;} [{}^{\ominus}OCH_2CH_2{}^{13}CHO] \;->\; {}^{\ominus}OCH_2CH_2{}^{13}CH_3 \\
\hspace{24em} H^{\ominus}\downarrow \\
\hspace{23em} HOCH_2CH_2{}^{13}CH_3
\end{array} \qquad [31]$$

The retention of the anionic oxygen in the $[{}^{\ominus}OCH_2CH_2{}^{13}CHO]$ intermediate is specific to the Cs promoter that prevents the dehydration of the alcoholate oxygen and favors hydrogenation of the free ${}^{13}CHO$ group. Such a path constitutes a reversal of the normal aldol synthesis pattern in which $CH_3CH_2{}^{13}CH_2OH$ propanol would be formed in the presence of hydrogen.

C. <u>C_3->C_4</u>

Over the alkali/MoS_2 and alkali/Co/MoS_2 catalysts, the C_3->C_4 growth step occurs mainly by linear CO insertion, giving rise to the dominance of 1-butanol in the C_4 product (<u>90</u>), and the ${}^{13}C$ label in ${}^{13}CH_3CH_2CH_2OH$ is found in the C-4 carbon of 1-butanol.

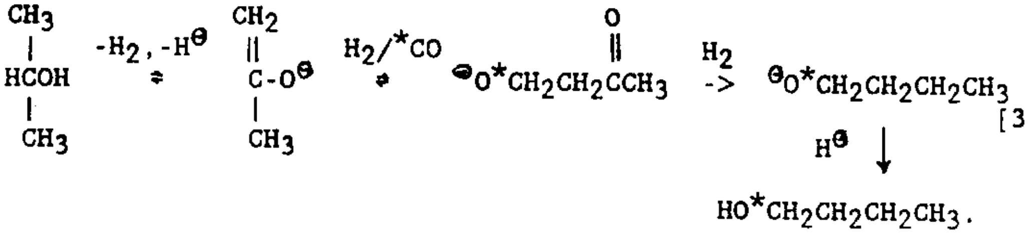
Over the Cu/ZnO and Cs/Cu/ZnO catalysts, injection of 1-propanol yields dominantly 2-methyl-1-propanol (with 1-butanol as a minor product), and the Cs promoter enhances the rate of the β-branching (72),



$$CH_3CH_2CH_2OH \xrightarrow[(Cs)/Cu/ZnO]{CO/H_2} \begin{cases} (CH_3)_2CHCH_2OH & \text{major} \\ CH_3CH_2CH_2CH_2OH & \text{minor} \end{cases}$$

[32]

The dominant β-addition to form 2-methyl-1-propanol occurs via a mechanistic path analogous to [31] as indicated by the ^{13}C isotope experiments of Nunan et al. (129). This aldol path with oxygen retention reversal is further corroborated by the outcome of 2-propanol injection into the synthesis gas (92) that resulted in the dominance of 1-butanol in the C_4 product,



$$CH_3CH(OH)CH_3 \xrightarrow{-H_2,\,-H^{\ominus}} CH_2{=}C(O^{\ominus})CH_3 \xrightarrow{H_2/{}^*CO} {}^{\ominus}O^*CH_2CH_2C(=O)CH_3 \xrightarrow{H_2} {}^{\ominus}O^*CH_2CH_2CH_2CH_3 \xrightarrow{H^{\ominus}} HO^*CH_2CH_2CH_2CH_3.$$

[33]

D. $\underline{C_4\text{->}C_5\pm}$

The patterns of steps C_1->C_4 continue over the different catalysts as shown above with the exception that 2-methyl-1-propanol does not give rise to any C_5 products over the copper-based catalysts. This is a known feature of β-addition not occurring at branched carbons in aldol synthesis. The α-addition of the type [25] between a branched C_4 and a C_1 aldehydic intermediate also appears to be forbidden, perhaps for steric as well as for electronic reasons. The high rate of β-addition at C_3 and the termination of the synthesis at the branched C_4 alcohol are the major factors determining the high selectivity for 2-methyl-1-propanol.

5.3.2.5 Other Catalytic Systems for Higher Alcohols

The activities and selectivities of copper-based catalysts were summarized in the review of methanol technology in Section 5.3.1.1 and in Section 5.3.2.2 in the summary of the IFP, Lurgi OCTAMIX, and LU HAS processes. In addition, a large number of Group VIII metal-based catalysts for C_1-C_5 alcohols has been investigated. In the 9th International Congress on Catalysis, a total of 21 reports dealt with Rh-based (8 papers) and Fe-, Co-, Ni- and Ru-based mixed catalysts (13 reports), primarily for methanol and ethanol mixtures. Several papers also reported on reactions of synthesis gas (SG) with olefins, methanol and amines, or initiated by acetylenes. The space time yields (STY's), selectivities, and reaction conditions are summarized in Table 5-16.

The impetus for research utilizing the Rh-based catalysts can be traced to the discovery at Union Carbide of a good selectivity of Rh-Fe catalysts to ethanol (130) and to the early work of Ichikawa (131) in which effects of various supports on the selectivity of Rh catalysts, particularly for ethanol, have been disclosed. Among the newer reports, particle size effects have been discovered (132) and confirmed (133) such that very small Rh particles (dispersion ≥ 0.6) promote the SG conversion to ethanol while large particles drive the synthesis to hydrocarbons and acetic acid. Arakawa et al. (134) classify the promoters of rhodium-based catalysts to those that increase dispersion, decrease dispersion, and those that accelerate CO dissociation. The suggested effects on selectivity in oxygenate synthesis are schematically represented in Figure 5-28. The investigations of the group of Rh-based catalysts represented in Table 5-16 and references therein demonstrate that 80-90 percent selectivity to oxygenates can be achieved. The STY's attain in some cases respectable values, e.g., 0.55 kg oxygenates/kg catalyst/hour over the $Rh/Mo/Al_2O_3$ catalyst (133). Further increases in selectivity appear to result in lower STY's, however.

Following another Union Carbide discovery (150) that Pt, Pd and Ir supported on silica are very selective catalysts for methanol, attempts

Table 5-16. Activities and Selectivities to Oxygenates (C_1-C_5 Alcohols, Acetic Acid, Esters) of Catalysts Based on Group VIII Metals

Source: 9th ICC, July 1988.

General Conditions: 1 - 10 MPa, H_2/CO - 1-2, low CO conversions, GHSV 5000-13,600.

Catalyst	Selectivity to oxygenates %	T °C	STY[a] of oxygenates g/kg(l)cat/hour	Reference
Rh/Fe^{I}II/SiO$_2$	45	150	20[b]	135
Rh/Mo/Al$_2$O$_3$	66	250	555	136
Rh/Mn/Li/SiO$_2$	80[c]	260	136[d]	134
Rh/Ti/Fe/Ir/SiO$_2$	69[c]	260	341	134
Rh/Fe^{I}II/SiO$_2$	88[e]	272	115	137
Rh/ZrO$_2$/K,P,Y,Mo,Mn	<50	250	113	138
Rh/Mn/Fe/SiO$_2$	77	220	n.a.[f]	139
Rh/SiO$_2$	93->30[g]	280	3->41	133
Fe/Pt,Pt,Pd/SiO$_2$	100	150	24	135
Fe/Ir/SiO$_2$	84	272	144	137
Fe/Rh,Pd,Ir,Pt/SiO$_2$	52-87	272	<80	137
Fe/N[h]	16	150-300	n.a.	140
Co/Ir,Pt	68-93	272	<80	137
Co/Cu/MgO	95->15	225->300	99->15	141
Ni/Ir	70	272	<15	137
Ni/ZnO	85	300	159	142
Ni/Pt	93	272	<30	137
Ni/Mo/K/SiO$_2$	55	300	296	143
NiPd/Cu membrane	<50	n.a.	n.a.	144
Ni/Pt				137
Ru/HT[i]	22	275	n.a.	144
Fe/acetylene[j,k]	>50	110-130	n.a.	146
Co carbonyl[k]	oxo reaction	110-270	n.a.	147
Co[k]	MeOH incorporation	180-200	n.a.	148
Ru,RuRh[k,l]	amine synthesis	120-260	-	149
NaOCH$_3$[k]	carbonylation	70-110	-	142

Table 5-16 (continued)

[a] STY = Space Time Yield, given in g of oxygenated product per hour per kg of catalyst (including support) where available, otherwise per liter of catalyst.

[b] Estimated.

[c] Ethanol plus acetic acid >50 percent of oxygenated product.

[d] Estimated, assuming runs were over 1 g of catalyst.

[e] Mainly methanol.

[f] Purpose of experiment was surface ketene trapping.

[g] Purpose of experiment was to establish Rh particle size effect; the smallest particles give the highest selectivity to oxygenates.

[h] Nitrided iron catalyst.

[i] HT = Hydrotalcite $Mg_3Al(OH)_8(CO_3)_{0.5} \cdot 2H_2O$ basic support.

[j] Reaction of synthesis gas initiated by acetylenes over Fischer-Tropsch iron catalysts.

[k] Reactions of synthesis gas with acetylene, olefins, methanol and amines

[l] Aminomethylations with synthesis gas and ammonia or amines.

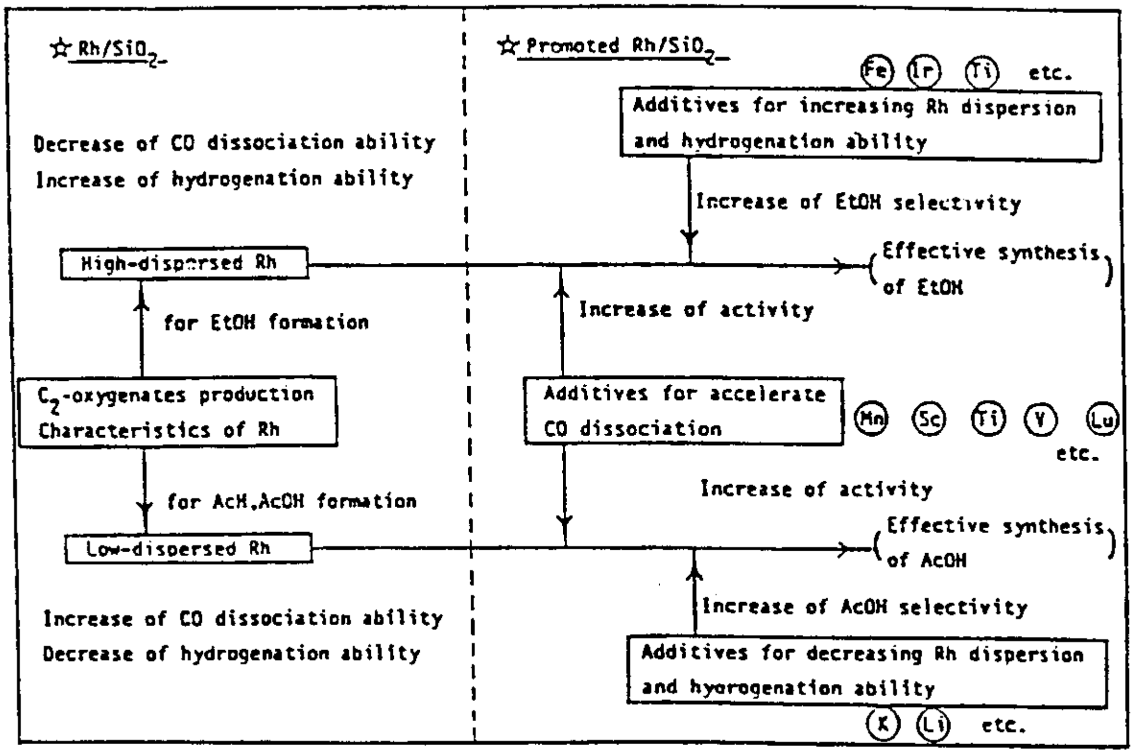


Figure 5-28. The Roles of Additives for Effective Synthesis of EtOH and AcOH

were made to improve their activity by adding a non-noble Group VIII metal such as Fe, Co, and Ni. The results are summarized in the second section of Table 5-16. In some cases high selectivities to oxygenates were attained at temperatures of 150-300°C, but both the maximum and the average STY's were lower than for the Rh-based catalysts.

More encouraging results were obtained when a non-noble Group VIII metal such as Fe, Co, and Ni was mixed with a component that is a known methanol synthesis catalyst such as ZnO, Cu, or Cu/ZnO (cf. Table 5-16, second section) but the selectivities to, and STY's of, oxygenates were significantly lower than in the systems described in Section 5.3.2.2.

In the third section of Table 5-16 are described some novel and improved processes for adding building blocks formed from SG to olefins (the oxo reaction), methanol (homologation and carbonylation), and amines (aminoalkylation). Included as well are SG polymerizations initiated by acetylenes at mild conditions wherein the group originating from the acetylene ends up as a terminal block of an oligomer formed by successive CO insertions. Although generalizations are premature, the results summarized in Table 5-16 indicate that the Rh-based catalysts give higher yields of alcohols and, except for supported Pt and Pd, also higher selectivities than the remaining Group VIII metals studied (Fe, Co, Ni, Ru, Fe/Pt, Fe/Ir, Fe/Rh, Co/Ir, Co/Pt, Ni/Ir, Ni/Pt, nitrided iron, and similar catalysts). Of the Rh-based catalysts a combination with molybdenum reported by Mills et al. (136) gives oxygenate yields comparable to or higher than those over the alkali/copper-based or alkali/MoS_2 catalysts, but the selectivities to alcohols appear lower. Among the C_2+ alcohols ethanol appears to be the main product over the Rh-based catalysts, and if ethanol is the desired product, the singly or doubly promoted Rh catalysts hold greater promise than the remaining Group VIII metals.

Some new reports also dealt with the alkali/MoS_2 catalysts with or without additional Group VIII metal sulfides such as CoS, NiS, or FeS, and effects of various supports were studied. These developments are summarized in Table 5-17, in which some of the information overlaps with

Table 5-17. Activities and Selectivities to Oxygenates (Methanol and C_2+ Alcohols) of Catalysts Based on Alkalized MoS_2

Source: 9th ICC, July 1988.

General Conditions: 5 - 20 MPa, $H_2/CO=1/1$, GHSV 2000-13,600.

Catalyst	Selectivity to oxygenates %	T °C	STY[a] of oxygenates g/kg(l)cat/hour	Reference
K/CoS/MoS_2	90	290	238[b,c]	118
K/CoS/MoS_2	84	305	275[b,d]	118
K/CoS/MoS_2	85	310-320	374[b]	118
K/NiS/MoS_2	80	310-320	314[b]	118
K/FeS/MoS_2	72	310-320	205[b]	118
Cs/MoS_2	84	295	310[e]	90
Cs/MoS_2	80	300	256[g]	104
Rb/MoS_2	66	300	101[g]	104
K/MoS_2	81	300	144[g]	104
Na/MoS_2	53	300	19[g]	104
Li/MoS_2	24	300	13[g]	104
K/Ketjen-165 (K/CoS/MoS_2/c-Al_2O_3)	13	~300	16[b]	118
K/MoS_2	86	320	500[f]	151
K/MoS_2	94	300	330[f]	151

[a] STY = Space Time Yield, given in g of oxygenated product per kg of catalyst (including support) where available, otherwise per liter of catalyst.

[b] STY in g/l cat/hour; pressure 10.3 MPa; $H_2/CO = 1$; ca. 50 percent Ethanol in product.

[c] GHSV = 2000.

[d] GHSV = 3300.

[e] STY in g/kg cat/hour; pressure 8.2 MPa; $H_2/CO = 1$; GHSV = 7750; ca. 30 percent Ethanol in product.

[f] Pressure 10 MPa, $H_2/CO = 2/1$, GHSV = 5000.

[g] Pressure 2.7 MPa, $H_2/CO = 1/1$, GHSV = 12,000, STY in g/l cat/hour.

that discussed in greater detail in Section 5.3.2.2 under the heading The Dow HAS Process.

Following the announcement by Dow Chemicals of a new process for mixed alcohols in 1984 (103) that utilizes alkalized MoS_2 catalysts, a series of patent applications, patents, and papers dealt with the selectivity, STY's, long-term performance, resistance to poisons, and effects of sulfur-containing compounds in the feed (70-77). The essential features of this interesting system are summarized below:

- It has now been established by several independent laboratories that C_1-C_4 alcohol STY's above 300 g/kg (l) cat/hour can be obtained at pressures below 10 MPa and temperatures $\leq$ 300°C over the alkali/MoS_2 catalysts; a claim that STY's greater than 1000 g/l cat/hour can be reached -- a result comparing favorably with commercial methanol production (118) -- is likely to be substantiated.
- Selectivities to C_1-C_4 alcohols of both the alkali/MoS_2 and the alkali/MeS/MoS_2 (Me = Co, Ni) are in the range of 80-90 percent; the remaining products are hydrocarbons, primarily methane, and small amounts of esters; the selectivity is not a strong function of temperature.
- Group VIII metal sulfide promoters to alkali/MoS_2 catalysts enhance the formation of ethanol both directly from SG and by homologation of methanol. These promoters are preferred in the order CoS > NiS > FeS. 50 percent selectivity to ethanol in the oxygenated product is readily attained.
- Over alkali/MoS_2 catalysts, 30/70 ethanol/methanol mixture can be obtained at high STY's and selectivity to oxygenates; heavy alkali are better promoters than light alkali, Cs > K.
- H_2S in small concentrations (10-40 ppm) doubles the selectivity of the K/MoS_2 (but not K/Co/MoS_2) catalysts to C_2+ alcohols; this remarkable effect is reversible upon removal of H_2S.
- The alkali/MoS_2 and alkali/MeS/MoS_2 catalysts are remarkably stable, resistant to S-containing and $Fe(CO)_5$ poisons, and have been demonstrated to perform over a year-long period of time.

5.3.2.6 Research Trends

The research trends in higher-alcohol synthesis appear to be motivated by the desire to develop catalysts that

- minimize the hydrocarbon, particularly methane, make
- have a high productivity (STY's) for C_2+ alcohols (ethanol in one case and isobutanol in another)
- have a high water gas shift activity
- have a good heat conductivity
- minimize the production of C_6+ oxygenates, and
- improve the stability and long-term performance of the most active catalysts.

Several of these requirements have already been satisfied by reactions and processes reviewed in Sections 5.3.2.2 and 5.3.2.3. Further improvements can be expected with existing catalytic systems by manipulating the reaction conditions (including optimizing the pressure, temperature and the CO_2 content in SG for the best performance of a given catalyst) and by characterizing the catalysts in all stages of preparation and use.

Specific items that appear desirable are the following:

- Achieve a uniform dispersion of the catalyst components. This has been cited as a key to the successful preparation of the IFP catalysts. In terms of the dispersion of alkali promoters, it is known that they are distributed in molecular submonolayer dispersion on certain preparation of the copper-based catalysts (105) but are agglomerated in large particles, perhaps accompanied by a fine dispersion, on the MoS_2-type catalysts (90).
- Suppress the formation of hydrocarbons, particularly methane, over the Group VIII metal and MoS_2-based catalysts. This will be a difficult task as, at least for the latter catalyst, it was shown that methane and ethanol have a common precursor (90).