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column, TW-204, where the product water is taken as bottoms, cooled and sent to waste purification. The overheads containing alcohols and water are recycled back to the phase separator.

3. Cost of Production Estimates

Cost of production estimates have been performed to determine the critical process areas affecting the costs to upgrade synthesis gas to the crude ALKANOL product. In the ensuing analyses, we have evaluated production costs on two bases. The first method was formulated to include only those costs related to the synthesis loop, and it was accordingly assumed in this situation that synthesis gas at specified pressure would be delivered to the battery limits of the synthesis gas conversion section at no cost. In the second method, the cost of synthesis gas was included as a production cost item with the synthesis gas sensitized over the range of \$5 to \$12 per MM Btu. In both cases, total capital-related charges including amortization, maintenance, interest, etc. were kept constant at a rate equivalent to 30 percent of the total capital investment.

The other assumptions used in performing the estimated cost of production calculations were as follows:

- Stream Factor: 8000 hours per year
- Cooling Water Cost: 5.9 ¢ per 1000 gal
- Purchased Power: 3.5 ¢ per kwh
- 400 psig Steam Credit: \$3.87 per 100 lb
- Boiler Feed Water: \$0.99 per 1000 gal
- Inert Circulating Oil: \$1.30 per gallon with a one-year life
- ALKANOLS Synthesis Catalyst: \$300 per ft³ with a two-year life

The basis for determining the outside battery limits (OSBL) capital costs is as follows:

Product Storage:	14 days inventory
Inert Oil Storage:	14 days inventory
Cooling Water System:	Sized for 50,000 gpm equivalent to \$3.8 million
Electrical System:	\$240 per kw
General Utilities:	15% of inside battery limits (ISBL) cost

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The utility summary for the base case estimate is presented in Table VIII-3. The purchased equipment cost summary is presented in Table VIII-4 while the total installed cost summary is provided in Table VIII-5. The net overall factor relating inside battery limits installed costs to purchased costs was determined to be 2.24.

A production cost summary including catalyst and chemicals, utilities and capital related charges is shown in Table VIII-6. The estimated catalyst and chemical cost is \$6.03 per short ton of ALKANOLS product. The cost of catalyst is assumed to be \$300 per cubic foot with a two year life. Inert hydrocarbon is priced at \$1.30 per gallon and has a one year life. This assumes that a system inventory is made up over the course of a year due to leaks, spills, etc. In all likelihood, the oil makeup will correspond to some equilibrium fraction of the products, and no actual makeup other than the initial fill should be needed. It is further assumed that all hydrocarbons coproduced with the alcohols will boil below the boiling range of the inert oil. The cooling water and power amount to \$2.66 and \$12.27 per short ton, respectively. The steam produced from the reaction heat meets the plant requirement, therefore there is no net requirement for the base case design. At other operating severities considered in the process sensitivity analysis, there is a net yield of 400 psig steam which is taken as a credit against capital and operating costs. The estimated capital-related production cost is \$78.90 per short ton of ALKANOLS based on the assumed rate of 30% of total capital investment. The net estimated cost of production is \$99.86 per short ton or \$3.68/MM Btu of ALKANOLS. It should be noted that these costs exclude the cost of synthesis gas as well as the value of the purge gas.

4. Sensitivities of Process Parameters

A sensitivity analysis has been performed to quantify the effects of variations in process variables on the estimated cost of production of ALKANOLS. Seven cases were studied in addition to the base case design and the resultant estimated capital and production costs are summarized in Table VIII-7. The basis for generation of these cases is as follows:

TABLE VIII-3

UTILITY SUMMARY FOR BASE CASE ESTIMATE (1)

<u>Item No.</u>	<u>400 psig Steam lb/hr</u>	<u>Cooling Water gpm (2)</u>	<u>Power kwh</u>
GC-101			15,900
GC-102			1,350
HE-101 A-G	(427,000)		
HE-102		2,300	
HE-104		10,100	
P-101 A-I			1,200
HE-201 A,B		16,800	
HE-202 A,B	270,000		
HE-203		300	
HE-204		7,600	
HE-205	122,000		
HE-206		700	
HE-207	16,000		
HE-208	19,000		
HE-209		1,020	
HE-210		150	
Miscellaneous			<u>250</u>
TOTAL	0	38,970	18,700

(1) 550 psia feed gas pressure, 2050 psia reactor pressure,
3000 SL/hr/kg catalyst space velocity, 22% CO conversion per pass.

(2) Based on 25^oF increase.

TABLE VIII-4

INSIDE BATTERY LIMITS CAPITAL COSTS FOR BASE CASE ESTIMATE (1)

<u>Item No.</u>	<u>Description</u>	<u>Purchased Equipment Cost, \$M</u>
GC-101	Feed Gas Compressor (2 stage - 10,600 Hp ea)	6,890
GC-102	Recycle Compressor (1 stage - 1,800 Hp)	585
HE-101 A-G	Oil Cooler (2,600 ft ² ea, DP=2,200 psig)	130 ea
HE-102	Intercooler (4,400 ft ² , DP=1,200 psig)	132
HE-103	Feed Preheater (138,000 ft ² , DP=2,200 psig)	9,660
HE-104	Final Cooler (17,300 ft ² , DP=2,200 psig)	865
P-101 A-I	Oil Circulating Pump(2) (2500 GPM, ΔP=60 psi, 225 Hp ea)	38 ea
R-101 A-G	Reactor (8'd x 150' T/T, SS clad CS, DP=2,200 psig)	2,100 ea
V-101 A,B	V/L Separator (8'd x 24' T/T, CS, DP=2,200 psig)	400 ea
V-102	Degasser (10'd x 20' T/T, CS, DP=150 psig)	25
HE-201 A,B	Condenser (5,100 ft ² ea, DP=150 psig)	155 ea
HE-202 A,B	Reboiler (4,800 ft ² ea, DP=150 psig)	145 ea
HE-203	Alcohol Cooler (660 ft ² , DP=150 psig)	20
HE-204	Condenser (6,00 ft ² , DP=150 psig)	180
HE-205	Reboiler (10,900 ft ² , DP=150 psig)	327
HE-206	Water Cooler (1,700 ft ² , DP=150 psig)	51
HE-207	Reboiler (300 ft ² , DP=150 psig)	9
HE-208	Reboiler (300 ft ² , DP=150 psig)	9
HE-209	Recovery Condenser (700 ft ² , DP=150 psig)	21
HE-210	Product Cooler (250 ft ² , DP=150 psig)	7
TW-201 A,B	Extractive Distillation Column (11'd x 100' T/T, DP=150 psig)	365 ea
TW-202	Solvent Regeneration Column (11'6"d x 45' T/T, DP=50 psig)	160
TW-203	Dehydration Column (4'd x 80' T/T, DP=50 psig)	76
TW-204	Stripping Column (8'd x 160' T/T, DP=50 psig)	320
V-201 A,B	Reflux Drum (7' x 14' T/T, DP=150 psig)	10 ea
V-202	Reflux Drum-Decanter (13'd x 13' T/T, DP=150 psig)	30
Miscellaneous		200
<u>Total Purchased Equipment Cost</u>		<u>37,669</u>

(1) At 550 psia feed pressure, 2050 psia reactor pressure, 3000 SL/hr/kg catalyst space velocity, 22% CO conversion per pass.

(2) Includes two spares.

DP = Design Pressure

TABLE VIII-5

TOTAL INSTALLED CAPITAL COST SUMMARY FOR BASE CASE ESTIMATE (1)

<u>Inside Battery Limits (ISBL) Equipment</u>		<u>Installed Costs, \$M</u>
Reactors		28,800
Compressors		16,000
Exchangers		25,000
Purification Equipment		9,400
Other Equipment		5,400
Catalyst (Installed)		4,200
Total ISBL, \$M		88,800
<u>Outside Battery Limits (OSBL) Equipment</u>		
Product Storage	14 days	1,680
Oil Storage	14 days	180
Cooling Water System	50,000 GPM	3,800
Electrical System	\$240/Kw	4,490
General Utilities	15% ISBL	13,300
Total OSBL, \$M		\$ 23,450
Total Installed Capital Costs, \$M		\$112,250

(1) At 550 psia feed pressure, 2050 psia reactor pressure, 3000 SL/hr/kgm catalyst space velocity, 22% CO₂ conversion per pass.

TABLE VIII-6

ESTIMATED COST OF PRODUCTION (EXCL. SYN GAS)⁽¹⁾
FOR BASE CASE DESIGN

	<u>1st Qtr, 1981; U.S. Gulf Coast Basis</u>	
	<u>\$/Short Ton</u>	<u>\$/MM Btu</u>
<u>Raw Materials</u>		
Catalyst @ \$300/ft ³	4.92	0.18
Chemicals	<u>1.11</u>	<u>0.04</u>
	6.03	0.22
<u>Utilities</u>		
Cooling Water @ 5.9 ¢/M gal	2.66	0.10
Power @ 3.5 ¢/kwh	12.27	0.45
Steam (400 psig) @ \$3.87/M lb	0. ⁽²⁾	0.
	<u>14.93</u>	<u>0.55</u>
Capital-Related Charges @ 30% of Total Capital Investment	78.90	2.91
Cost of Production (Excl. Syn Gas Cost)	99.86	3.68

(1) 550 psia feed gas pressure, 2050 psia reactor pressure, 3000 SL/hr/kgm space velocity, 22% CO conversion per pass.

(2) No net heat requirement since the steam recovered from the circulating oil satisfies the plant energy requirement.

TABLE VIII-7

SENSITIVITY ANALYSIS FOR ALKANOLS PRODUCTION

Case No.	1 ⁽¹⁾	2	3	4	5	6	7	8
Feed Gas Press., psia	550	1,040	550	1,040	550	1,040	550	550
Reactor Press., psia	2,050	2,050	2,050	2,050	1,550	1,550	1,550	1,550
Catalyst Density (kg/cat/1 oil)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Space Velocity (S liters/hr-kg cat)	3,000	3,000	6,000	6,000	6,000	6,000	6,000	6,000
% Conversion Per Pass	22	22	22	22	22	22	30	40

ESTIMATED CAPITAL COSTS, \$MM

Reactors	28.8	28.8	14.4	14.4	10.4	10.4	8.7	7.5
Compressors	16.0	8.4	16.0	8.4	13.2	5.8	11.1	9.5
Exchangers	25.0	25.0	25.0	25.0	20.0	20.0	16.7	14.3
Purification Equipment	9.4	9.4	9.4	9.4	9.4	9.4	7.9	6.7
Other Equipment + Catalyst	9.6	9.6	6.6	6.6	6.2	6.2	5.2	4.5
Total Inside Battery Limits (ISBL) Costs	88.8	81.2	71.4	63.8	59.2	51.8	49.6	42.5
Outside Battery Limits (OSBL) Costs	23.4	20.2	20.8	17.5	18.2	15.1	16.4	15.1
Total Fixed Investment	112.2	101.4	92.2	81.3	77.4	66.9	66.0	57.6

ESTIMATED PRODUCTION COSTS, \$/SHORT TON ALKANOLS

Raw Materials (Excl. Syn Gas)

Catalyst & Chemicals	6.03	6.03	3.01	3.01	3.01	3.01	2.20	1.65
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Utilities

Cooling Water at 5.9 ¢/M gal	2.66	2.50	2.66	2.50	2.66	2.50	2.46	2.32
Power at 3.5 ¢/kwh	12.27	6.89	12.17	6.89	10.23	5.11	9.65	9.25
400 psig Steam at \$3.87/M lb	0.	0.	0.	0.	0.	0.	(1.52)	(2.60)
	20.96	15.42	17.94	12.40	15.90	10.62	12.79	10.62

(2)

Capital-Related Charges	78.90	71.30	64.80	57.10	54.40	47.00	46.40	40.50
Total Production Costs	99.86	86.72	82.74	69.50	70.30	57.62	59.19	51.12
\$/Million Btu ALKANOLS	3.68	3.20	3.05	2.56	2.59	2.13	2.18	1.89

(1) Base Case Design

(2) At 30% of total fixed capital investment

Case 1: Base case design formulated from data obtained in 300 hour test in Berty vapor-phase reactor.

Case 2: Study effect of increasing fresh feed gas supply pressure on base case costs. The high gas supply pressure results in the elimination of one stage of the feed gas compressor.

Case 3,4: Same as cases 1 and 2, respectively, with the exception of increased (by a factor of 2) space velocity. This results in 50 percent reductions in reactor volume, catalyst inventory and inert hydrocarbon oil inventory.

Case 5, 6: Same as cases 3 and 4, respectively, with the exception of reduced reactor pressure (1550 psia vs. 2050 psia for case 3 & 4).

Case 7: Same as case 5 with the exception that per pass carbon monoxide conversion is assumed to be 30 percent instead of 22 percent.

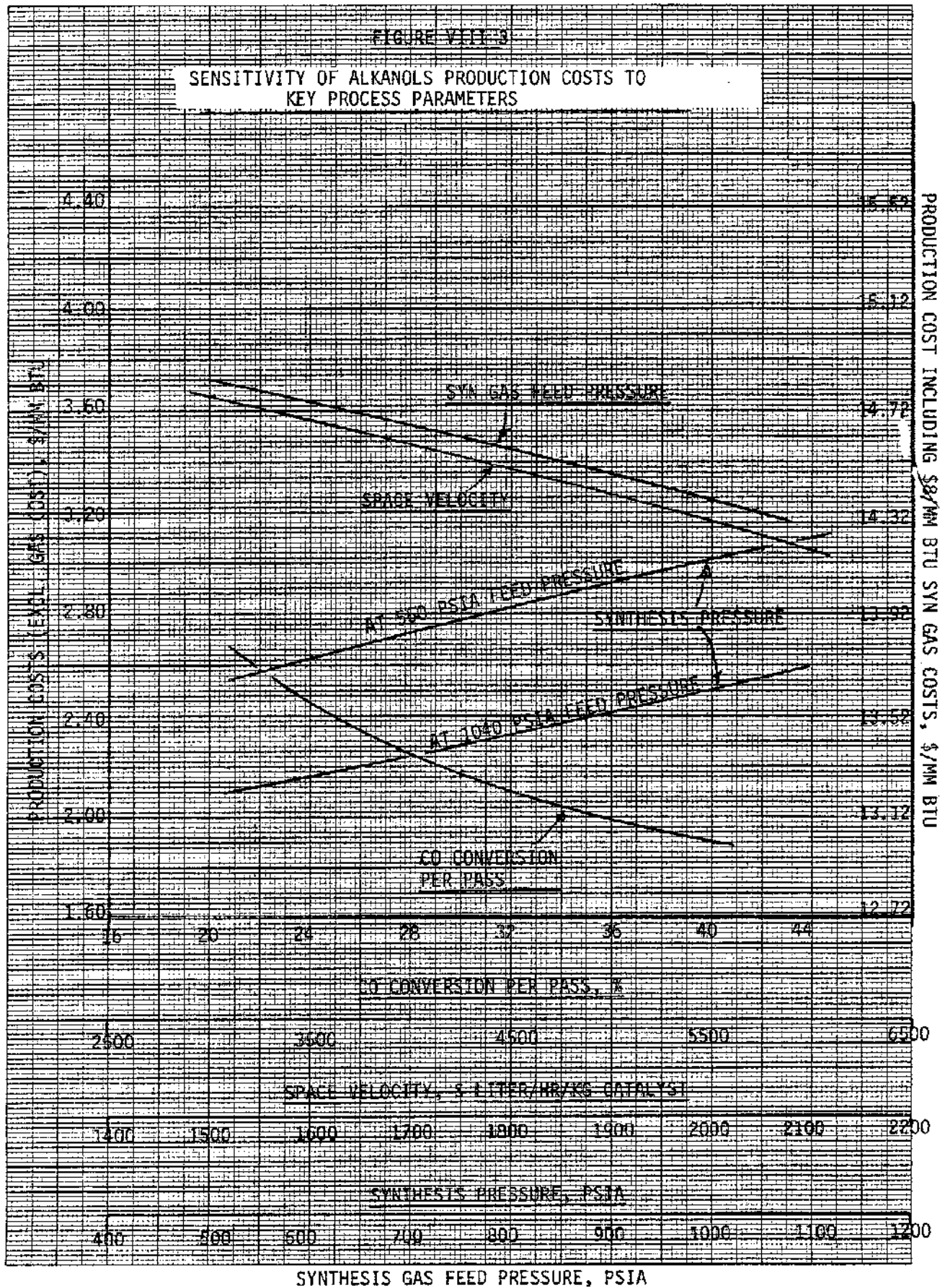
Case 8: Same as case 5 with the exception that per pass carbon monoxide conversion is assumed to be 40 percent instead of 22 percent.

The effect of the variations in the four key process parameters is illustrated in Figure VIII-3. It should be pointed out that cases 7 and 8 show the explicit effect of variations in carbon monoxide conversion per pass independently of reaction conditions, and thus the reactor operating severity for these two cases was assumed the same as that of case 5.

Estimated production costs varied from a low of \$1.89/MM Btu of ALKANOLS for case 8 (high assumed carbon monoxide conversion per pass) to a high of \$3.68/MM Btu for the conservative base case design. This variation is relatively low when the overall process of converting synthesis gas to ALKANOLS is considered. For the constant product slate assumed in this study, the net synthesis gas requirement (i.e., total synthesis gas feed minus purge gas) amounts to 37.75 MM Btu/short ton of ALKANOLS with an equivalent cost of \$11.12/MM Btu of ALKANOLS when the synthesis gas is

FIGURE VIII-3

SENSITIVITY OF ALKANOLS PRODUCTION COSTS TO KEY PROCESS PARAMETERS



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costed in at a value of \$8/MM Btu of synthesis gas. Thus, the range of estimated production costs for producing ALKANOLS from purchased synthesis gas is \$13.01 to \$14.80 per MM Btu of ALKANOLS.

It is evident that the sensitivity of estimated ALKANOLS production costs to variations in synthesis loop parameters is minimal as compared to the effect of synthesis gas costs. The estimated incremental cost of the ALKANOLS attributable to the synthesis gas costs is about 75-85 percent of the total ALKANOLS production costs when synthesis gas is priced at \$8/MM Btu. Obviously, as synthesis gas costs increase, the effect of the synthesis loop parameters on ALKANOLS production costs diminishes.

The preliminary process sensitivity analysis has pinpointed further process design areas which should be evaluated in more depth in future studies. Some of these include:

- Sensitivity of product slate to reactor feed gas composition;
- Optimization of the mechanical design of the reactor system;
- Phase separation equipment for the alcohols-hydrocarbons-water mixtures;
- Optimization of the product purification train which could result in significant reductions in plant utility requirement, thereby increasing the byproduct revenues from export of high pressure steam.

5. Comparative Economics of ALKANOLS Vs. Methanol
and Mobil MTG Gasoline

Coal-derived liquids can be produced either by direct coal hydrogenation or by indirect coal liquefaction, i.e., coal gasification followed by synthesis gas conversion to hydrocarbons or alcohols. Transportation fuels to be used in internal combustion engines are generally characterized by having relatively high volatility (430⁰F end point) and high aromatic content. Coal syncrudes produced by direct hydrogenation of coal distill into roughly two equal distillate fractions (C₅-430⁰F gasoline range and 430-800⁰F fuel oil range) and a residual fraction. Generally, the naphtha fraction is highly aromatic making this material

excellent gasoline reformer feedstock. However, conversion of highly aromatic fuel oil range material to transportation fuels (gasoline or diesel) will be extremely difficult and economically unattractive. Thus, indirect coal liquefaction is an alternative route to producing a liquid product that can be totally utilized as transportation fuel.

ALKANOLS production via conversion of coal-derived synthesis gases has been compared to two mature indirect liquefaction routes: synthesis gas to methyl fuel by commercial, low pressure, methanol synthesis technology and the soon-to-be commercialized methanol to synthetic gasoline process (Mobil MTG). In order to make an equitable comparison, production costs for these two synthesis fuels were calculated on the same basis as that used for the ALKANOLS production cost estimates. In both cases, it was assumed that a balanced synthesis gas would be delivered to the battery limits of the respective plants. Table VIII-8 is a summary of the capital and operating costs for synthetic gasoline, exclusive of the synthesis gas costs, by the two-step route of converting synthesis gas to methanol followed by fixed-bed conversion of methanol to synthetic gasoline. The 97 million gallon per year production rate of synthetic gasoline was specified to yield the same equivalent energy content as that of the 1280 stpd ALKANOLS production rate. The estimated cost of production (excluding synthesis gas costs) of synthetic gasoline by the Mobil MTG Process of \$2.50/MM Btu is essentially equivalent to that of ALKANOLS production (\$2.59/MM Btu for case 5).

The effect of increased capacity of the synthesis loops for both the MTG gasoline and ALKANOLS synthesis fuels is shown in Table VIII-9.

TABLE VIII-9
EFFECT OF SYNTHESIS LOOP CAPACITY

<u>Capacity</u>		
MM Gal/yr gasoline	97	700
Stpd ALKANOLS	1280	9237
MMM Btu/day	36	260
<u>Production Costs Excluding Syn Gas Costs, \$/MM Btu</u>		
Mobil MTG	2.50	2.11
ALKANOLS (Case #5)	2.59	2.23

TABLE VIII-8MOBIL MTG PROCESS PLANT INVESTMENT AND PRODUCTION COST ESTIMATES

Inside Battery Limits (ISBL), \$MM	83.7
Outside Battery Limits (OSBL), \$MM	<u>28.0</u>
TOTAL FIXED CAPITAL INVESTMENT, MM	111.7

\$/1000 gal Synthetic Gasoline

Raw Materials,	
Catalyst and Chemicals	11.6
Utilities,	
Steam	
600 psig (\$4.10/M lb)	(46.2)
200 psig (\$3.87/M lb)	(9.5)
45 psig (\$3.82/M lb)	71.3
Power at 3.5¢/Kwh	34.0
Boiler Feed Water at 99¢/M Gal	2.6
Cooling Water at 5.9¢/M Gal	1.8
Fuel Gas at \$3.37/MM Btu	(17.0)
LPG at \$5.05/MM Btu	(35.3)
Mix. Butanes at \$5.05/MM Btu	(55.1)
Inert Gas at \$1.13/MSCF	<u>0.2</u>
	(41.6)
Capital-Related Charges	
(30% Capital Investment)	<u>345.4</u>
Total Production Costs (Excl. syn gas costs)	
Expressed as \$/1000 gal	303.8
Expressed as \$/MM Btu	2.50

Production costs were also generated for conversion of synthesis gas to methyl fuel by a typical low pressure, methanol synthesis process and the results of these calculations are shown in Table VIII-10.

In order to fairly assess the three indirect liquefaction routes, it is necessary to compare the respective production costs including the net cost of synthesis gas. The stoichiometric synthesis gas requirements and the purge rates necessary to maintain the reaction systems in balance differ for each of the three processes. Thus, in Tables VII-11, the synthesis gas feed costs are calculated on a net basis by subtracting the purge gas rate from the corresponding fresh synthesis gas rate. Again, it can be seen that the net feed requirement for the ALKANOLS synthesis is intermediate between that of the methanol and MTG syntheses.

A sensitivity analysis of the effect of synthesis gas costs on syncrude product costs is shown in Figure VIII-4 for ALKANOLS cases #5 and #8, Mobil MTG and methyl fuel. The differential costs between conversion of synthesis gas to methyl fuel and to ALKANOL fuels vary slightly depending upon cost of the synthesis gas. At the lower level synthesis gas costs (e.g., \$6/MM Btu), estimated ALKANOLS production costs are about \$1-1.80 per MM Btu (\$0.09-0.16 per gallon ALKANOLS) higher than those of methyl fuel and about \$1.80-2.20 per MM Btu (\$0.16-0.20 per gallon ALKANOLS) lower than those of Mobil MTG gasoline. At the higher level of synthesis gas costs (e.g., \$12.00/MM Btu), estimated ALKANOLS production costs are about \$1.80-2.80 MM Btu (\$0.16-0.25 per gallon ALKANOLS) higher than those of methyl fuel and about \$2.80-3.50/MM Btu (\$0.25-0.31 per gallon ALKANOLS) lower than those of Mobil MTG gasoline.

C. Utilization of ALKANOL Fuels

Among the several alternative fuels that can be used either as blending stocks or as substitutes for petroleum-derived gasoline, lower saturated alcohols (methanol through hexanol) have been receiving much attention. There are important technical and cost differences among the various lower alcohols when considering their utilization as transportation fuels. ALKANOL fuels have the potential for providing a gasoline blending stock superior to that of straight-run methanol. The addition of higher

TABLE VIII-10

PLANT AND PRODUCTION COSTS (EXCL. SYN GAS)
FOR 1800 STPD METHYL FUEL FROM SYN GAS
 1st Quarter, 1981, U.S. Gulf Coast Basis

Inside Battery Limits (ISBL), \$MM	46.15
Outside Battery Limits (OSBL), \$MM	<u>13.50</u>
Total Fixed Capital Costs, \$MM	59.65

\$/Short Ton Methyl Fuel

Raw Materials

Catalysts & Chemicals	1.26
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Utilities

600 psig steam @ \$4.10/Mlb	(3.43)
200 psig steam @ \$3.87/Mlb	(3.33)
45 psig steam @ \$3.82/Mlb	8.67
Fuel @ \$3.37/MM Btu	(2.09)
Power @ 3.5 ¢/kwh	4.62
BFW @ 99 ¢/M Gal	0.25
CW @ 5.9 ¢/M Gal	<u>0.21</u>
SUBTOTAL	6.16

Capital-Related Charges (@ 30% of Total Fixed Capital)	29.80
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Total Production Costs (Excl. Syn Gas Costs)	
Expressed as \$/Short Ton	35.96
Expressed as \$/MM Btu	1.87

TABLE VIII-11

IMPACT OF SYNTHESIS GAS COSTS ON
THREE INDIRECT LIQUEFACTION PROCESSES

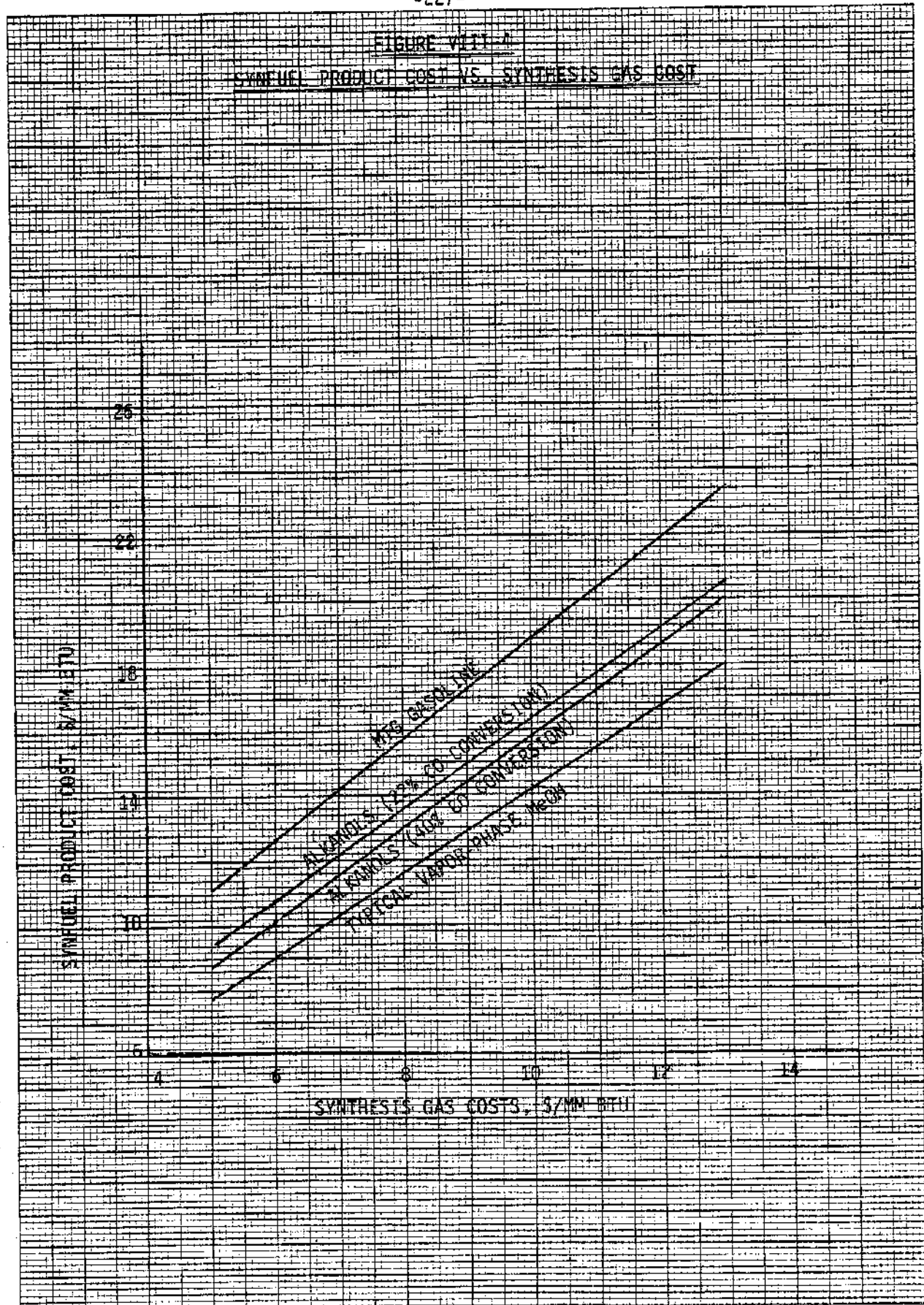
	<u>ALKANOLS</u>		<u>Methyl⁽¹⁾</u> <u>Fuel</u>	<u>Mobil MTG</u>
	<u>Case 5</u>	<u>Case 8</u>		
Fresh Syn Gas Requirement, MM Btu/Hr	2824.6	2824.6	1849.9	2466.5
Purge Gas Rate, MM Btu/Hr	<u>811.4</u>	<u>811.4</u>	<u>65.7</u>	<u>99.0</u>
Net Feed Gas Requirement, MM Btu/Hr	2013.2	2013.2	1784.2	2367.5
Ratio of Net Feed to That of Methyl Fuel Case	1.13	1.13	1.00	1.33
Net Feed/Product Energy Ratio ⁽²⁾	1.39	1.39	1.23	1.63
Net Feed Gas Cost ⁽³⁾ , \$/MM Btu	11.12	11.12	9.84	13.04
Production Cost (Excl. Syn Gas), \$/MM Btu	2.59	1.89	1.86	2.50
Total Synfuel Cost, \$/MM Btu	13.71	13.01	11.70	15.54

(1) Based on typical, vapor-phase, commercial methanol synthesis process.

(2) Btu content of net syn gas feed divided by Btu content of synfuel product.

(3) Syn gas priced @ \$8/MM Btu.

FIGURE VIII-2
SYNFUEL PRODUCT COST VS. SYNTHESIS GAS COST



(C₂-C₆) alcohols to methanol as cosolvents reduces the vapor pressure penalty associated with the use of lower alcohols in gasoline while still maintaining excellent anti-knock properties. Water sensitivity with the ALKANOL fuels is also improved as compared to that of methanol usage in gasoline.

1. Properties of ALKANOL Fuels

Although the current interest is in the use of ALKANOLS as gasoline blending components, ALKANOLS may be used as straight-run motor fuels in modified internal combustion engines. Octane ratings for the lower saturated alcohols are as high as petroleum gasoline and do not need lead anti-knock compounds. Flame temperatures for alcohols are lower than for gasoline, thereby lowering NO_x emissions at the engine exhaust. Water added to neat alcohol fuels results in significant increases in octane numbers (1.2 MON units per one weight percent water added to ethanol). Volumetric fuel economy for alcohol fuels is less than that for gasoline, and for a given travel radius, a motor vehicle will require a fuel tank larger than would be needed for the case of gasoline fuel. In the case of fleet car/truck applications in large urban centers, this problem may not be severe and existing vehicle fuel tanks could suffice.

ALKANOLS are less volatile than methanol and potential safety problems with the use of alcohols are reduced when ALKANOLS are used instead of methanol. ALKANOLS have higher volumetric energy contents than methanol and the resultant fuel economy, i.e., miles per gallon, will be higher as can be seen from in Table VIII-12.

TABLE VIII-12
PROPERTIES OF ALKANOL MIXTURES

	<u>ALKANOL A</u>	<u>ALKANOL B</u>	<u>ALKANOL C</u>	<u>Methanol</u>
Composition, Wt%				
MeOH	70	20	35	100
C ₂ -C ₆ Alcohols	30	80	42	0
Coproducted C ₄ -C ₉ H.C.	0	0	23	0
Calculated HHV, Btu/Gal	74,100	86,500	89,000	64,386

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It can be seen from the table that ALKANOL B & C mixtures should have about a 34-38% theoretically higher MPG rating than methanol at equivalent engine efficiencies.

A preferred route to introducing alcohols into the automobile fuel supply networks is via blending with petroleum-derived gasoline. Methanol, ethanol and t-butanol have already been incorporated into the motor gasoline supply system as blends with gasoline (e.g., "Gasohol", "Arconol", "Oxinol"). There are four major technical advantages that ALKANOL fuel has over methanol when used as a gasoline blending stock. These are:

1. Improved volatility and driveability,
2. Improved hydrocarbon solubility,
3. Improved water tolerance, and
4. Higher volumetric heats of combustion.

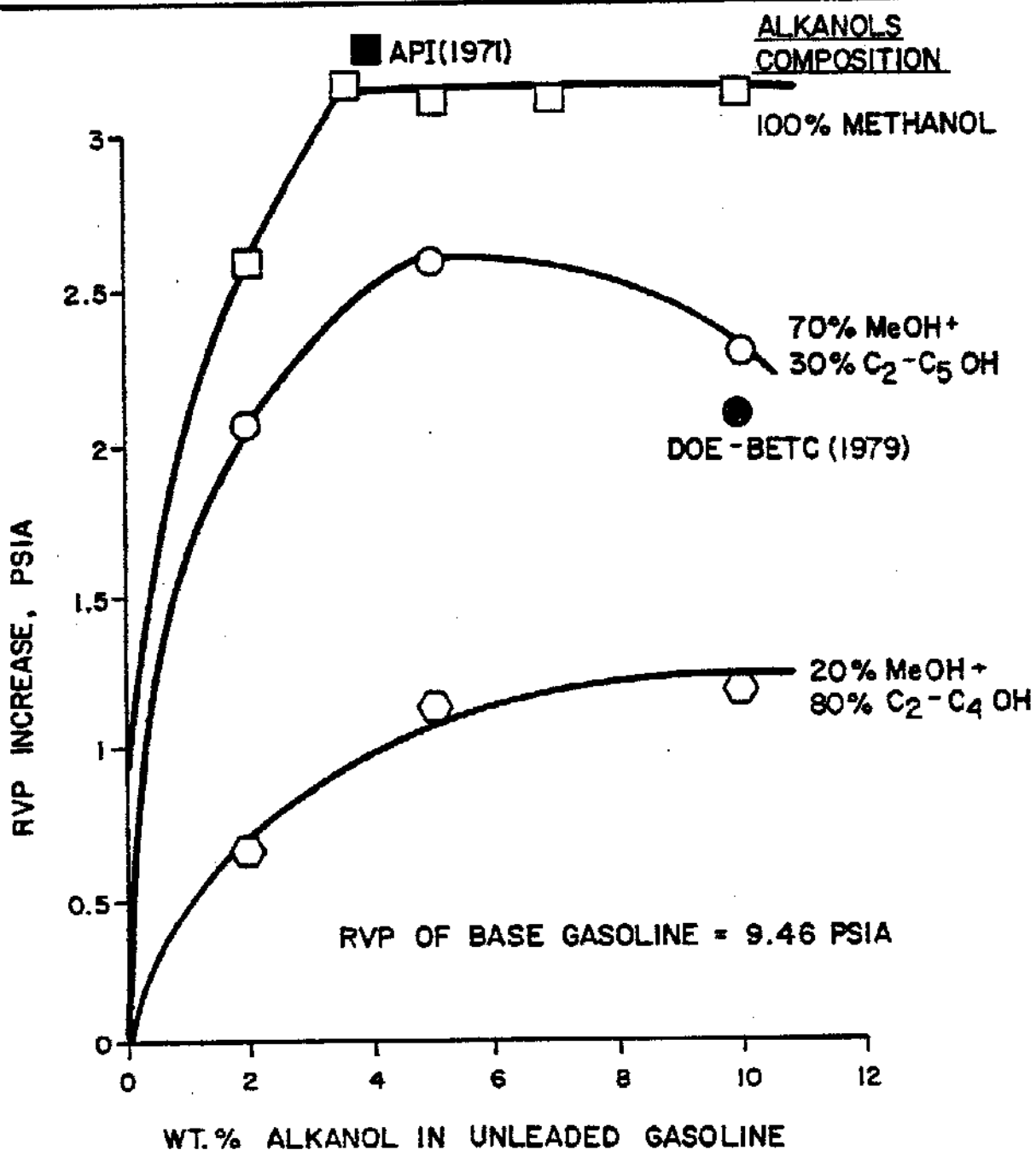
ALKANOL mixtures A & B were synthesized and evaluated in terms of octane improvement (i.e., RdBVON), Reid vapor pressure (RVP) characteristics, water tolerance and hydrocarbon solubility. A third mixture (ALKANOL C) was also synthesized and subjected to water tolerance tests. The available literature was reviewed and data on other ALKANOL mixtures were obtained and compared to the three synthesized ALKANOL mixtures.

Volatility and Driveability

The addition of methanol to gasoline results in a significant increase in the Reid Vapor Pressure (RVP) of the fuel blend as seen in Figure VIII-5^(55,56). Higher alcohols, namely, ethanol, propanols, butanols, and pentanols also increase the Reid vapor pressure of the mixtures but to a lesser extent. This reduced RVP elevation characteristic of the ALKANOL fuels does tend to reduce vapor lock problems. It also minimizes the amount of butanes that would have to be backed out of methanol-gasoline blends in order to adjust RVP characteristics.

FIGURE VIII-5

EFFECT OF ALKANOLS COMPOSITION ON INCREASE IN GASOLINE REID VAPOR PRESSURE (RVP) AS A FUNCTION OF ALKANOLS CONTENT IN GASOLINE



Conventional cars are undriveable on straight alcohol fuels because the stoichiometric air/fuel ratios of these fuels are so low that the mixture delivered by a carburetor designed for gasoline is too lean to fire⁽⁵⁷⁾. However, conventional cars will operate on blends of 5-20% alcohols in gasoline, but the warm-up driveability deteriorates proportionately to the total alcohol content. By modifying conventional carburetion with fuel injection and with the air/fuel ratio controlled by an exhaust gas analyzer-controller, driveability demerits were low. As shown in Figure VIII-6, the ALKANOL-gasoline fuel mixture containing 25% C₂-C₄ alcohols in the alcohol fraction had a driveability slightly better than that of the gasoline stock (11 vs. 18), while the mixture containing 100% methanol had higher driveability demerits than that of the gasoline (38 vs. 18).

Hydrocarbon Solubility

Methanol is partially soluble in paraffins with the solubility decreasing as the temperature decreases. Conversely, methanol solubility increases as the aromaticity of gasoline increases. Typical cat reforming gasolines are generally rich in aromatic content while cat cracker and alkylate gasolines are generally richer in paraffins and/or naphthenes. Thus, the composition of the gasoline pool materials will have a great effect on alcohol solubility in gasoline-alcohol blends. Table VIII-13 shows the effect of methanol and ALKANOLS addition, as measured by the cloud point test (ASTM D2500-66) on alcohol solubility in gasoline hydrocarbons⁽⁵⁸⁾. The addition of C₂-C₅ alcohols to methanol clearly improves alcohol solubility for all gasoline compositions delineated in the table.

Water Tolerance

The water tolerance of alcohol-gasoline blends is the amount of water a blend can dissolve before breaking into two phases - an upper gasoline-rich phase and a lower alcohol-rich phase. This separation can have some undesirable effects such as corrosion of parts of the automobile fuel system, engine stalls, etc. Figure VIII-7 shows the water tolerance

TABLE VIII-13

EFFECT OF ALKANOLS ADDITION ON ALCOHOLS SOLUBILITY
IN 10% ALCOHOL/90% GASOLINE BLENDS

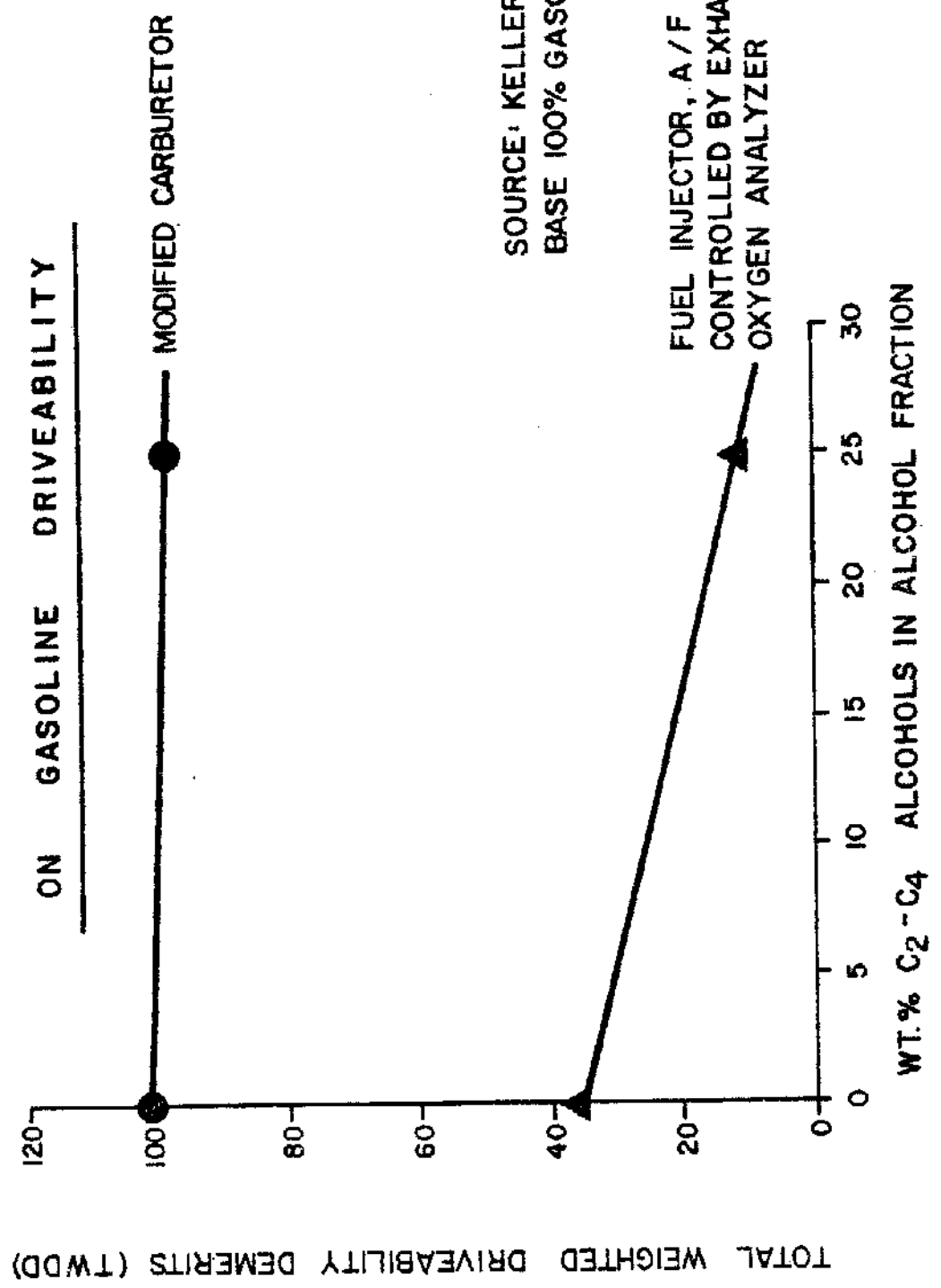
Test No.	<u>Gasoline Composition*</u>		Cloud Pt., °C			
	<u>% Saturates</u>	<u>% Aromatics</u>	ALKANOL Composition, Wt%			
			<u>100% MeOH</u>	<u>80% MeOH 20% iPrOH</u>	<u>70% MeOH, 30% C₂-C₅ Alcohols</u>	<u>20% MeOH, 80% C₂-C₄ Alcohols</u>
1	100	0	+27	+22	--	--
2	65	21	+7	-16	-37	-51
3	43	2	-7	-39	--	--
4	20	78	-16	-41	--	--

*Balance - olefins

Source - A. W. Crowley, 1975

FIGURE VIII-6

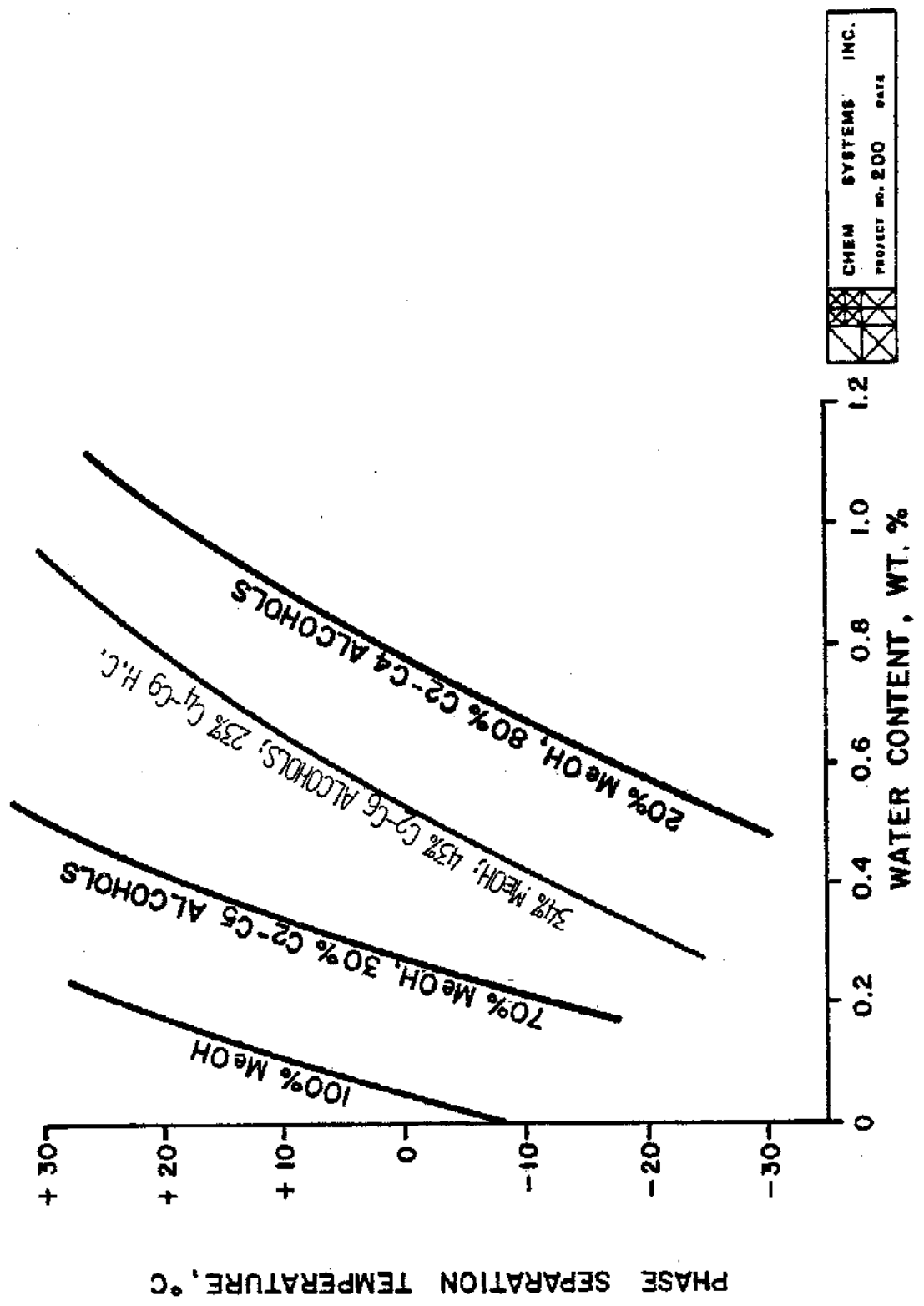
EFFECT OF C₂-C₄ ALCOHOL CONTENT OF
ALCOHOL (15-18%) / GASOLINE (82-85%) BLENDS
ON GASOLINE DRIVEABILITY



SOURCE: KELLER (1979)
BASE 100% GASOLINE: 18 TWDD

FIGURE VIII-7

WATER TOLERANCE OF 13% ALKANOL / 87% GASOLINE BLENDS



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	200	

of 13% alcohol/87% gasoline blends for four different alcohol compositions: 100% methanol, 100% ethanol and two ALKANOL mixtures⁽⁵⁸⁾. Methanol clearly has the lowest tolerance of all the lower (C₁-C₅) alcohols, below about 0.2%. ALKANOL mixtures, which act as cosolvents for methanol, can improve the water tolerance to levels above 0.2% and as high as 1%. Further improvements in water tolerance may be achieved by increasing the percentage of alcohols in gasoline to the 15-20% levels. Of particular significance is the observation that at the phase separation points for the two ALKANOL blends, the alcohol content of the water phase was very low. For the case of the methanol phase separation point, the methanol content of the water phase was high.

Heats of Combustion/Octane

Thermal efficiency is potentially better with alcohols because they have more favorable thermochemical properties, can be burned leaner and can operate at higher compression ratios. However, volumetric mileage may decrease as a direct result of the lower energy content of the alcohols. When considering 10% ALKANOL/90% gasoline blends, the volumetric energy content of the blends varies from about 96 to 97% (depending upon ALKANOL composition) of that of the gasoline stock. The three to four percent reduction in average energy content will probably be offset by the improved octane of the alcohols thereby resulting in no significant variation in the MPG (miles per gallon) rating. Table VII-14 summarizes the heating value and octane numbers of typical ALKANOL mixtures.

2. Economics of Use of ALKANOLS as Gasoline Blending Stocks

The value of ALKANOLS to a refiner as a gasoline pool blending stock is best understood in terms of octane improvement economics. The petroleum refiner has several methods for controlling incremental octane number costs including tetraethyl lead addition; C₅-C₆ isomerization; toluene and other aromatics addition; increased FCC conversion; and high severity cat reforming. Octane improvement via direct addition of oxygenated blending agents, such as ALKANOLS, can be compared to the conventional routes described above when these oxygenates are purchased (or assigned a

TABLE VIII-14

THERMOCHEMICAL PROPERTIES OF 10% ALKANOL/90% GASOLINE BLENDS

<u>Blend Properties</u>	<u>ALKANOL Composition of 10% ALKANOL/ 90% Gasoline Blends</u>			<u>Virgin Gasoline</u>
	<u>100% MEOH</u>	<u>70% MeOH, 30% C₂-C₅ Alcohols</u>	<u>20% MeOH, 80% C₂-C₄ Alcohols</u>	
Higher Heat Content, Btu/Gal	118,942	119,910	121,130	125,000
RON	95.1 ^(b)	95.7	94.9	90.6
MON	84.6 ^(b)	85.9	85.9	82.4
Road ON	89.9 ^(b)	90.8	90.4	86.5
Road Blending Value Octane Number of ALKANOL Component	120 ^(a)	129.5	125.5	--

(a) Source: H. L. Hoffman, Hydrocarbon Processing (Feb. 1980)

(b) Calculated based on Rd BVON of 120 for methanol

value within a refinery) as a gasoline pool blending stock. A convenient method of measuring and analyzing octane improvement costs is to use the concept of cents per octane number per gallon. Because the denominator of the term is a unit of improvement, octane-gallons may be lost by strict material balance while still showing improvements in quality. The procedure for calculating octane improvement costs for oxygenates is more complicated than for the case of lead anti-knocks since the oxygenates not only affect pool octane, but also the volumetric energy content, the density and the Reid vapor pressure (RVP) of the finished gasoline blends. Generally, alcohols have relatively higher vapor pressures and thus a butane adjustment is required. Butane itself is a high-octane blending component of gasoline and if butane has to be withdrawn from the pool in order to meet the RVP specifications, its value is downgraded from gasoline value (\$7.30/MM Btu for 91.3 ¢/gal gasoline) to fuel gas value (\$5.52/MM Btu at 57 ¢/gal butane). In the range of 5-10% alcohols addition rates to gasoline, the penalty for high density and low volumetric energy content is very small and therefore is not included in the calculations of octane improvement economics.

The most important factor affecting the octane improvement economics of oxygenated fuels is the road blending value octane number (RdBVON). RdBVON is a calculated parameter that reflects the amount of gasoline having a fixed road octane number (average of Research and Motor Octane numbers) and the amount of octane improver, i.e., alcohol fuel, needed to elevate the octane number of the mixture to the desired value. The Road Blending Value Octane Number (RdBVON) of an oxygenated fuel can be determined from the following expression:

$$\left(\frac{R+M}{2}\right)_G \times X_G + \text{RdBVON} \times X_{OX} = \left(\frac{R+M}{2}\right)_M \quad (1)$$

Where: $(R+M)/2$ = Road Octane Number (average of research and motor methods);

X = weight fraction of respective component;

Subscript G refers to gasoline component;

Subscript OX refers to oxygenates component; and

Subscript M refers to gasoline-oxygenates mixture.

The RdBVON cost improvement is the difference between the RdBVON of the oxygenated fuel component and the road octane number of the original gasoline multiplied by the cost per unit road octane number for octane improvement:

$$\text{RdBVON Cost Improvement} = \left[\text{RdBVON} - \left(\frac{R + M}{2} \right) M \right] \times \text{\$/ON gallon} \quad (2)$$

Where $\text{\$/ON gallon}$ represents the cost of the current method of octane improvement being used by a particular refiner, expressed as cents per octane number-gallon.

The following table lists estimates of the cost of octane improvement ($\text{\$/ONG}$) of some currently used refining routes:

TABLE VIII-15

ESTIMATED OCTANE IMPROVEMENT COSTS GULF COAST BASIS, 1985

	<u>\\$/ON Gallon</u>
<u>CATALYTIC REFORMING</u>	
Existing reformer, 95-100 RONC reformate	0.8-1.0
New reformer, balanced refinery, 85-100 RONC reformate	1.3-1.6
<u>C₅-C₆ ISOMERIZATION</u>	
	0.9-1.2
<u>TOLUENE ADDITION</u>	
@ \$1.27/gal	2.2
@ 2.50/gal	3.8
<u>TETRA ETHYL LEAD ADDITION</u>	
	0.2-0.3

Based on the preceding analysis, we have estimated the values of two ALKANOL mixtures as gasoline blending stocks to a refiner who is currently practicing octane improvement by toluene addition with toluene valued at \$1.27/gallon. The results of the analysis are presented in Table VIII-16 along with estimates of refining values of other oxygenated fuels. The cost of production of the two ALKANOL mixtures specified in the table were estimated to be 95 $\text{\$/gal}$ (\$12.76/MM Btu) for ALKANOL A and \$1.15/gal (\$12.76/MM Btu) for ALKANOL B. In both the ALKANOL and methanol cases, it was assumed that synthesis gas costs were \$6.63/MM Btu with a 20 percent

TABLE VIII-16

ESTIMATED REFINING VALUES OF OXYGENATED FUELS AT 5-10% ADDITION
RATES TO 88 RdON UNLEADED GASOLINE

<u>Oxygenated Fuel</u>	<u>ALKANOL A</u>	<u>ALKANOL B</u>	<u>Methanol</u>	<u>Ethanol</u>	<u>MTBE</u>	<u>t-BA</u>
<u>RdBVON</u>	129.5	125.5	120	112.5	109	97.5
<u>Cost of Production, including 20% ROI, ¢/gal</u>	95	115	70	180	76	114
<u>Refining Value of Oxygenated Fuel Relative To Toluene Addition, ¢/Gal</u>	161	161	107	142	137	115

Notes:

1. Unleaded gasoline priced at 91.3 ¢/gal; butane at 57 ¢/gal; toluene at 127 ¢/gal.
2. ALKANOL A (70% MeOH, 30% C₂-C₆ Alcohols) and ALKANOL B (20% MeOH, 80% C₂-C₆ alcohols) costs of production estimated.
3. RdBVON's for ALKANOLS based on octane tests with Sunoco unleaded gasoline having 65% saturates, 21% aromatics and 14% olefin content.
4. t-BA sold as byproduct of propylene oxide process and cost taken at equivalent value per octane number gallon as toluene.
5. Methanol production costs by low pressure methanol synthesis from coal-derived synthesis gas priced at \$6.63/MM Btu.

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straight return on total capital investment. It was further assumed that the upgrading costs on an energy basis for these two ALKANOL mixtures were the same as those for the ALKANOL composition considered in the conceptual design study.

The driving force for use of ALKANOLS and other oxygenated fuels as octane improvers obviously exists only when the cost of production is less than the relative refining value of the oxygenated fuel. There is a driving force (i.e., refining value exceeds cost of production) for using all of the ALKANOL and oxygenated fuels listed in the table when these fuels are valued relative to the use of toluene addition (priced at 127 ¢/gal) as the current octane improvement method in use by a refiner.

The data in Table VIII-16 for the two ALKANOL fuels were based on RdBVON's determined for a 10% ALKANOL/90% unleaded gasoline containing 65% saturates, 21% aromatics and 14% olefins. The RdBVON values for the other oxygenated fuels are from the literature. The octane improvement economics for ALKANOLS as well as other oxygenated fuels are very dependent upon RdBVON's and RVP measurements. The RdBVON and the RVP characteristics are themselves a function of gasoline composition and oxygenated fuel addition rates. Some of the oxygenates have non-linear RVP and RdBVON responses to oxygenates dosage. Thus, the cost calculations presented in Table VIII-16 assess the value of ALKANOLS for one particular gasoline composition over a relatively narrow range of ALKANOLS addition rates.

The values of estimated octane improvement costs shown in Table VIII-15 reflect the sensitivity of RdBVON on the refining value of oxygenated fuels. If the deviation in the RdBVON measurement of an oxygenated fuel is, for example, 10 octane number units, then the estimated refining value of that fuel would vary by an amount equal to 10 multiplied by the ¢/ONG for the particular octane improvement method being utilized. Thus, for the case of toluene addition, the deviation in the refining value of an oxygenated fuel would be ± 22 ¢/gal with toluene priced at 127 ¢/gal. The

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measured RdBVON for ALKANOL A (70% methanol, 30% C₂-C₆ alcohols) would have to decrease from the determined value of 129.5 to a value below 90 in order for the use of ALKANOL A not to be competitive with toluene addition. For the case of ALKANOL B, the parity point occurs at a RdBVON of 104 compared to the test value of 125.5. Similar relationships can be derived for determining the sensitivity of RdBVON on refining values of ALKANOL fuels relative to the other octane improvement routes described in Table VIII-15.