Section 1

INTRODUCTION AND BACKGROUND

This project was initiated in early 1975, and the previous years work was reported in Annual Reports published by EPRI in August, 1975 and May, 1978 under the headings:

Liquid Phase Methanol	Liquid Phase Methanol
EPRI AF - 202	EPRI AF - 693
Research Project 317-1	Research Project 317-2
August, 1976	May, 1978

The above information, supplemented by recent studies conducted since then, has been reorganized and is included in this final report.

PROCESS DESCRIPTION

The simplest form of the reaction scheme development consists of a three-phase fluidized bed reactor as shown in Figure 1-1. Synthesis gas containing CO, CO_2, and H_2 is passed upward in the reactor concurrently with an inert liquid which serves to both fluidize the catalyst and absorb the exothermic heat of the methanol synthesis reactions indicated below.

$$CO + 2H_2 \rightleftharpoons CH_3OH$$
$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

The conversion level is limited by equilibrium considerations, but a reasonably close approach is realizable by this system. The exothermic reaction heat is taken up by the liquid primarily as sensible heat and rejected as steam. The overhead product gases are condensed to remove the product methanol and water and to recover any vaporized liquid for recycle. The main liquid flow is circulated through a heat exchanger for temperature control. Unreacted synthesis gas can either be recycled to the reactor for production of additional methanol or burned directly for base-load generation, depending on the application.

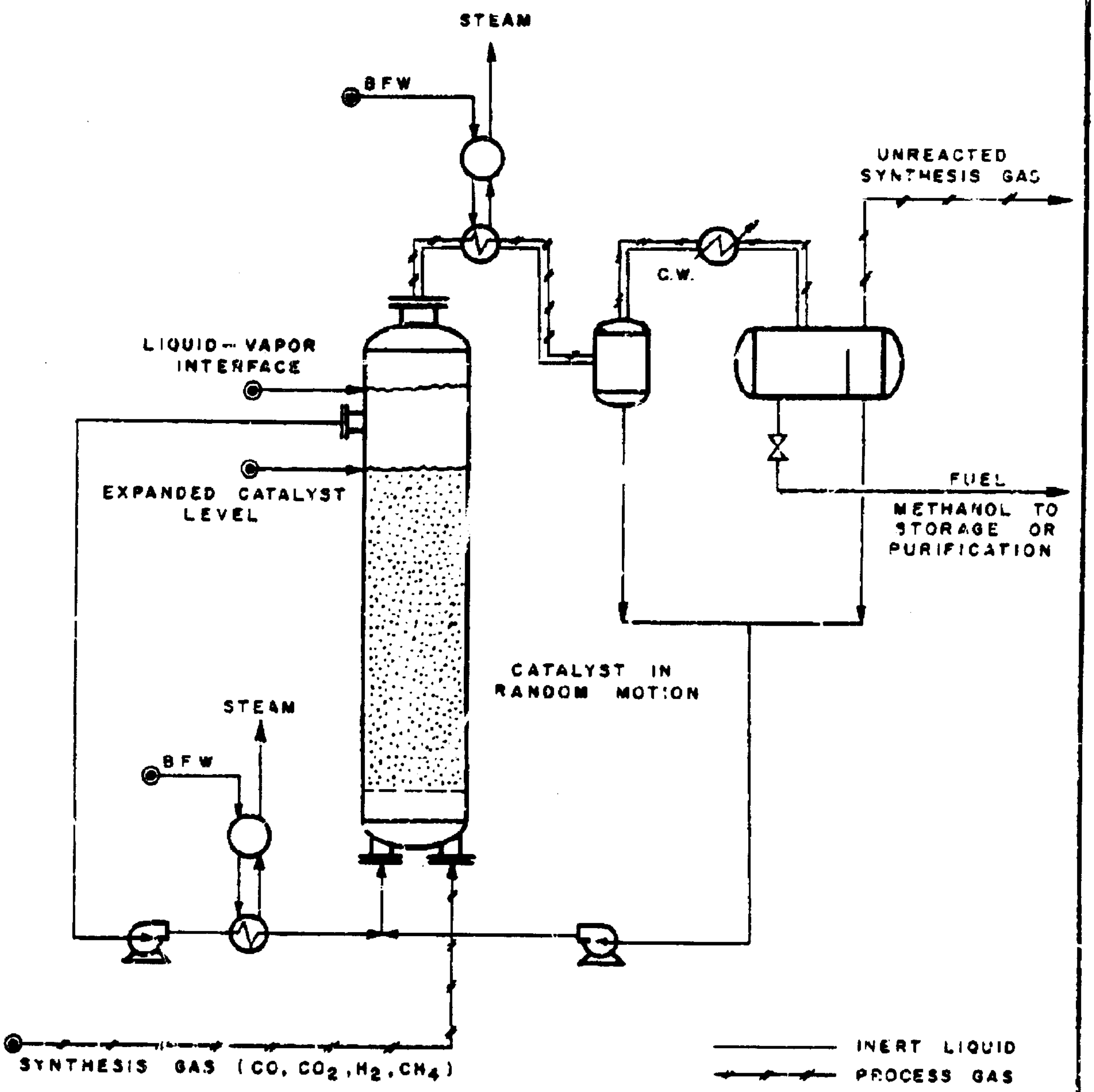

FIGURE 1-1

CHEM SYSTEMS INC.
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METHANOL
REACTION SYSTEM

NO. 226

The advantages of this reaction system are:

- The reaction temperature can be precisely controlled and maintained at levels which optimize the combination of both reaction rate and equilibrium conversions.
- Small sized catalyst particles can be used, maximizing reactor productivity.
- Catalyst can be easily added and withdrawn from the system to maintain activity at a constant desired level.

PROCESS APPLICATIONS

This new system holds the promise of improving the economics of present synthesis systems due to its ability to operate at very high gas conversions, which are close to equilibrium levels, while maintaining an essentially isothermal reactor.

Methanol fuel can be produced by such a plant for export to utility stations for intermediate and peak load plant use. Secondly, methanol production may be used as an efficient method of energy storage from coal-based gasification power plants. This would allow a gasifier to run at constant throughput, maximizing its efficiency, while demand fluctuations on the utility side can be followed by inventory changes in the energy storage systems. Synthesis gas produced from an oxygen-blown system can be used not only directly in a power plant, but also can be readily converted to storable energy. The production of methanol has several advantages:

- Methanol has already been successfully demonstrated as a fuel for peak-shaving turbines.
- Methanol can be incorporated into fuel cell systems.
- Methanol, as opposed to hydrocarbon liquids, has the highest ratio of stored energy/exothermic heat of formation.

ACCOMPLISHMENTS

Highlights of the Phase I program were:

- An automated Bench Scale Unit (BSU) was constructed for the program.
- Satisfactory inexpensive hydrocarbon liquids were demonstrated to be effective in the process.
- Commercial catalysts were shown to be suitable to the process though their physical form required alteration.
- At comparable conditions, methanol concentrations in the reactor exit gases are from 2-1/3 to 4 times greater than conventional processes can achieve.
- Simulated (sulfur free) coal product gases were utilized directly without the need for shift conversion.
- Single pass energy conversions to liquid forms of 25 to 35 percent were realized at 1000 psig. (The lower value is for a Lurgi gas which has over 40 percent of its energy in the form of methane which is non-reactive.)
- The reaction temperature for maximum catalyst productivity was found to be 220-250°C. The literature indicates that temperatures above 280°C lead to catalyst deactivation and less favorable equilibrium conditions.
- Reaction rates increase nearly proportionally with pressure in the range of interest.
- Catalyst productivity is inversely proportional to catalyst diameter in the one to two millimeter range.
- The presence of small quantities of CO_2 in the feed gas (1-3 percent) enhances catalyst productivity.
- Catalyst productivities (lb methanol/lb catalyst-hr) greater than that for commercial processes were realized.

In Phase II of this project, Chem Systems tested a number of operating variations of the Liquid Phase Methanol Synthesis and scaled up the operation by 50 fold to a larger Process Development Unit (PDU).

The following was found in relation to the operating variations tested:

- Chemical displacement of the methanol equilibrium by effecting a simultaneous reaction to form higher alcohols or ether detracted too greatly from the system's activity to be of value.
- Operation of a combined shift methanol reaction could be accomplished and would be applicable to hydrogen deficient gases.
- Slurry phase operation (with very fine catalyst) significantly increased catalyst activity.
- Increased production rates of methanol could be attained by flashing product from the recycled liquid.

In addition,

- Quantitative catalyst poisoning tests were run with olefins, sulfur, chlorine and nitrogen oxides.
- Catalysts developed during the program were tested and then used in a long duration activity maintenance test of over 600 hours duration.
- The process was scaled up 50 fold and operated in an existing PDU reactor system.
- A number of engineering studies were performed on the system.

The details of the Phase I and Phase II work are presented in this report.

SECTION 2

SUMMARY

Development work on Chem Systems' Liquid Phase Methanol Process started in early 1975 and continued through 1978. The major area of the development program included the following:

- Demonstration of concept feasibility
- Design, construction and operation of a three-phase bench scale unit
- Catalyst development
- Process variable studies
- Scale-up in a larger process development unit
- Long term continuous runs
- Engineering studies

DEMONSTRATION OF CONCEPT FEASIBILITY

One of the original premises for developing a new, more efficient methanol process was to allow the conversion of a certain percentage of coal-derived synthesis gas to a storable form, i.e., methanol, with minimal effect in the overall efficiency of both the coal conversion and methanol conversion processes. Based on synthesis gas compositions as would typically be obtained from Lurgi and Koppers-Totzek gasifiers, thermodynamic calculations indicated that from 10 to 30 percent of the Btu content of the gas could be converted to methanol in a single pass through a methanol synthesis reactor. Synthesis gas from a Lurgi gasifier, after acid gas and water removal, having a H_2/CO ratio of ~ 2/1 with 25% inerts (primarily CH_4) could give 10 to 20 percent conversion to methanol between 30 and 50 atmospheres. With Koppers-Totzek gas, on the other hand, containing a $H_2//CO$ ratio of ~0.6 and only 3 percent inerts, 15 to 30 percent conversion of its Btu content to methanol could be achieved.

These calculations were confirmed experimentally in a fixed bed reactor using the liquid phase system. Three different catalysts were tested in this unit using a paraffinic process liquid (WITCO 40 mineral oil). Feed gas compositions simulating the Lurgi and K-T coal gasifier synthesis gases were tested. In most of these tests, a slow cocurrent stream of mineral oil was fed with the feed gas. However, in some of these tests, the mineral oil was circulated around the system over the fixed catalyst bed.

The results of these initial tests proved:

- Commercial methanol catalyst could operate effectively in the presence of an inert liquid phase
- Methanol conversions could be obtained from a high CO containing feed gas (K-T) as well as from a more typical ($H_2/CO = 2$) methanol synthesis feed gas (LURGI)
- The methanol product produced could be phase separated from the hydrocarbon process liquid. The product purity remained consistently high, even at CO conversions of 30 percent per pass or greater.

THREE-PHASE BENCH SCALE UNIT

While the initial feasibility tests were being conducted in a small fixed bed unit, an automated bench scale reaction unit was designed and built. This system was designed for three-phase fluidized bed operation. The catalyst in the reactor is fluidized by the process liquid circulation. Synthesis gas feed is introduced along with the liquid at the bottom of the reactor. The system was constructed of 316 stainless steel and is capable of 1,000 SCFD. The process liquid superficial velocity can be varied from 20 to 100 gpm/ft^2 (0.04 - 0.22 ft/sec). Gas space velocity can be varied from 1,000 to 10,000 SCF/Ft^3 cat-hr. The reactor is a nominal 1" diameter tube by 6 feet long. The bench scale unit contains all equipment for heating and cooling feed and product gases, collecting the product methanol and recycling the process liquid. Analytical equipment is provided to continuously monitor reaction feed and effluent streams.

CATALYST DEVELOPMENT

In the first half of the development program, experimental runs were performed in the bench scale unit (BSU) using commercial methanol catalyst which was physically crushed from its original shape of 3/16" to 1/4" diameter tablets to irregular particles, sieved to give a size range of either 12 to 16 mesh ($\sim$1/16" dia.) or 16 to 20 mesh ($\sim$ 1/32" dia). A considerable number of process variable scans (described below) were conducted in the BSU using this crushed catalyst.

The second half of the development program was concerned with producing a catalyst particle that would be acceptable from both activity and attrition resistance for use in a liquid-fluidized three-phase reactor. In one series of tests, a catalyst vendor tried extruding and spheroidizing 1/16" dia. catalysts from the powder that is used to produce the commercial catalyst tablets used in vapor phase reactors. The extrudates produced were not of acceptable crush strength to warrant testing. An alternative approach was used by the catalyst vendor to produce 3/32" x 3/32" tablets (mini-tablets) in a variety of crush strengths and graphite addition levels. Several of these catalyst samples were run in the bench scale reactor. The results indicated that the activity was not as high as obtained with the crushed commercial catalyst. However, neither the crush strength nor the level of graphite had any significant effect on catalyst activity as measured by CO conversion. In addition, a 600-hour continuous run in a larger PDU (see below) with the 5 pound per square inch average crush strength catalyst indicated that its attrition resistance was not acceptable for a commercial catalyst.

More work needs to be done to develop a catalyst suitable for a liquid-fluidized reactor. This is being pursued under a separate EPRI contract. There is another viable approach to solve this problem. This is to use the catalyst powder directly in a catalyst liquid slurry system without producing tablets or extrudates. An added advantage of this approach is that some preliminary tests indicate that the catalyst activity of such a system would be enhanced several-fold over that obtained with the crushed commercial tablets.

PROCESS VARIABLE STUDIES

The experimental program conducted in the BSU investigated a large number of process variables as described in the following paragraphs.

Process Liquids

Three different types of process liquids were tested; aliphatic, aromatic and oxygenated. The first two were found to be suitable for use in the process. The aliphatic oil used in the experiments was a mineral oil with a carbon number range predominantly of C_{14} to C_{21}. The composition was 72 percent paraffinic, 28 percent naphthenic with an ASTM boiling range of 518° to 660°F. The aromatic oil had a composition of 73 percent C_{10}, 18 percent C_{11} with some lighter and heavier aromatic components. The boiling range was 360°F - 410°F. Ethylene glycol was the oxygenated hydrocarbon tested and it underwent rapid decomposition. The mineral oil is slightly preferred over the aromatic due to its lower vapor pressure. Also, methanol is less soluble in the mineral oil than in the aromatic, which may also contribute to higher system productivities.

Synthesis Gas Composition

Most of the experimental work was done with feed gases simulating either a Koppers-Totzek coal gasifier after acid gas removal or a Lurgi coal gasifier after complete H_2S removal and partial CO_2 removal. Other feed gas compositions were examined to investigate the reactivity of both CO and CO_2. For gas compositions where equilibrium calculations indicated that only CO should react to form methanol, a minimum amount of CO_2 is required in the feed gas to the synthesis reactor. This behavior is similar to other methanol synthesis processes. The CO_2 appears to behave as a catalyst promoter, significantly boosting CO conversion levels (close approach to equilibrium) while passing through without measurably reacting itself. On the other hand, with feed gases containing high levels of CO_2 (7 to 14 percent) and high H_2 concentration, ca. 75 percent, a substantial conversion of CO_2 to methanol is achieved; 60 to 90 percent of that predicted by equilibrium.

Alcohol Product Analysis

The methanol product composition produced in the Chem Systems' process is slightly affected by the feed gas composition. Feed gases with a H_2 to CO ratio less than the stoichiometric 2/1 ratio tend to produce more higher alcohols. Table 2-1 shows typical crude methanol compositions for a Lurgi feed gas and a Koppers-Totzek feed gas.

TABLE 2-1

Product MeOH Composition (*) (Weight percent)

	Lurgi Gas	Koppers-Totzek	
Component	BSU	BSU	PDU
Methanol	96.16	91.44	89.60
Methyl Formate	0.17	0.24	0.39
Ethanol	0.32	2.55	2.46
i-Propanol	tr	tr	tr
Methyl Acetate	0.07	0.78	1.02
n-Propanol	0.14	1.23	1.31
C_4 Alcohols	0.23	1.43	2.67
C_5 Alcohols	0.33	1.40	1.14
C_{6+} Alcohols	0.06	0.55	1.09
Water	2.71	0.51	0.33

(*) Oil-free basis, oil level is a function of composition (especially water concentration) and temperature. See Figure 8-14.

Maximizing CO Conversion to Alcohol

The addition of bases and acids as modifiers to the basic catalyst composition was investigated as a means of increasing the system productivity beyond what methanol equilibrium would allow. It was believed that base addition would increase the yield of higher alcohols while acid addition would promote the formation of dimethyl ether and other volatile ethers. Several catalyst formulations were prepared to test these alternatives. Neither approach met with any appreciable success and both approaches were terminated.

A physical means was investigated as another method of increasing methanol productivity. This involved removal of dissolved methanol from the process liquid stream before it is recirculated to the reactor. This could be done by reducing the pressure of the process liquid to allow the dissolved methanol to "flash" off. This methanol is then condensed and combined with the methanol product that would normally come out in the reactor vapor effluent.

The "lean" process liquid is repressured to reactor pressure to absorb additional methanol. Several experiments were performed confirming that this flash vaporization scheme can indeed work. However, a considerable amount of synthesis gas, which is also dissolved in the process liquid, is flashed off along with the methanol. An economic analysis of this scheme indicated that it has advantages in certain situations, i.e., where the synthesis gas flashed off need not be recompressed to reaction pressure.

Catalyst Particle Size

Since the initial process variable scans indicated that catalyst of nominal 1/32" diameter were more active than catalyst of nominal 1/16" diameter, a few runs were performed with even smaller catalyst particles; 0.21 - 0.30 mm diameter. The results indicated a 30 - 40 percent increase in catalyst activity. These tests were performed in the BSU which was not designed for small catalyst particles that will be entrained with the process liquids. The equipment must be modified in order to test a slurry phase system.

SCALE-UP IN A LARGER PROCESS DEVELOPMENT UNIT

A process development unit (PDU) built as part of the Liquid Phase Methanation development program was used for larger scale testing of the Liquid Phase Methanol process. The PDU has a 3.62" inside diameter by 7' high reactor and can handle synthesis gas feed rates of nominally 1500 SCFH. Operation in the PDU represents approximately a 50 fold scale-up from the BSU. Several runs were made in January, 1977 with a Lurgi-type feed gas composition using 3/32" diameter 5 pound crush strength catalyst mini-tablets. In two runs of 80 and 120 hours respectively, catalyst activity, as measured by CO conversion, declined faster than an analogous BSU run being done at the same time. This was later attributed to nickel and iron contamination of the catalyst. A third run of 120 hours was made with crushed vapor phase catalyst. Activity remained constant indicating that trace metal impurities had been scavenged from the system.

A 645 hour PDU run was performed in October - November, 1978 concurrent with a similar run in the BSU. Feed gas for this run simulated a Koppers-Totzek gas with an H_2/CO ratio of 0.6. A new batch of 3/32" diameter 5 pound crush strength mini-tablets was used. Process conditions were maintained at 250°C, 1000 psig and 3000 hr^{-1} space velocity. Initial results from the PDU were equivalent to BSU results. Catalyst attrition occurred throughout the PDU run indicating that the catalyst mini-tablet did not possess sufficient strength.

LONG TERM CONTINUOUS RUNS

Three long-term runs were performed. The first one was in the BSU and lasted for 605 hours. A Lurgi feed gas composition was used with 3/32" diameter, 5 pound crush strength mini-tablets. Catalyst activity declined slowly throughout the run, from an initial CO conversion of 40 percent to a final value of 30 percent. This could have been due to trace metal contamination of the catalyst or to an operating upset that occurred between the 115th and 130th hour. A Koppers-Totzek type feed gas was inadvertently used during this period, when feed gas cylinders were being switched. The CO conversion naturally dropped due to the lower H_2/CO ratio of the Koppers-Totzek gas. When the proper Lurgi feed gas composition was restored as feed, the CO conversion rose, but not to the level just prior to the feed gas switch. Over the next 250 hours, the CO conversion rose slightly and then slowly declined for the final 200 hours of operation.

The second and third long term runs were concurrent runs in the BSU and PDU respectively. Again, the 3/32" diameter, 5 pound crush strength catalyst mini-tablets were used. The feed-gas composition for these runs was Koppers-Totzek gas. The BSU run lasted for 720 hours. The CO conversion declined slowly from 16 percent initially to 11.5 percent at the end. The catalyst recovered from the BSU reactor was 95 percent of that initially loaded, with only slightly reduced catalyst dimensions. Despite the use of a zinc oxide guard chamber upstream of the methanol reactor, the spent BSU catalyst contained 480 ppm nickel and 600 ppm iron, contrasted with 15 ppm and 90 ppm levels in fresh catalyst.

The PDU run lasted for 645 hours. The catalyst removed was only 54 percent of that loaded. Inspection of individual recovered catalyst particles shows a physical reduction in size. The results of this run indicated that the catalyst mini-tablets used did not possess sufficient strength for the liquid-fluidized process. Additional work is required in catalyst development in order to improve attrition resistance for the liquid-fluidized mode of operation.

Spent catalyst from the PDU reactor also measured high levels of iron and nickel, indicating that some activity loss was due to contamination.

ENGINEERING STUDIES

Empirical Model

A preliminary empirical model was developed to correlate experimental results and to use for reactor scale-up and design studies. The model is based on calculating the CO conversion in terms of an approach to equilibrium (measured in ^{0}C) rather than as an absolute value. Experimental data for both Lurgi and Koppers-Totzek type feed gases were found to correlate well over a wide range of temperatures, pressures, space velocities and catalyst particle sizes. Actually, there were insufficient data for the Koppers-Totzek feed gas composition to make firm conclusions about relative catalyst activity. Additional experimental data are required to further test and refine the model.

Process Design Studies

During the development work, process design information was requested by several engineering contractors performing certain evaluation services for EPRI. The LPMeOH process was included as part of a coal conversion complex producing liquid fuels for several cases and as part of plant producing intermediate BTU gas and methanol for combined cycle power generation. The process design information prepared included process flow sheets, material balances, equipment specifications, overall energy balances, and catalyst and chemical requirements. The process designs covered a methanol production range of 2400 tons per day to 16,400 tons per day. The larger size plants required several parallel reactor trains.

An economic evaluation of the flash vaporization scheme was also performed. In addition, design information for this mode of operation was provided to another EPRI contractor who was evaluating the combined cycle power generation complex. Approximately 25 percent of the synthesis gas energy value was converted to methanol.

Section 3

DEMONSTRATION OF THE BASIC CONCEPT

PROCESS THERMODYNAMICS

There are two major reactions which normally occur in the production of methanol from synthesis gas:

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad (1)$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad (2)$$

Several side reactions do occur to some extent, particularly:

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad (3)$$

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \qquad (4)$$

Preliminary calculations have not included these latter two reactions because they unnecessarily complicate the presentation of the pertinent results and are usually negligable. In addition, the pair of reactions noted as Equations 1 and 2 can be written in an equivalent form that is far easier to manipulate analytically, that is:

$$CO + 2H_2 \overset{K_1}{\rightleftharpoons} CH_3OH \qquad (1)$$

$$CO_2 + H_2 \overset{K_2}{\rightleftharpoons} CO + H_2O \qquad (5)$$

For a given set of process conditions, the equilibrium compositions can now be calculated as follows: If X moles of CO react and Y moles of CO_2 react, then the feed and product composition are as shown in Table 3-1.

TABLE 3-1

EQUILIBRIUM COMPOSITIONS

Component	Feed Composition, Moles	Product Composition, Moles
Inerts	I^o	I^o
CO	CO^o	$CO^o - X + Y$
CO_2	CO_2^o	$CO_2^o - Y$
H_2	H_2^o	$H_2^o - 2X - Y$
H_2O	W^o	$W^o + Y$
CH_3OH	M^o	$M^o + X$
	Total^o	Total^o - 2X

The reaction equilibrium constants can be expressed in terms of the component concentrations as follows:

$$K_1 = \frac{K_{a_1}P^2}{K_{\gamma_1}} = \frac{(M^o+X)}{(CO^o-X+Y)} \cdot \frac{(\text{Total}^o-2X)^2}{(H_2^o-2X-Y)^2}$$

$$K_2 = \frac{K_{a_2}}{K_{\gamma_2}} = \frac{(CO^o-X+Y)}{(CO_2^o-Y)} \cdot \frac{(W^o+Y)}{(H_2^o-2X-Y)}$$

Here, K_a is the reaction equilibrium constant based on partial pressures of reactants at a total pressure of 1 atmosphere and K_γ is the fugacity ratio of the chemical reaction. K_a is a function of temperature only, while K_γ is a function of both temperature and pressure. The calculated values for these constants are given on the following page (for pressures less than 100 atmospheres). (1)

(1) CEP Symposium Series 98, Volume 66, pp. 54-68, 1970.

$$K_{a_1} = 3.27 \times 10^{-13} e^{11678/T}$$
$$K_{Y_1} = 1 - A_1P$$
$$A_1 = 1.95 \times 10^{-4} e^{1703/T}$$
$$K_{a_2} = 1.17 \times 10^{2} e^{-4827/T}$$
$$K_{Y_2} = 1 - A_2P$$
$$A_2 = 4.24 \times 10^{-4} e^{1107/T}$$

For any feed gas composition, temperature and pressure, Equations 6 and 7 can be solved for their equilibrium values of X and Y. The calculations performed by Chem Systems have initially been limited to synthesis gases from two coal gasification processes, Lurgi and Koppers-Totzek, which cover a wide variation in H_2/CO ratio. A typical synthesis gas composition for these two processes is shown in Table 3-2.

After acid gas removal (assuming 75 percent CO_2 and 100 percent H_2S removal) and condensation of water, the compositions are as shown in Table 3-3. Equilibrium calculations using these feed gas compositions were performed over a temperature range of 250°-300°C and a pressure range of 30-50 atmospheres.

In addition, for the Lurgi gas, the effect of (1) increasing the H_2 level to the stoichiometric amount required for complete reaction of CO and CO_2, and (2) removing additional CO_2 down to the 2 percent level was also examined. The feed composition for these additional cases is given in Table 3-4.

The results of these calculations can best be presented in terms of the percentage of Btu's available in the feed gas converted to a storageable energy form as a function of the process conditions. The heat of reaction liberated in the reactor is recovered as high pressure steam by heat exchange with the circulating process liquid. The energy recovered

TABLE 3-2

SYNTHESIS GAS COMPOSITION

Component	Lurgi	Koppers-Totzek
CH_4	6.92	-
C_2H_4, C_2H_5	0.63	-
N_2, Ar	0.20	0.90
CO	12.21	49.4
CO_2	18.05	6.2
H_2	24.23	30.92
H_2S	0.20	1.74
H_2O	37.56	10.70
	100.00	100.00

TABLE 3-3

METHANOL SYNTHESIS FEED GAS

Component	Case 1: Lurgi	Case 2: Koppers-Totzek
CH_4	14.17	-
C_2H_4, C_2H_6	1.29	-
N_2, Ar	0.41	1.08
CO	25.01	59.56
CO_2	9.26	1.89
H_2	49.63	37.24
H_2O	0.23	0.23
	100.00	100.00
H_2/CO	1.98	0.63
$H_2/(2CO + 3CO_2)$	0.64	0.30

TABLE 3-4

METHANOL SYNTHESIS FEED GAS

Component	Low Level CO_2 Case 3: Lurgi	Stoichiometric H_2 Case 4: Lurgi
CH_4	15.31	13.75
C_2H_4, C_2H_6	1.39	1.25
N_2, Ar	0.45	0.41
CO	27.01	12.12
CO_2	2.00	12.00
H_2	53.61	60.24
H_2O	0.23	0.23
	100.00	100.00
H_2/CO	1.98	4.96
$H_2/(2CO + 3CO_2)$	0.89	1.00

in this manner is roughly proportional to the conversion level and equal to about one-sixth of the storageable energy. Figures 3-1, -2, -3 and -4 review the individual case results, while Figures 3-5 and 3-6 show a direct comparison for the four different cases. Figure 3-7 shows the equilibrium conversion as a function of pressure at a constant temperature of 250°C. Note that for a recycle system with the Lurgi-derived synthesis gas, the results would be essentially the same since the actual inlet gas composition would remain unchanged. A recycle system employing a Koppers-Totzek derived synthesis gas would require extensive shifting prior to entering the synthesis loop.

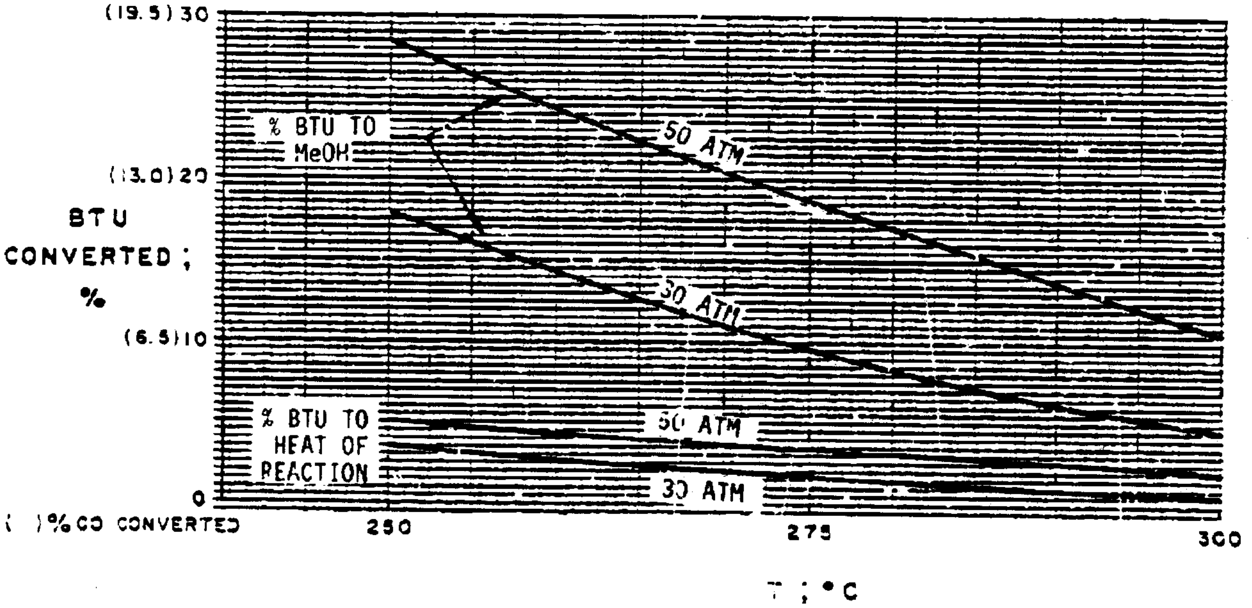
Both Figures 3-5 and 3-6 indicate that, in terms of storageable energy, the Koppers-Totzek synthesis gas provides the greatest degree of energy conversion. This is due primarily to two factors: (1) the methane content of a Lurgi-derived synthesis gas, about 15 volume percent, contains roughly one-third of the feed gas Btu's, all of which is unavailable for conversion to methanol, and (2) the methane content behaves much as a diluent in terms of the driving force for the reaction and hence lowers the ultimate equilibrium conversion level obtainable.

Still higher levels of conversion can be readily obtained by operating the synthesis loop at higher pressures. This can be most economically accomplished on a once-through basis with a Koppers-Totzek-derived synthesis gas and by a gas recycle system with a Lurgi-derived synthesis gas. The summary results presented in Figures 3-5, 3-6, and 3-7 also indicate that increasing the level of CO_2 removal prior to reaction results in a modest relative increase (~10 percent) in the storageable energy. On the other hand, incremental shifting without CO_2 removal of a Lurgi chemical synthesis gas sharply reduces the yield of storageable energy by about 25 percent.

FIGURE 3-1

EQUILIBRIUM CONVERSION — KT GAS

(AFTER ACID GAS AND WATER REMOVAL)



FEED COMPOSITION

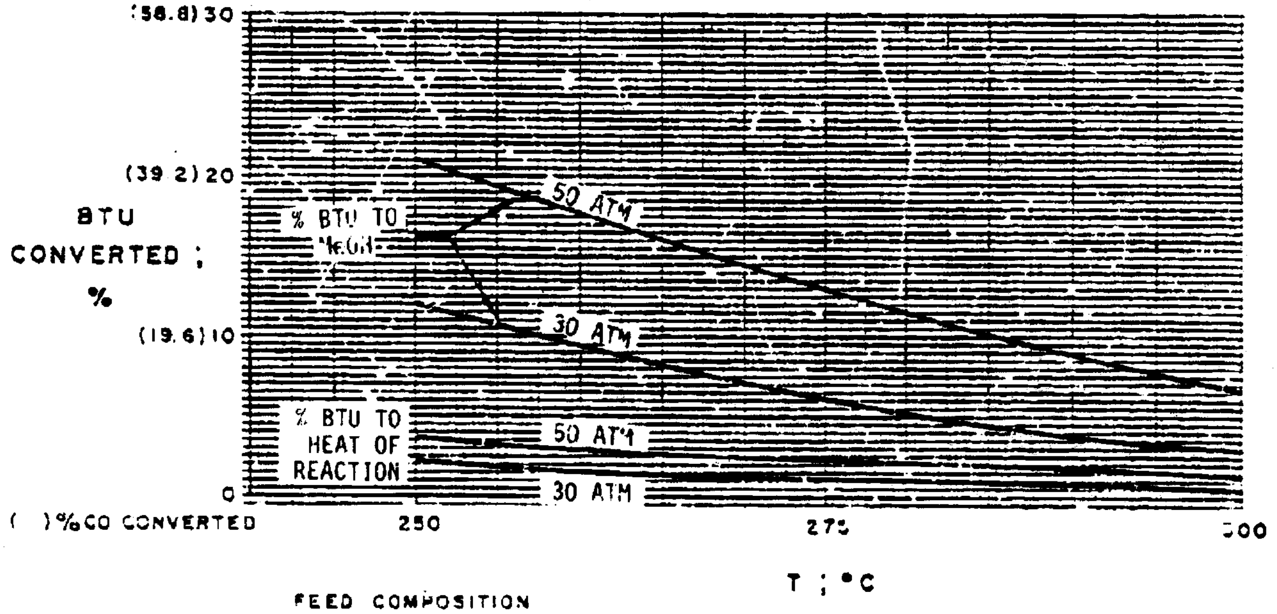
COMPONENT	MOLE %
N_2, Ar	1.08
CO	59.56
CO_2	1.89
H_2	37.24
H_2O	0.23

312 BTU/SCF

FIGURE 3-2

EQUILIBRIUM CONVERSION — LURGI GAS

(AFTER ACID GAS AND WATER REMOVAL)



FEED COMPOSITION

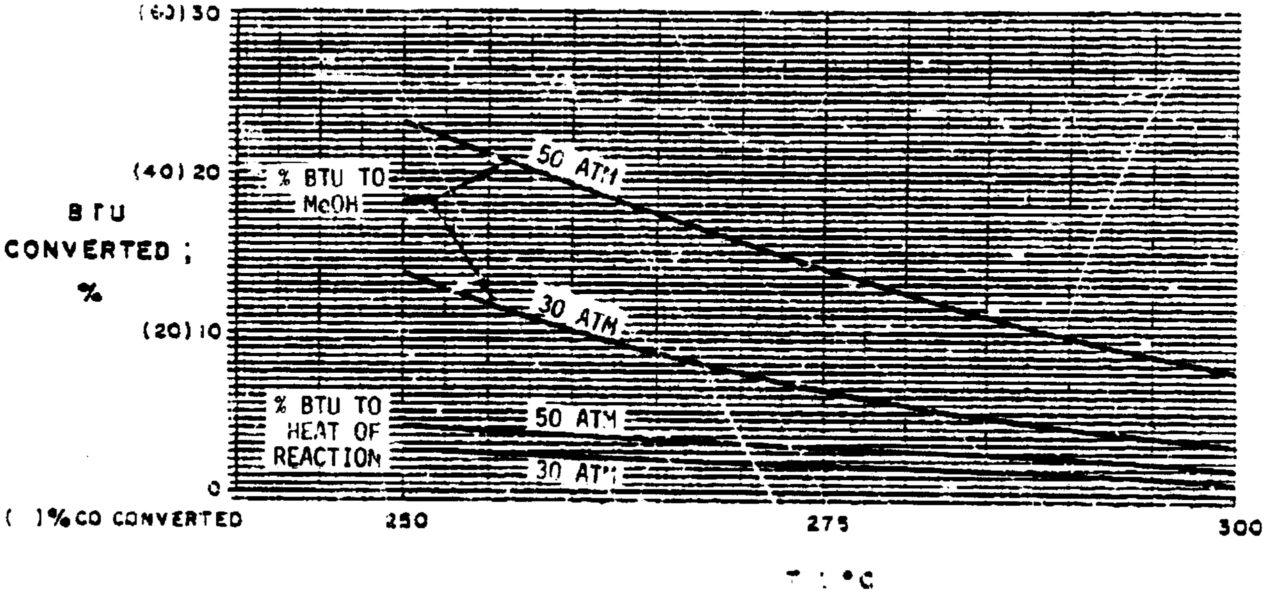
COMPONENT	MOLE %
N_2, Ar	0.41
CH_4	14.17
C_2, C_2'	1.29
CO	25.01
CO_2	9.26
H_2	49.63
H_2O	0.23

407 BTU/SCF

FIGURE 3-3

EQUILIBRIUM CONVERSION
LURGI GAS AFTER CO_2 REMOVAL

(AFTER ACID GAS AND WATER REMOVAL, CO_2 = 2 %)



FEED COMPOSITION

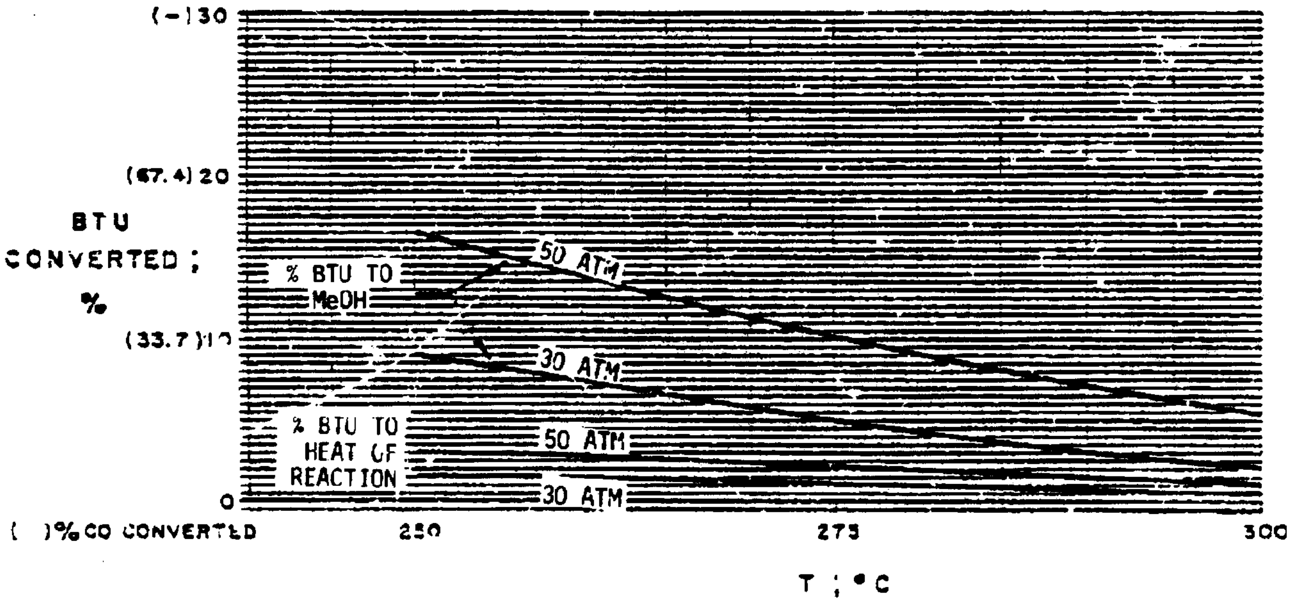
COMPONENT	MOLE %
N_2, Ar	0.44
CH_4	15.31
C_2, $C_2^=$	1.39
CO	27.01
CO_2	2.00
H_2	53.61
H_2O	0.23

440 BTU/SCF

FIGURE 3-4

EQUILIBRIUM CONVERSION
LURGI BALANCED GAS

(65.5% SHIFTED AT 900°F AND 30ATM TO GIVE
$[H_2/(2CO+3CO_2)]=1$ AFTER ACID GAS AND
WATER REMOVAL)



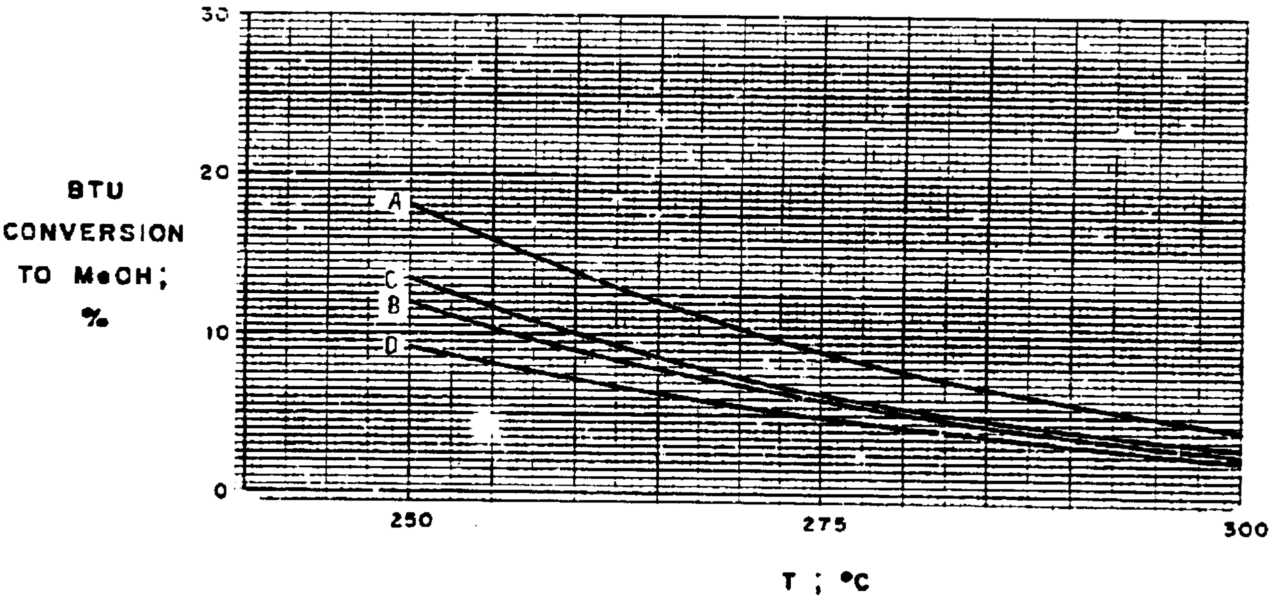
FEED COMPOSITION

COMPONENT	MOLE %
N_2, Ar	0.40
CH_4	13.75
C_2, $C_2^=$	1.25
CO	12.14
CO_2	12.00
H_2	60.26
H_2O	0.23

395 BTU/SCF

FIGURE 3-5

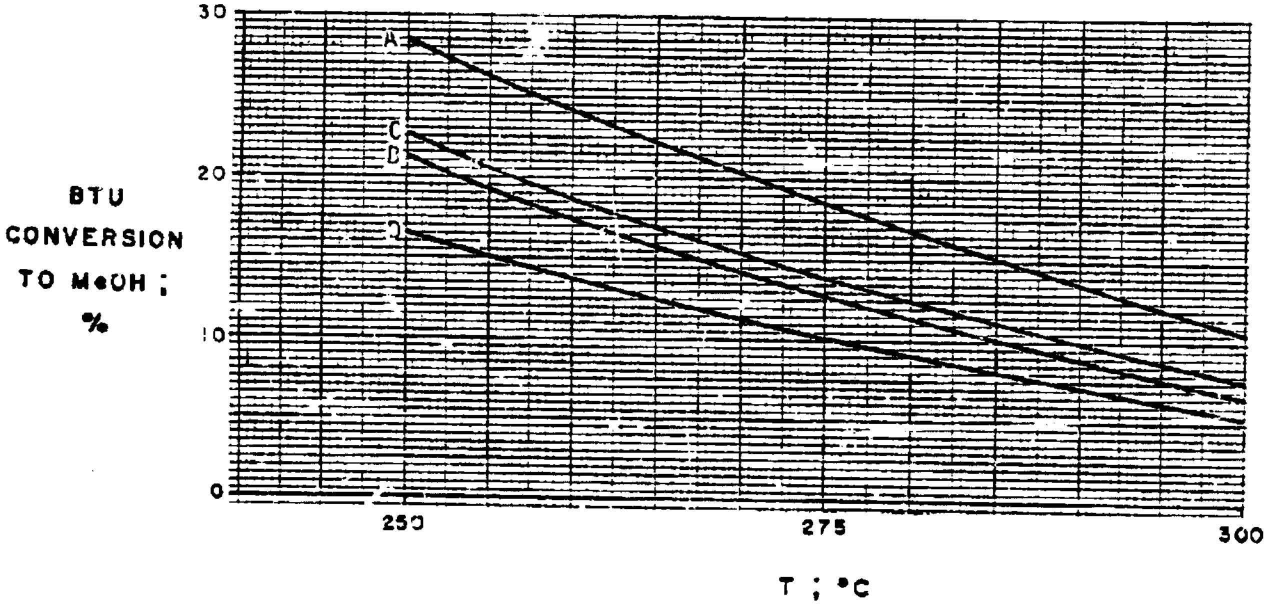
EQUILIBRIUM CONVERSION
CASE SUMMARY AT 30 ATM



A KOPPERS-TOTZEK (ACID GAS AND WATER REMOVAL)
B LURGI (ACID GAS AND WATER REMOVAL)
C LURGI (ACID GAS AND WATER REMOVAL - CO_2 = 2%)
D LURGI (SHIFTED, ACID GAS AND WATER REMOVAL)

FIGURE 3-6

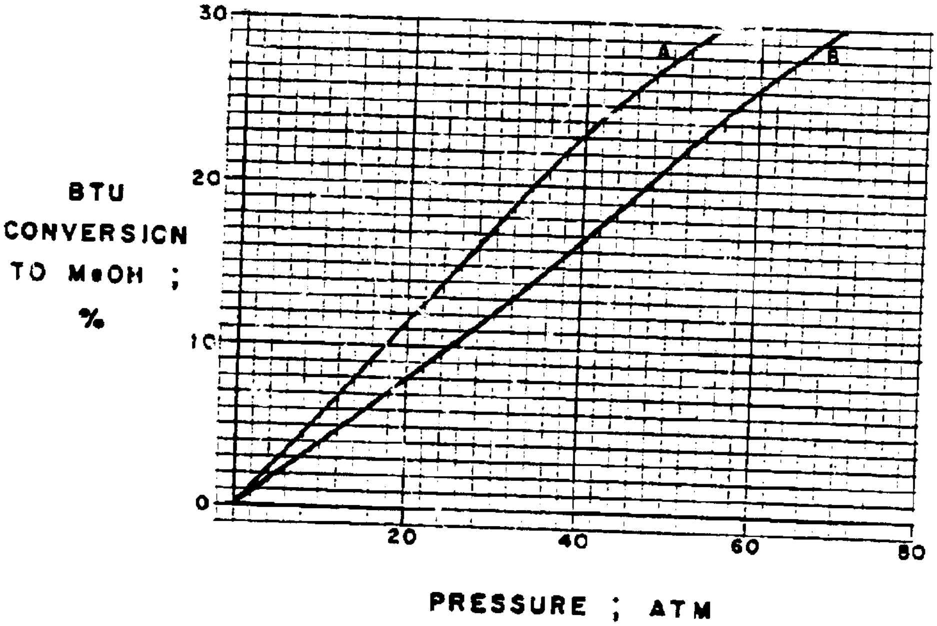
EQUILIBRIUM CONVERSION
CASE SUMMARY AT 50 ATM



A	KOPPERS - TOTZEK	(ACID GAS AND WATER REMOVAL)
B	LURGI	(ACID GAS AND WATER REMOVAL)
C	LURGI	(ACID GAS AND WATER REMOVAL - CO_2 = 2%)
D	LURGI	(SHIFTED, ACID GAS AND WATER REMOVAL)

FIGURE 3-7

EQUILIBRIUM CONVERSION
CASE SUMMARY AT 250°C



A KOPPERS – TOTZEK (ACID GAS AND WATER REMOVAL)
B LURGI (ACID GAS AND WATER REMOVAL)