膨胀机装置中利用甲醇控制水化作用*

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内容提要: 本文为利用甲醇控制天然气水化作用的透平膨胀机装置提供了设计资料。内容主要包括: 水化物的一般特性; 利用甲醇或乙二醇降低水化作用, 以及通过图表和克劳休斯—克莱普朗 (Clausius-Clapeyron) 近似公式表达水化点降与冰点降之间的关系; 运用哈默施密特 (Hammerschmidt) 公式, 预测一般天然气与防冻剂的稀水溶液接触时, 水化点降的半经验公式; 用于浓甲醇的哈默施密特修正公式; 注入和回收甲醇的工艺流程; 膨胀机装置中利用甲醇控制水化物系统的基本设计步骤和计算实例; 甲醇脱水同固体床脱水的经济比较等。文章最后指出: 用甲醇注入装置处理含水量低 (4磅水/百万标准立方英尺) 的天然气同用活性铝脱水装置相比, 其投资和运行费用均较低。当处理天然气规模为20亿或1.2亿标准立方英尺/日时, 其结论都一样; 用甲醇脱水装置处理高含水天然气 (23磅水/百万标准立方英尺) 比用分子筛脱水装置投资少, 而两者的运行费用却大体相同。本文还附有有关的计算图表和曲线。

Use of Methanol for Hydrate Control in Expander Plants**

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INTRODUCTION

The first turboexpander plant, designed and built by Fluor in 1963 for Coastal States Gas Producing Company, used methanol for hydrate control.[1,2] Since then the majority of expander installations have used

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solid bed dehydration. The reasons for this are obscure, especially since in many instances methanol grants greater ease of operation as well as lower capital and operating costs. This is particularly true when the water content of the feed gas is low or when recompression is required.

This paper presents design information for turboexpander plants using methanol for hydrate control. Hopefully, this information will permit users to take advantage of cost savings available when the use of methanol for hydrate control is appropriate.

HYDRATES—GENERAL

Natural gas generally contains water before processing. High pressure, low temperature, or both favor the combination of water with light hydrocarbon gases to form hydrates. Hydrate forming gases include the C_1 to C_4 paraffins and olefins, carbon dioxide, and hydrogen sulfide while hydrocarbons higher than isobutane do not form hydrates. Free water must always be present for hydrates to form.

Hydrates, which are solid crystals resembling wet snow, cause problems by plugging pipelines, valves, and other process equipment. Therefore, proper equipment design requires the accurate prediction of the limiting conditions at which hydrates are formed from a gas of given composition, i.e., the hydrate point. As a general rule, the hydrate point should be evaluated anytime a gas stream containing hydrate formers and free water is cooled below 80°F.

HYDRATE DEPRESSION

It is well known that primary or polyfunctional alcohols, e.g., methanol or glycols, can be used as antifreeze agents to depress the freezing point of water. Alcohols also depress the hydrate formation temperature of a hydrate forming gas. There is an unfortunate tendency to confuse the two phenomena.

Consider the phase diagram for the water-methanol system as shown in Figure 1.[3] If a 25 weight percent aqueous methanol solution (about 16 mole percent) is cooled without any hydrate forming gases present, ice begins to form at −20°C (-4°F). Since pure water freezes at 32°F, methanol depresses the ice point 32°F − (-4°F) or 36°F, while −4°F is defined as the depressed ice point.

Consider the same 25 weight percent methanol solution in contact with a typical gas at 1000 psia. According to experiments conducted by Hammerschmidt[4], this gas formed a hydrate at 63°F when in contact with

pure water. In another experiment, the same gas at 1000 psia formed a hydrate at 39°F when in contact with a 25 weight percent aqueous methanol solution. The normal hydrate point is defined to be 63°F while the depressed hydrate point is 39°F and the hydrate depression is 63°F − (39°F) or 24°F. Figure 2 summarizes Hammerschmidt's experiments.

Examining Figure 2, we observe that the normal and depressed hydrate points are pressure dependent, but that the difference between these two temperatures, the hydrate depression, is presssure independent.

Also note that the hydrate depression of a 25 weight percent methanol solution, 24°F, is less than the ice point depression, which is 36°F. *In general, the hydrate depression is always less than the ice point depression.*

This can be shown on a phase diagram. For example, if the hydrate locus for a typical natural gas is plotted on a ln P versus T diagram, the result will be similar to Figure 3 which is the phase diagram for the ethane-water system.[5]

On Figure 3:

S = Ice phase

H = Hydrate phase

G = Hydrocarbon vapor phase

L_1 = Water-rich liquid phase

L_2 = Hydrocarbon-rich liquid phase

If a small amount of solute, such as methanol, is added to the water-rich phase, the line SLG, the water-ice-hydrocarbon vapor locus, is displaced a distance ΔT and the line L_1HG, the water-hydrate-gas locus, is displaced a distance $\Delta T'$ as shown in Figure 4.

Note that by inspection Figure 4 shows that $\Delta T'$, the hydrate depression, is less than ΔT, the ice point depression. In fact, using Figure 4 and the Clausius-Clapeyron equation it can be shown that the relationship between ΔT, the freezing point depression of the water-ice line, and the depression of the water-hydrate line, $\Delta T'$, is approximately:

$$\Delta T' \simeq \Delta T (1 - \frac{\Delta H_2}{\Delta H_1})$$

where:

$\Delta T = T_0 - T$

$\Delta T' = T_0 - T'$

ΔH_2 = the heat of transition $S + G \rightleftharpoons H$

ΔH_1 = the heat of fusion for $L_1 + G \rightleftharpoons H$

T′ = hydrate forming temperature

T = ice forming temperature

T_0 = normal quadruple point

As ΔH_2 is less than ΔH_1, the hydrate depression of a given solution is always less than the ice point depression. Therefore, it must be emphasized that while there is a relationship between hydrate and ice formation, *freezing curves such as Figure 1 cannot be used for design without some modification*.

THE HAMMERSCHMIDT EQUATION

In the 1930's Hammerschmidt presented a semi-empirical equation for predicting the hydrate depression of typical natural gases in contact with dilute aqueous solutions of antifreeze agents such as methanol or any glycol.[4] Hammerschmidt's equation is:

$$\Delta T = \frac{2335W}{100M - MW}$$

where:

M = the molecular weight of the antifreeze agent, e.g., methanol

W = the weight percent of the antifreeze agent in the solution

ΔT = the hydrate depression or the difference between the normal and depressed hydrate point in °F

The origin of this equation is the relationship for the freezing point depression of an ideal solution.[6]

$$\Delta T \simeq \frac{RT_0^2}{\Delta H} \ln\left(1 + \frac{N}{S}\right)$$

where:

ΔT = the freezing point depression

T_0 = the normal freezing point (absolute temperature)

ΔH = the enthalpy of fusion per mole of solvent

N = moles of solute (antifreeze agent)

S = moles of solvent

R = the gas constant

If the solution is dilute, N is smaller than S and the logarithm can be expanded in terms of N/S.

$$\ln\left(1 + \frac{N}{S}\right) = \frac{N}{S} - \frac{1}{2}\left(\frac{N}{S}\right)^2 + \frac{1}{3}\left(\frac{N}{S}\right)^3 - \cdots\cdots$$

For very dilute solutions where N is very small, all powers of N/S above the first can be neglected and:

$$\Delta T \simeq \frac{RT_0^2}{\Delta H} \times \frac{N}{S}$$

Now:

$$\frac{N}{S} = \frac{WM_1}{100M - MW}$$

where M_1 is the molecular weight of the solvent and the other variables are defined as before.

Therefore:

$$\Delta T = \frac{M_1 RT_0^2}{\Delta H} \times \frac{W}{100M - MW}$$

Using a typical natural gas and various dilute solutions, Hammerschmidt fitted this equation to hydrate depression and solution concentration data to obtain:

$$\frac{M_1 RT_0^2}{\Delta H} = 2335$$

or

$$\Delta T = \frac{2335W}{100M - MW}, \ \Delta T \text{ in } °F$$

The Hammerschmidt equation *applies only to typical natural gases and to solute concentrations less than* 0.20 *mole fraction.* Glycol injection systems operating down to -10°F fall within these limitations.

Surprisingly, operating data show that the Hammerschmidt equation can be used to design glycol injection systems operating at temperatures as low as -40°F or -50°F requiring about 0.4 mole fraction ethylene glycol.[5] The success of the equation at these conditions seems to be due to a number of compensating factors; the most important of these has to be the strong negative deviations from Raoult's law that water exhibits in glycol solutions.*

THE MODIFIED HAMMERSCHMIDT EQUATION
FOR CONCENTRATED METHANOL

As discussed earlier, the Hammerschmidt equation can be expressed as:

$$\Delta T = \frac{RT_0^2}{\Delta H} \ln X_{water}$$

Since $\ln(1 + \frac{N}{S}) = -\ln X_w$

*Design data given in standard glycol design references such as Dow's **Gas conditioning Fact Book** are actually plots of the Hammerschmidt equation.

Therefore, using earlier results:

$$\Delta T = -\frac{2335}{M_1} \ln X_{water}$$

Now $M_1 = 18.02$ and $X_{water} = 1 - X_{MeOH}$
Therefore:

$\Delta T = -129.6 \ln (1 - X_{MeOH})$, wherein ΔT is in degrees Fahrenheit is a form of the Hammerschmidt equation more appropriate for concentrated methanol solutions. Although this equation is an approximation, experience has shown that it can be used for the design of practical methanol hydrate control systems operating as low as -160°F.

The following table gives the hydrate depression, ΔT, in °F and °C as obtained from the modified Hammerschmidt equation as a function of methanol concentration.

Table I

X_{MeOH} Mole Fraction	wt % MeOH	ΔT °C	ΔT °F
0.0	0.0	0.0	0.0
0.1	16.5	7.6	13.7
0.2	30.8	16.1	28.9
0.3	43.2	25.7	46.2
0.4	54.2	36.8	66.2
0.5	64.0	49.9	89.8
0.6	72.7	66.0	118.8
0.7	80.6	86.7	156.0
0.8	87.7	115.9	208.6
0.835*	90.0*	129.7*	233.5*

*Approximately 0.835 mole fraction methanol or 90 weight percent methanol gives the maximum hydrate depression available as with methanol concentrations greater than this, solid methanol begins to form. See Figure 1 and Figure 7.

This table can be used to set the methanol concentration required for hydrate control. In most cases the methanol concentration is set at 90 weight percent. The maximum hydrate depression recommended for design is the calculated depressed hydrate points plus 35°F. See Figure 7 and

the sample calculation for the use of these data. Note that the depressed
hydrate point locus for the sample calculation gas intersects the solid
methanol curve at -113.5°C. Obviously it is academic if a hydrate could
exist below this temperature since solid methanol would start plating
out in the equipment. Methanol injection control for expander outlet
temperatures below -102°C must be more accurate in order to keep the aqueous
methanol concentration above the freezing line in the eutectic range. The
recommended 35°F safety margin for the maximum hydrate depression will
keep the designer out of the eutectic range and out of trouble in almost
all situations.

Operating temperatures colder than -160°F are possible, but design
for these conditions is beyond the scope of this paper. In this realm,
the safety margin of 35°F is often no longer available and the modified
Hammerschmidt equation is no longer appropriate. A more exact form
of the freezing point depression equation should be used. [7]

$$\ln (\gamma X) = \frac{\Delta H}{RT} (\frac{T}{T_0} - 1) + \frac{\Delta C_p}{R} (\frac{T_0}{T} - 1) + \frac{\Delta C_p}{R} \ln (\frac{T}{T_0})$$

TYPICAL METHANOL INJECTION SYSTEM

Figure 5 shows a typical methanol injection and recovery system found
in a cold oil absorption or turboexpander plant. Feed gas is passed
through a free-water knockout drum and into a gas-gas exchanger and
provisions are also made to spray methanol on the exchanger tubesheets.
The methanol inhibits hydrate formation as an aqueous methanol solution
condenses in the exchanger and chiller. The methanol water solution is
removed from the separator and sent to the methanol still for methanol
recovery. A significant amount of methanol will dissolve in the hydrocar-
bon liquid. Essentially all this methanol will appear in the propane
product if the hydrocarbon liquid is fractionated. To recover the dissolv-
ed methanol, water from the methanol still bottoms is used to wash
either the propane product or the raw hydrocarbon liquid from the
demethanizer. If the raw liquid is recovered and fractionated at the same
location, it is usually more economical to wash the propane product.

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Conference, Norman, Oklahoma, 1972.

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FIGURE 1
SOLID – LIQUID PHASE DIAGRAM
OF THE METHANOL – WATER
SYSTEM
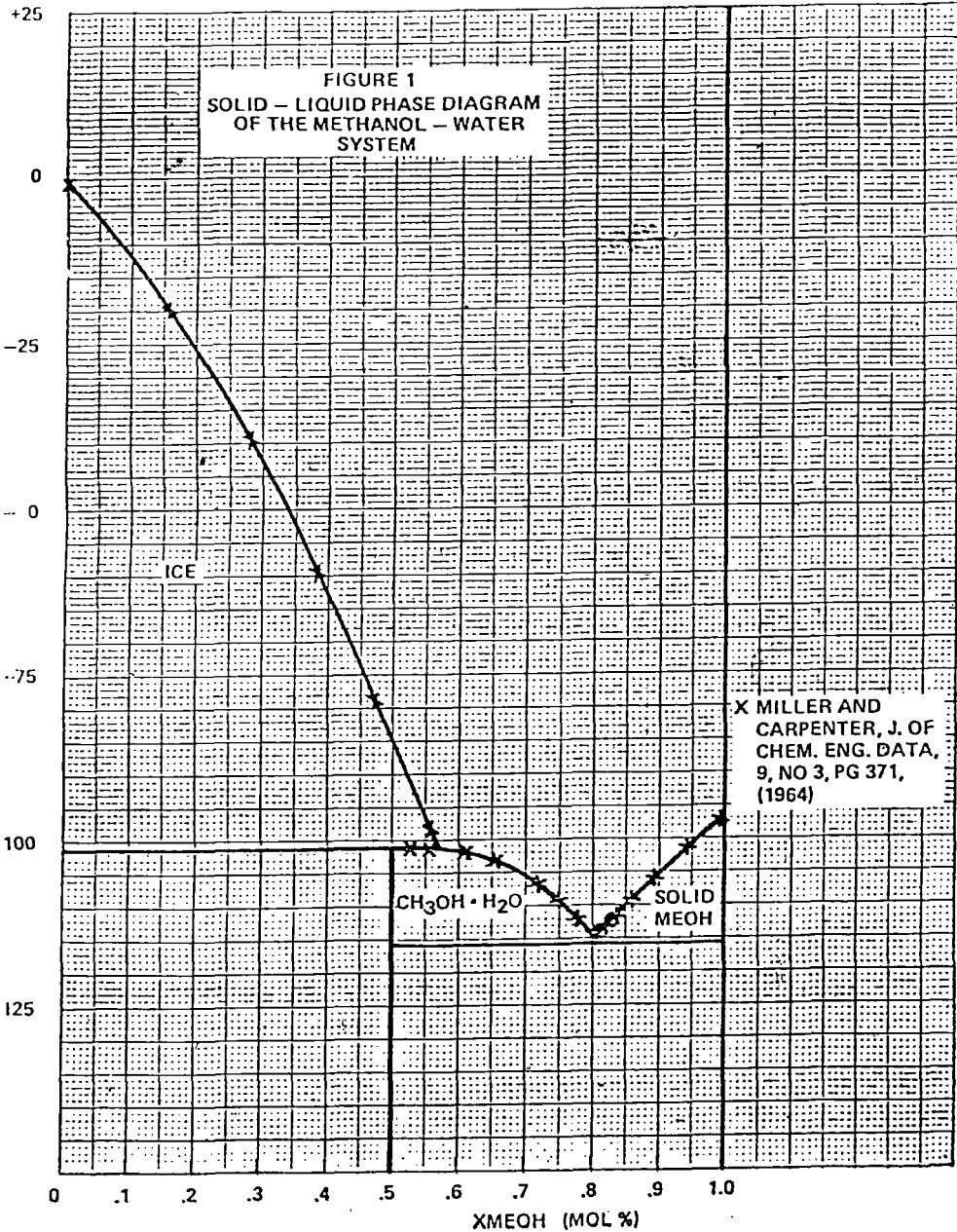
5. Reamer, H. H., Selleck, F. T. and Sage, B. H., "Some Properties of Mixed Paraffinic and Olefinic Hydrates, " **Petroleum Transactions**, 195, pg. 197 (1952).

6. Adam, N. K., **Physical Chemistry**, Oxford University Press, 1956, pg. 284.

7. Prausnitz, J. M., **Molecular Thermodynamics of Fluid Phase Equilibrium**, Prentice Hall, 1969, pp. 388-391.

FIGURE 2

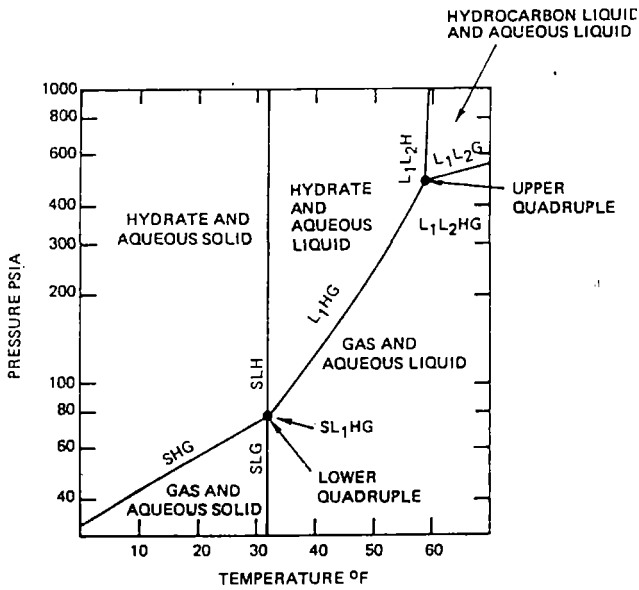FREEZING POINT LOWERING OF GAS HYDRATES IN METHANOL SOLUTION.
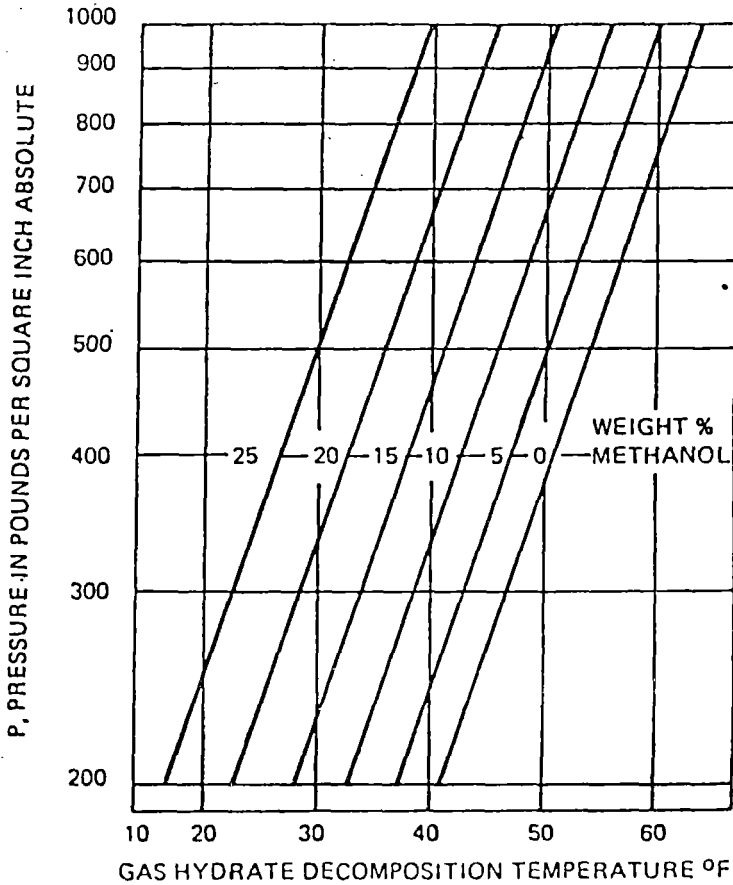
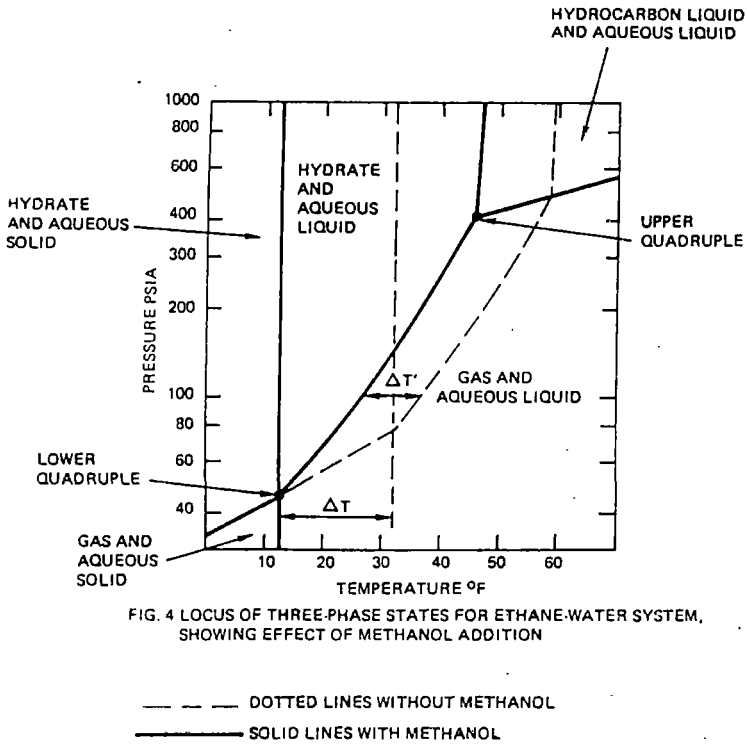FIG. 3 LOCUS OF THREE-PHASE STATES FOR ETHANE WATER SYSTEM.

FIG. 4 LOCUS OF THREE-PHASE STATES FOR ETHANE-WATER SYSTEM, SHOWING EFFECT OF METHANOL ADDITION

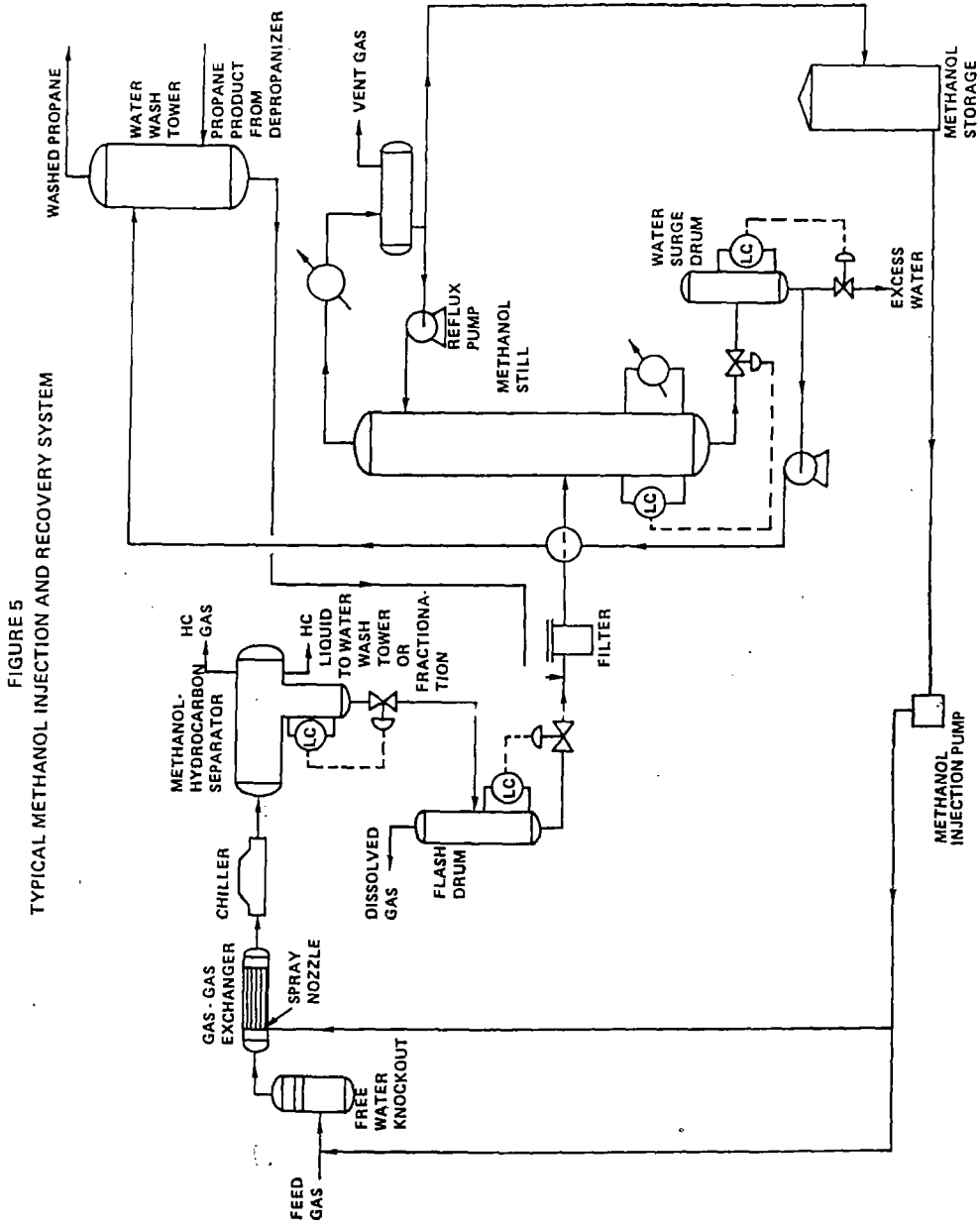— — — DOTTED LINES WITHOUT METHANOL

———— SOLID LINES WITH METHANOL

FIGURE 5

TYPICAL METHANOL INJECTION AND RECOVERY SYSTEM

WASHED PROPANE

WATER WASH TOWER

PROPANE PRODUCT FROM DEPROPANIZER

VENT GAS

METHANOL STORAGE

WATER SURGE DRUM

LC

EXCESS WATER

REFLUX PUMP

METHANOL STILL

LC

LC

FILTER

METHANOL-HYDROCARBON SEPARATOR

HC GAS

HC LIQUID TO WATER WASH TOWER OR FRACTIONA-TION

C

DISSOLVED GAS

FLASH DRUM

LC

CHILLER

GAS-GAS EXCHANGER

SPRAY NOZZLE

FREE WATER KNOCKOUT

FEED GAS

METHANOL INJECTION PUMP