BNL 51075 212 3-20-80

DR. 918

MASTER

ALTERNATIVE PROCESS SCHEMES FOR COAL CONVERSION

PROGRESS REPORT NO. 2
FEBRUARY 1 - APRIL 30, 1979

May 1979

PROCESS SCIENCES DIVISION
DEPARTMENT OF ENERGY AND ENVIRONMENT

BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.

UNDER CONTRACT NO. EY-76-C-02-0016 WITH THE
UNITED STATES DEPARTMENT OF ENERGY

bnl
aui

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

BNL 51075
UC-90
(Coal Conversion and Utilization -
TID-4500)

MASTER

ALTERNATIVE PROCESS SCHEMES FOR COAL CONVERSION

PROGRESS REPORT NO. 2
FEBRUARY 1 - APRIL 30, 1979

Principal Investigator: MICHAEL J. SANSONE

Contributors:
Anthony S. Albanese
Meyer Steinberg

Work performed for
OFFICE OF FOSSIL ENERGY,
U.S. DEPARTMENT OF ENERGY
WASHINGTON, D.C. 20545

MEYER STEINBERG, HEAD
PROCESS SCIENCES DIVISION
DEPARTMENT OF ENERGY AND ENVIRONMENT

BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

NOTICE

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
50
Price: Printed Copy ~~$4.50;~~ Microfiche $3.~~00~~
6.00
October 1979 300 copies

Table of Contents

Summary

A conceptual process for the separation of H_2/CH_4 and $H_2/CO/CH_4$ mixtures using gas hydrates is outlined. A flowsheet has been developed and material and energy balances completed. The process energetics are then compared with a simple single stage partial liquefaction scheme for H_2/CH_4 separation. The gas hydrate separation requires about 50% more energy but becomes more competitive if the gasification process is operated at pressures above the assumed 500 psia. The lack of kinetic data makes it impossible to determine if the process is kinetically feasible, but design calculations for a range of rates have been included.

Introduction

In the first progress report, the importance of gas separation methods to the economics of hydrogasification and catalytic gasification processes was emphasized. This importance is due to the fact that these processes require large amounts of recycled hydrogen or hydrogen and carbon monoxide from which the product methane must be removed via some economical method. For example, the Exxon catalytic gasification process utilizes a cryogenic distillation to achieve the separation of CH_4 from H_2 and CO.

In this report, the energetics of a cryogenic separation process for hydrogen-methane mixtures are calculated and compared with the energy requirements for the separation of H_2/CH_4 and $H_2/CO/CH_4$ mixtures using a gas hydrate separation scheme. It must be stated at the outset that the success of the proposed hydrate process depends upon the kinetics of hydrate formation for which we have no data. Nevertheless, it is still worthwhile to examine such a process within a thermodynamic framework to determine if such a scheme is at least energetically, if not kinetically, feasible.

Cryogenic Separation

The separation of a mixture of H_2 and CH_4 via a single stage condensation process is illustrated in Figure 1. Since the vapor-liquid equilibrium constants (K=y/x) are very different for these two gases, high degrees of separation are achievable without the use of further rectification. Following the procedure described in King,[1] the equations for calculating the compositions and relative amounts of the vapor and liquid streams in the separation drum are

$$x_{H_2} = \frac{1-K_{CH_4}}{K_{H_2}-K_{CH_4}}$$

$$y_{H_2} = K_{H_2} x_{H_2}$$

$$V/F = \frac{z_{H_2}-x_{H_2}}{y_{H_2}-x_{H_2}}$$

where z_{H_2} = mole fraction H_2 in the feed F

y_{H_2} = mole fraction H_2 in the vapor V

x_{H_2} = mole fraction H_2 in the liquid L

The results of some of these calculations are given in Table 1. From the first twelve rows it can be seen that the percent methane recovered increases with decreasing temperature and with increasing pressure. In all these cases, however, the residual hydrogen (up to 6% in the product stream) is a potential problem since current government restrictions on pipeline gas require 1% H_2 or less. King shows that the energy required for refrigeration in this single stage process is given roughly by the latent heat of vaporization of methane at the existing process pressure. This means that the latent heat is not recoverable in the exchanger since it is available at too high a temperature.

Consider row 7 in Table 1. The energy required for operating the separation process at -250°F and 500 psia is calculated from the latent heat of CH_4 (λ_{CH_4}) by assuming a Carnot refrigeration cycle operating between ambient temperature and -250°F.

$$W = Q \frac{T_a - T_{ref}}{T_{ref}}$$

At 500 psia, λ_{CH_4} = 1664 Btu/lb-mole so that Q = 1664 Btu/lb-mole x 0.4 $\cong$ 666 Btu/lb-mole feed. Therefore

$$W = (666) \frac{530-210}{210} = 1015 \text{ Btu/lb-mole feed}$$

If it is further assumed that typical refrigeration cycles operate at 40% of the Carnot efficiencies (see Dodge[2]), then

W = 2538 Btu/lb-mole feed = 7169 Btu/lb-mole CH_4 = 3983 cal/g-mole CH_4

The separation step is shown in Figure 2. The fraction of methane recovered in the product liquid is given by

Table 1

Effect of Temperature, Pressure, and Feed Composition on H_2/CH_4 Separation

Basis: 1 mole feed

	T(^{o}F)	P(psia)	K_{CH_4}	K_{H_2}	z_{CH_4}	V	y_{CH_4}	L	x_{CH_4}	% CH_4 Recovered in L Stream
1	-200	500	0.37	19	0.4	0.931	0.354	0.069	0.966	16.7
2	-200	500	0.37	19	0.5	0.766	0.354	0.234	0.966	45.2
3	-220	200	0.32	50	0.4	0.874	0.316	0.126	0.986	31.2
4	-240	200	0.20	61	0.4	0.743	0.197	0.257	0.986	63.3
5	-250	200	0.14	70	0.4	0.692	0.138	0.308	0.988	76.1
6	-250	300	0.10	46	0.4	0.658	0.098	0.342	0.980	83.9
7	-250	500	0.075	31	0.4	0.635	0.073	0.365	0.970	88.5
8	-250	500	0.075	31	0.5	0.524	0.073	0.476	0.970	92.3
9	-250	1000	0.06	15	0.3	0.723	0.056	0.277	0.937	86.5
10	-250	1000	0.06	15	0.4	0.610	0.056	0.390	0.937	91.4
11	-250	1000	0.06	15	0.5	0.496	0.056	0.504	0.937	94.4
12	-297	500	0.014	48	0.3	0.704	0.014	0.296	0.980	96.7
13	-297	500	0.014	48	0.4	0.600	0.014	0.400	0.980	98.0
14	-297	500	0.014	48	0.5	0.497	0.014	0.503	0.980	98.0

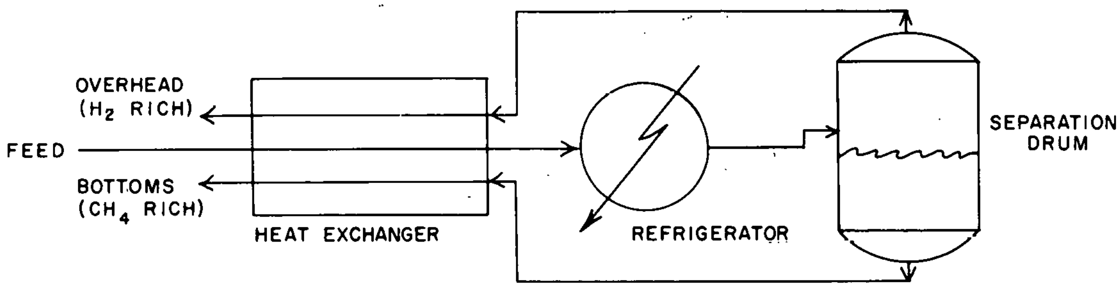


Figure 1. Single stage partial condensation for H_2/CH_4 separation

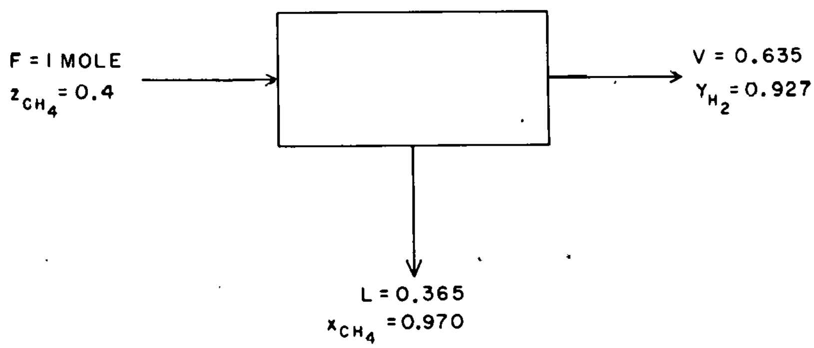


Figure 2.

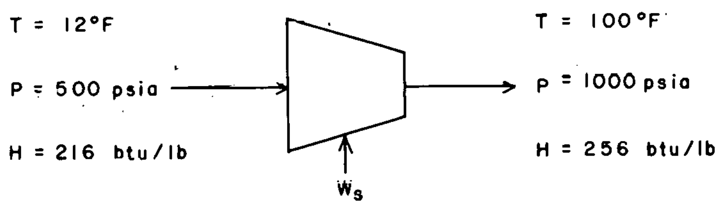


Figure 3.

$$\frac{(L)(x_{CH_4})}{(F)(z_{CH_4})} = \frac{(0.365)(0.970)}{(1.0)\ (0.4)} = 0.885.$$

The preceding separation calculations are valid for H_2/CH_4 separations. Similar calculations could be done for $H_2/CH_4/CO$ mixtures if the appropriate VLE data was available.

Finally, it is necessary to compress the product methane to pipeline pressure (1000 psia). The stream is first heated to 12°F and then compressed adiabatically to 1000 psia and a final temperature of 100°F as shown in Figure 3.

$$\begin{aligned} W_s &= -\Delta H \\ &= -(256-216)\text{Btu/lb} \times 16\ \text{lb/lb-mole } CH_4 \times 1/0.8 \\ &= 800\ \text{Btu/lb-mole } CH_4 = 444\ \text{cal/g-mole } CH_4 \end{aligned}$$

Thus, the total work is 3983 + 444 = 4427 cal/g-mole CH_4.

<u>Separations Using Gas Hydrates</u>

Clathrate compounds are chemical species which are formed by the combination of one stable compound with another element or compound in which the former provides a cage-like structure within which the latter resides. There are no chemical bonds between the guest species and the host compounds. The most important clathrate structures are held together by hydrogen bonds. There are several different classes of clathrate compounds.[3]

Gas hydrates comprise an interesting and important class of clathrates. When water is solidified in the presence of certain atomic or molecular species, solids resembling wet snow are formed. These solids are less dense than normal ice and cannot exist in the absence of the guest molecule. There are two common gas hydrate structures both belonging to the cubic system. The first structure[4] (Structure I) consists of 46 molecules of water hydrogen bonded in such a way as to form six medium cages (4.30A) and two smaller cages (3.95A). If all the cavities are occupied, the empirical formula is given by $X \cdot 5.75\ H_2O$ where X is the guest molecule.

If only the larger cages are filled, the stoichiometry becomes X·7.67. The second structure[5] (Structure II) consists of 136 molecules of water forming 16 cavities of size 3.91 A and 8 cavities of size 4.73 A. Hydrates of this structure are formed by molecules which are too large for accommodation in Structure I. For example, methane forms gas hydrates with the first structure, while propane crystallizes with the second structure. Mixed hydrates also occur in which larger molecules like propane occupy the larger cavities of Structure II while smaller molecules like methane occupy the smaller cavities as well as some of the larger ones.

Methane and ethane form gas hydrates with Structure I while propane and isobutane form hydrates with Structure II. Hydrates are formed by the isomeric butanes or by longer chain molecules only with great difficulty. CO_2 and H_2S also form gas hydrates, while H_2 and CO do not.

A typical phase diagram for a mixture of a light hydrocarbon and water system is shown in Figure 4. To the right of line 1-2, it is similar to a one component phase diagram. The line B-C is slightly above the vapor pressure curve for the pure hydrocarbon. Point C is the three phase (liquid, gas, water) critical point. The line A-B represents the conditions of T and P at which hydrocarbon gas and water combine to form hydrate. Points A and B are invariant quadruple points at which four phases are in equilibrium. This is readily seen by application of Gibb's phase rule

$$F = C + 2 - P$$
$$= 2 + 2 - 4 = 0$$

with F = degrees of freedom

C = no. of components

P = no. of phases

The lines in Figure 4 are univariant since

$$F = 2 + 2 - 3 = 1$$

while the open areas are bivariant

$$F = 2 + 2 - 2 = 2.$$

The point A occurs at approximately $0^{o}C$, the freezing point of water.

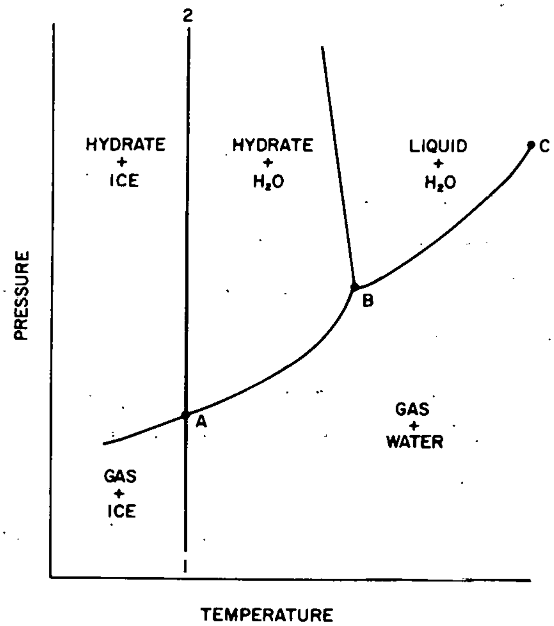


Figure 4. Qualitative phase diagram for hydrate forming system

Table 2 lists some thermodynamic properties of several gas hydrates.[6] The dissociation pressure of CH_4 hydrate at 0°C is 26 atm. This pressure decreases for other members of the homologous series. Since our primary concern is the separation of CH_4/H_2 mixtures containing up to 40% CH_4, this requires high total pressures to achieve the requisite partial pressures of CH_4 for hydrate formation. Clearly separations of ethane/hydrogen and propane/hydrogen would be far less energy intensive

Figure 5 presents a plot of experimental P-T data for several alkane-water systems.[7] Methane forms hydrates at higher temperatures than do ethane and propane. The pressure required for hydrate formation decreases with increasing molecular size

As mentioned previously, a mixed system of methane and propane will form hydrates at pressures intermediate between those for the pure components separately.[8] The hydrate formation conditions for the CH_4-C_3H_8-H_2O are given in Figure 6. At 35°F, five percent propane in methane lowers the pressure required for hydrate formation from 450 psia to about 120 psia. The composition of the mixed hydrate system[9] as a function of pressure at 26.6°F (-3°C) is given in Table 3. The corresponding phase diagram[10] is given in Figure 7. At a total pressure of 10 atmospheres with $y_{CH_4} \cong 0.98$ and $y_{C_3H_8} \cong 0.02$, the hydrate compound in equilibrium with this gas has the empirical formula

$$CH_4 \cdot 0.686\ C_3H_8 \cdot 12.30\ H_2O$$

as computed from the data in Table 3. It is apparent that the addition of small amounts of C_3H_8 to methane/hydrogen mixtures will lower the pressure required for hydrate formation but have the adverse effect of lowering per pass conversion to hydrate. The number of moles of water required per methane molecule encaged also increases which increases the energy requirements. (Each mole of water condensed requires approximately 1440 calories, the heat of fusion of water.)

The thermodynamics of methane hydrate formation were reviewed by Glew[11] and the principal reactions and enthalpies are summarized below.

$$CH_4(g) \rightleftarrows CH_4(l) \qquad \Delta H = -4668 \text{ cal/mole}$$

$$CH_4(l) + nH_2O(l) \rightleftarrows CH_4 \cdot nH_2O(h) \qquad \Delta H = -8228$$

$$CH_4(g) + nH_2O(l) \rightleftarrows CH_4 \cdot nH_2O(h) \qquad \Delta H = -12896$$

Table 2

Thermodynamic Data and Lattice Constants of Some Hydrates

Solute (in order of increasing bp)	Dissoc. pressure at 0°C	Max. temp. at which hydrates exist, °C	Heat of formation from pure water and gas at 0°C kcal/mole solute	Lattice constant, A
A	95.5 atm	no maximum exists		
CH_4	26.0 atm	no maximum exists	14.5	
Kr	14.5 atm	no maximum exists	13.9±0.5	
Xe	1.15 atm	no maximum exists	16.7±0.5	12.0
C_2H_4	5.44 atm	no maximum exists	15.0	
C_2H_6	5.2 atm	14.5	16.3	
N_2O	10 atm	12	14.7	12.03
C_2H_2	5.7 atm	16	15	
CO_2	12.47 atm	10.20	14.4	12.07
H_2S	698 mm	29.5	14.8	12.02
Cl_2	252 mm	28.7	16.0	12.03
CH_3Cl	311 mm	21	18.1	12.00
SO_2	297 mm	12.1	16.6	11.97
CH_3Br	187 mm	14.5	19.5	12.09
CH_3SH	239 mm	12	16.6	12.12
Br_2	43.90 mm	5.81	20.83	12.1
C_3H_8	1.74 atm	5.69	32	17.40
$CHCl_2F$	115 mm	8.61	32.7	
C_2H_5Cl	201 mm	4.8	31.9	17.30
CH_2Cl_2	116 mm	1.7	29	17.33
CH_3I	74 mm	4.3	31.4	17.14
$CHCl_3$	(50 mm)	1.6	31	17.33

Table 3

Composition of the Mixed Hydrate (Structure II) of Methane and Propane, when in Equilibrium with Ice and Gas at $-3^{\circ}C$ as a Function of Pressure

Pressure atm	Fraction of smaller cavities occupied by CH_4 y_{M1}	Fraction of larger cavities: Occupied by CH_4 y_{M2}	Fraction of larger cavities: Occupied by C_3H_8 y_{P2}	Remarks
35.8	0.8836	0.8522	0	metastable CH_4-hydrate
20	0.8088	0.1795	0.7646	
10	0.6762	0.0309	0.9496	stable "homogeneous" solutions
5	0.4952	0.0060	0.9860	stable "homogeneous" solutions
3	0.3317	0.0017	0.9937	stable "homogeneous" solutions
2	0.1736	0.0005	0.9965	
1.48	0	0	0.99795	C_3H_8-hydrate

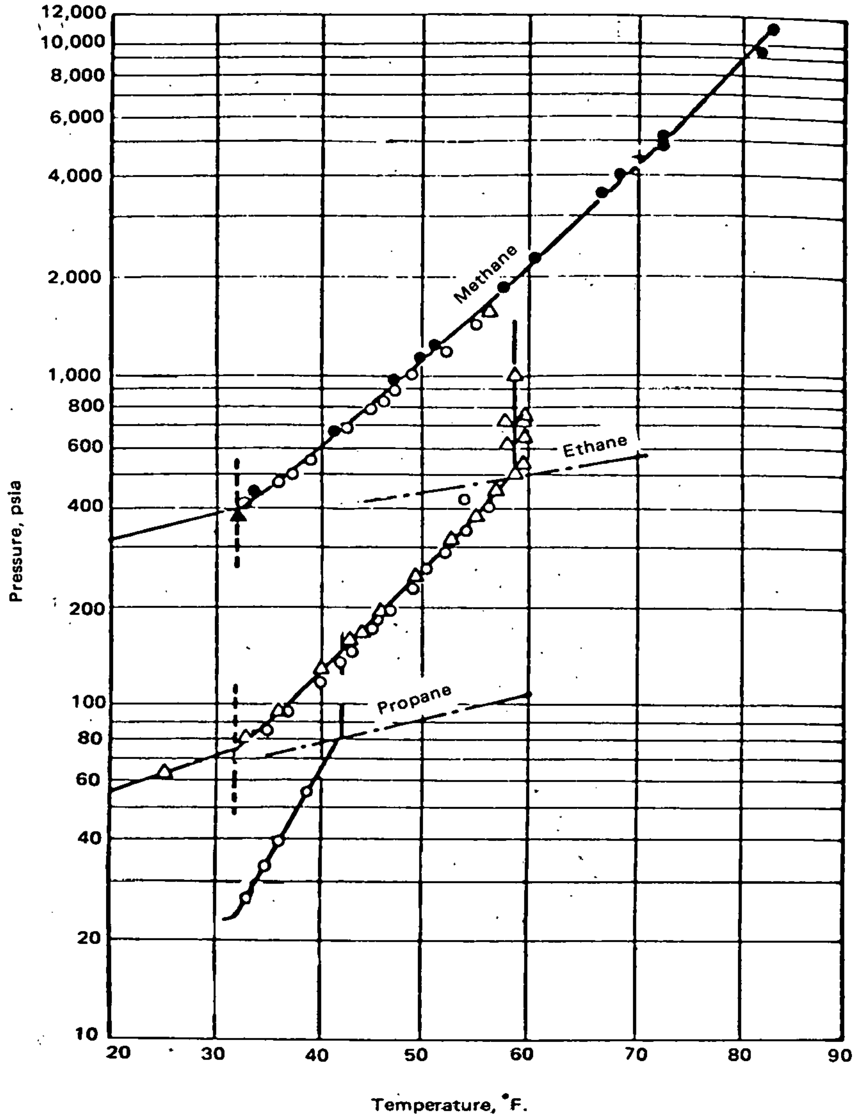


Figure 5. Hydrate forming conditions for paraffin hydrocarbons

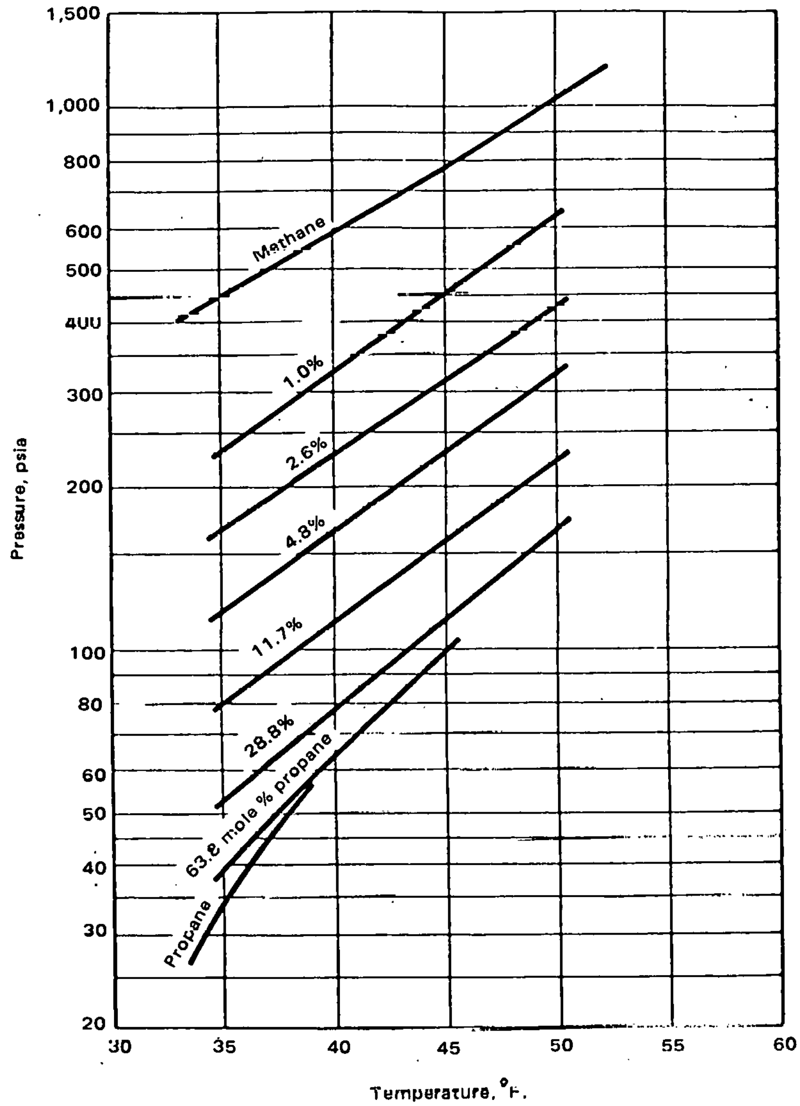


Figure 6. Hydrate forming conditions of methane-propane mixtures

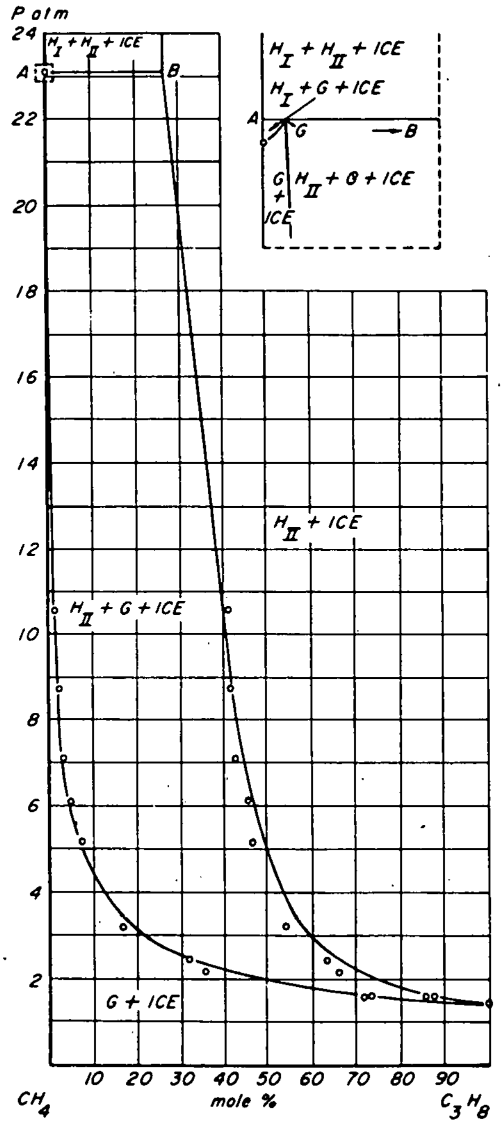


Figure 7. Isothermal cross section of the system H_2O-CH_4-C_3H_8 on a water-free basis at -3°C

The subscripts g, l, and h correspond to gas, liquid, and solid hydrate, respectively and n = 5.75 which implies that all cavities are filled. This contradicts the theoretical occupancy of 83% as derived by van der Waals and Platteeuw.[12]

Process Flowsheet

A conceptual process flowsheet for a process utilizing gas hydrates for CH_4/H_2 separation is shown in Figure 8. Feed gas from the hydrogasifier enters the process after acid gas removal. The CH_4 concentration ranges from 30 to 50% at a total pressure of 500 to 2000 psia. After compression, the gas is cooled to 32^oF and fed to the hydrate reactor. This reactor will probably be a sparged bubble column and may require agitation. In order to ensure adequate partial pressure of CH_4 for hydrate formation, the vessel will be operated at 2000 psia resulting in the required methane partial pressure of 400 psia (20% CH_4 in the effluent stream).

The hydrate crystals are removed from the bottom of the reactor, separated from the brine, and transferred to the decomposer.

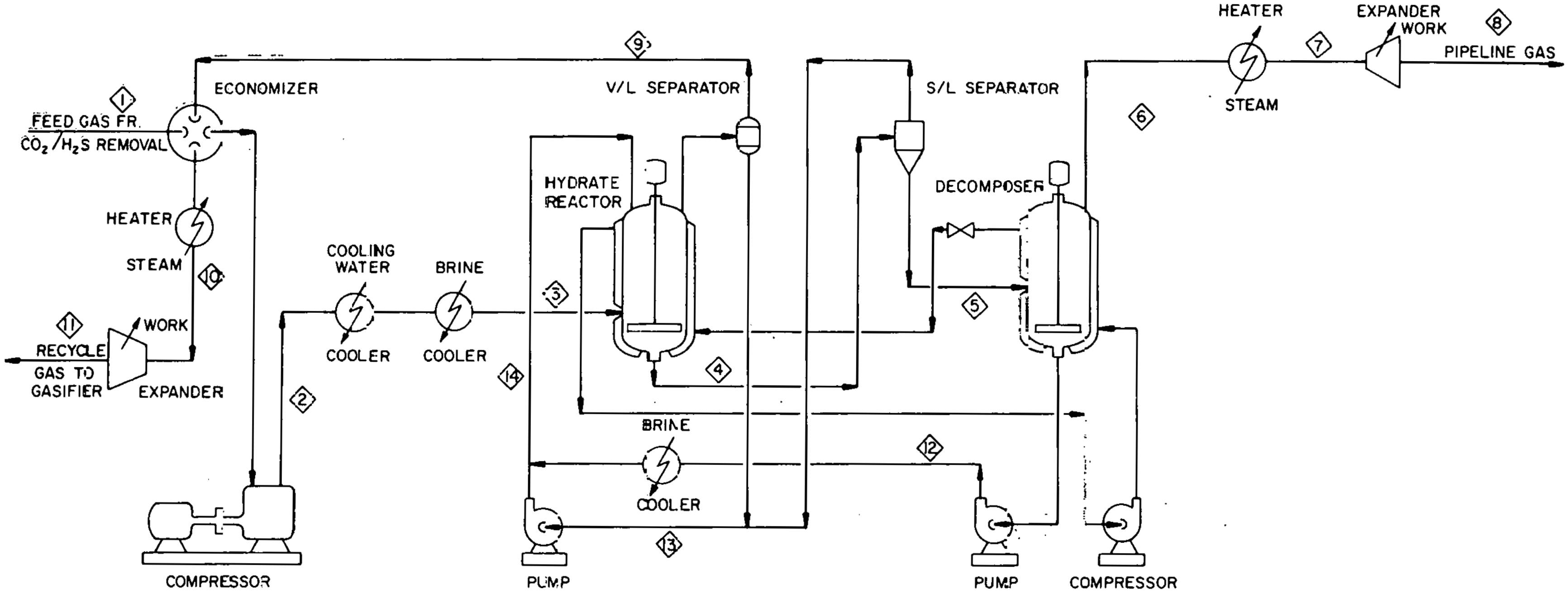
The decomposer is operated at 2000 psia and 60^oF. The product methane is dried, heated, and expanded in a turbo-expander to 1000 psia. Notice that the incoming stream (1) and the recycle stream (11) are both at 500 psia and 100^oF which are chosen as the reference conditions. The process as described is applicable both to hydrogasification processes (H_2/CH_4 separation) and to processes such as Exxon catalytic gasification ($H_2/CH_4/CO$ separations) since only methane forms gas hydrates.

The material balance given in Figure 8 does not include the gases dissolved in the aqueous streams. The slurry leaving the hydrate reactor is assumed to be 15% solid hydrate. Obviously, higher slurry concentrations would be beneficial since this would reduce the required water recycle load.

The energy requirements for the hydrate separation process are summarized in Table 4 below and the calculations included in the Appendix. A refrigeration cycle is being operated between the decomposer and the reaction vessel to transport the heat of fusion between the two units. Two turboexpanders, one on the product stream and the other on the recycle stream, are being used for power recovery. Refrigeration requirements are computed at 40% of the ideal Carnot efficiencies. Cooling water pumping requirements are not included.

Table 4

Feed Gas Compression	102,629 hp	
Feed Gas Cooling	7,593 hp	
Heat Pump Between Reactor and Decomposer	35,559 hp	
Power Recovery (Product Stream)	(6,222)hp	
Product Stream Heating	2,555 hp	$4.97 \times 10^5 \ \frac{Btu}{min}$
Power Recovery (Recycle Stream)	(48,633 hp)	
Recycle Stream Heating	31,260 hp	$2.68 \times 10^6 \ \frac{Btu}{min}$
Water Pumping	8,344 hp	
	133,085 hp	



STREAM NO.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
TEMP. (°F)	100	378	32	32	32	60	205	100	32	330	100	60	32	32
PRESSURE (PSIA)	500	2000	2000	2000	2000	2000	2000	1000	2000	2000	500	2000	2000	2000
FLOW (MOLES/HR)														
$CO + H_2$	65963	65963	65963	0	0	0	0	0	65963	65963	65963	0	0	0
CH_4	43975	43975	43975	0	0	27487	27487	27487	16488	16483	16488	0	0	0
$CH_4 \cdot nH_2O$	0	0	0	27487	27487	0	0	0	0	0	0	0	0	0
H_2O	0	0	0	1034070	158050		0	0	0	0	0	158050	1034070	1192120
TOTAL	109938	109938	109938	1061557	185537	27487	27487	27487	32451	32451	82451	158050	1034070	1192120

Figure 8. Conceptual process flow diagram methane separation by hydrate formation

The largest single energy requirement is the compression of the feed gas from 500 to 2000 psia. Since hydrogasification processes will probably operate at higher pressures (1000 to 2000 psia) these costs may be substantially less. The water pumping costs are those incurred for handling the large flow of brine solution (42,933 gpm) between the reactor and decomposer.

Reactor Size

The size of the reactor vessel will be determined by the kinetics of the hydrate process. Since there is no available data, it seems worthwhile to estimate the size required for a series of different rates. The reaction will be assumed to be pseudo first order, i.e., independent of H_2O concentration since this component is always present in constant concentration of 55.5 moles/liter and first order in methane concentration.

In order for reaction to occur, methane must first dissolve in the liquid. Since the product of this reaction is a solid hydrate, the reaction vessel should not contain packing since product removal would become a problem and the column might become clogged with product. Therefore, a sparged or agitated bubble column reactor might be the best choice. It should be noted that if the intrinsic kinetics of the hydrate formation are rapid compared with mass transfer of methane from the gas to the liquid phase, then reactors which maximize surface to volume ratios such as spray or packed columns are more efficient than bubble columns. For slow reactions, the bubble columns become more efficient.

Mass transfer with chemical reaction is treated at length by Danckwerts[13] and in several papers by van Krevelen and Hoftijzer,[14] and Bridgewater and Carberry.[15] The simplest treatment utilizes the concept of film theory wherein a thin gas film and a thin liquid film exist at the gas-liquid interface. It is assumed that reactant A is transported from the bulk gas through the gas film and across the interface into the liquid film. Depending on the reaction rate, reaction occurs somewhere totally within the liquid film, in the film and in the bulk, or, for very slow reactions, totally within the bulk liquid phase. It is further assumed that the liquid phase reactant B is non-volatile. The reaction can be gas phase controlled, liquid phase controlled, chemically controlled, or a combination of these depending on the relative rates of the mass transfer and kinetic processes. A schematic diagram is presented in Figure 9.

A complete analytical solution for mass transfer with accompanying pseudo first order reaction has been given by Kramers and Westerterp[16] and is summarized below for the reaction A(gas) + B(liquid) → products.

$$E = \frac{K_L}{K_L^o} = \frac{\text{rate of absorption with reaction}}{\text{rate of absorption without reaction}} = \frac{K_L A_i a_T}{K_L^o A_i a_T}$$

$$= \Phi \frac{\Phi(\alpha-1) + \tanh\Phi}{1+\Phi(\alpha-1)\tanh\Phi} \qquad (1)$$

$$\text{where } \alpha = \frac{V_L}{a_T \delta}, \quad \Phi = \delta\sqrt{\frac{K_2 B}{D_A}} = \frac{\sqrt{K_2 B D_A}}{K_L^o}$$

and V_L = total liquid volume

a_T = total interfacial area

δ = liquid film thickness

$K_2 B = K_1$ = pseudo first order rate constant

B = concentration of B in the bulk

D_A = liquid phase diffusivity of A

K_L^o = liquid phase mass transfer coefficient without reaction

K_L = " " " " " with reaction

E = enhancement factor

A plot of E vs Φ with α as parameter is given in Figure 10. The following limiting cases are of interest.

Case I. Very fast reactions

In this case Φ > 2 so that $\sqrt{K_L B D_A} > K_L^o$ and $\tanh\Phi \to 1$. Then

$$E = \frac{K_L}{K_L^o} = \Phi = \frac{\sqrt{K_L B D_A}}{K_L^o} \qquad (2)$$

and the reaction rate is at least twice as fast as the unenhanced rate.

Case II. Fast reaction

For $0.5 < \Phi < 2.0$, K_L/K_L^o must be calculated according to (1) above since there are no simple limiting approximations. K_L is still greater

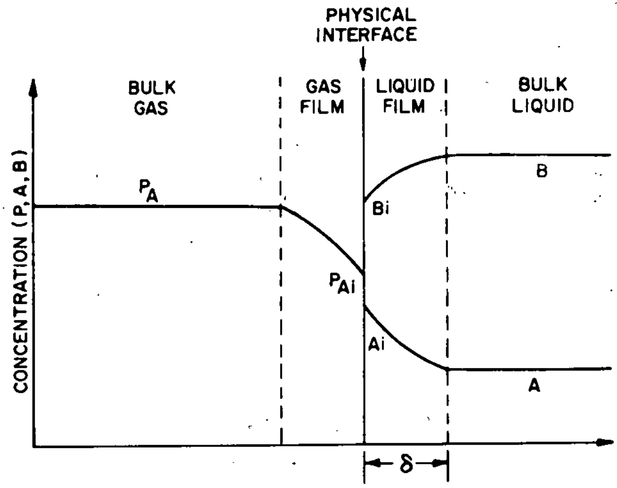


Figure 9. Film model for diffusion with reaction

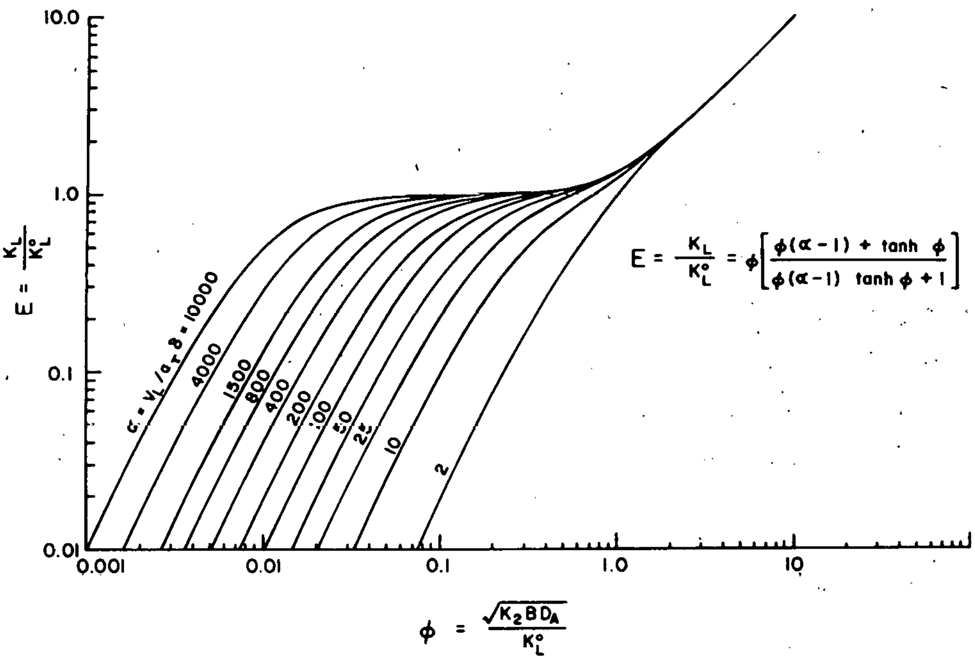


Figure 10.

than K_L^o so that absorption is enhanced.

Case III. Intermediate reaction

If K_2B is small, then Φ is small and $\tanh\Phi \to \Phi$.

Equation 1 becomes

$$\frac{K_L}{K_L^o} = \frac{\alpha\Phi^2}{\alpha\Phi^2 - \Phi^2 + 1} \tag{3}$$

If at the same time α is large, then $\alpha\Phi^2 >> 1 - \Phi^2$ and (1) becomes

$$\frac{K_L}{K_L^o} \simeq 1$$

As noted on Figure 10, this regime is represented by horizontal lines where the reaction rate is such that reaction occurs throughout the laminar film and some reaction takes place in the bulk liquid.

Case IV. Slow reaction

This is another transitional region. Φ is small so that $\tanh\Phi \to \Phi$ and equation 1 becomes

$$\begin{aligned} E &= \Phi \; \frac{\Phi(\alpha - 1) + \Phi}{(\alpha - 1)\Phi^2 + 1} \\ &= \frac{\alpha\Phi^2}{1 + \alpha\Phi^2} \end{aligned} \tag{5}$$

In the regime K_L/K_L^o lies roughly between 0.1 and 1.0 and much of the reaction takes place in the bulk.

Case V. Very slow reaction

If K_2B is small and, in addition, α is small so that $\alpha\Phi^2 << 1$ then

$$\frac{K_L}{K_L^o} \to \alpha\Phi^2 \tag{6}$$

The regime is shown in Figure 10 as that part where the slope of the α lines are all 2.0 and K_L/K_L^o is smaller than 0.1. The reaction is so slow that bulk chemical reaction is now rate controlling.

Table 5, adopted from Levenspiel,[19] presents typical values of interfacial area/unit liquid volume (a), volume of liquid/volume of film (α), and volume fraction of liquid (f) for various gas liquid contactors. It is clear from this table and Figure 10 that for values of Φ below 1.0, the type of contactor becomes important with bubble columns being far preferable to spray towers or packed columns.

It has been assumed throughout the above discussion that gas phase resistance is negligible. This is generally the case when the reacting gas has a low solubility in the liquid provided that its concentration in the gas phase is not too low. This is definitely the case with the system under study.

From Perry's Handbook,[17] the value of $K_L^o a$ for the system O_2-H_2O in a sparged bubble column at a superficial gas velocity U_G = 0.7 ft/sec is $K_L^o a(O_2\text{-}H_2O) = 550\ hr^{-1}$. The diffusivities for O_2-H_2O and CH_4-H_2O at about the same temperature are

$$D_{25^oC}(O_2\text{-}H_2O) = 2.41 \times 10^{-5}\ cm^2/sec$$

$$D_{20^oC}(CH_4\text{-}H_2O) = 1.49 \times 10^{-5}\ cm^2/sec$$

Using Eq. 18-146 in Perry's leads to the following value of $K_L^o a$.

$$K_L^o a\ (CH_4\text{-}H_2O) = 550\ \left(\frac{1.49}{2.41}\right)^{1/2} = 432\ hr^{-1}.$$

The total gas volume to be handled by the reactor is calculated to be:

$$1 \times 10^9\ scf/day \times \frac{day}{24\ hr} \times \frac{hr}{3600\ sec} = 11{,}574\ scf/sec$$

$$11{,}574\ scf/sec \times \frac{14.7}{2000} \times \frac{492}{530} \simeq 79\ acf/sec$$

where acf is actual cubic feet.

If the superficial velocity is U_G = 0.7 ft/sec, then

Table 5

Contactor	$a = \frac{\text{Interfacial Area}}{\text{Volume of Liquid}}$ (cm^{-1})	$\alpha = \frac{\text{Volume of Liquid}}{\text{Volume of Film}} = V_L/a\bar{T}\delta$	Volume Fraction of Liquid (f)
Spray Column	∿ 12	∿ 2-10	∿ 0.05
Packed Column	12	10-100	0.08
Plate Column	10	40-100	0.15
Agitated Bubble Column	2	150-800	0.9
Bubble Column	0.2	4000-10000	0.98

$$\frac{\frac{79\ ft^3}{sec}}{0.7\ \frac{ft}{sec}} \cong 113\ ft^2$$

requiring a column of diameter D = 12 feet. A superficial gas velocity of 0.7 ft/sec is quite high and would result in a high degree of backmixing in the reactor. The hydrodynamic regime would be highly turbulent.

A general design equation for columns is derived in Levenspiel[18] and will be used for order of magnitude estimates for calculating the required tower height. G' has been assumed constant for convenience.

$$h = \frac{G'P_I}{\pi} \int_{Y_{A_1}}^{Y_{A_2}} \frac{dY_A}{(-r_A)a} \tag{7}$$

where

h = height of tower (feet)

P_I = partial pressure of inert gases (atm)

π = total pressure (atm)

G' = total molar flow rate of gas $(\frac{\text{lb-moles}}{ft^2\text{-hr}})$

$Y_A = \frac{\text{moles methane}}{\text{moles inerts}}$

Since $Y_A = P_A/P_I$, the equation can be rewritten as follows:

$$h = \frac{G'}{\pi} \int_{\frac{P_{A_1}}{P_I}}^{\frac{P_{A_2}}{P_I}} \frac{dP_A}{(-r_A)a} \tag{8}$$

Consider Case I above where $E = K_L/K_L^o$ so that the rate is enhanced by chemical reaction. Then

$$(-r_A)a = K_L^o a A_1 E = \frac{K_L^o a P_A E}{H} \tag{9}$$

so that

$$h = \frac{G'H}{\pi K_L^o aE} \int \frac{dP_A}{P_A}$$

$$= \frac{G'}{\pi} \frac{H}{K_L^o aE} \ln \frac{P_{A2}}{P_{A_1}} \tag{10}$$

Now $G' = 972.9 \frac{\text{lb-mole}}{\text{hr-ft}^2}$ assuming a column diameter of 12 feet.

Therefore

$$h = 972.9 \frac{\frac{\text{lb-mole}}{\text{hr-ft}^2}}{\frac{2000}{14.7}\text{ atm}} \times \frac{404 \text{ l-atm}}{\text{g-mole}} \times \frac{454 \text{ g}}{\text{lb}} \times \frac{\text{ft}^3}{28.3 \text{ l}} \times \frac{\text{hr}}{432} \times \ln\frac{800}{400} \times \frac{1}{E}$$

$$= \frac{174}{E} \text{ feet} \qquad (11)$$

Thus, the tower height is inversely proportional to the enhancement factor which is directly proportional to the square root of the pseudo first order rate constant. Note that for Case III, where the rate is unenchanced E = 1 and the required tower height would be 74 feet.

For slow reaction, Equation 10 should be modified by substitution of the bulk reaction rate for Equation 9 (see Levenspiel[20]).

$$h = \frac{G'}{\pi f} \int_{\frac{P_{A_1}}{P_I}}^{\frac{P_{A_2}}{P_T}} \frac{dP_A}{-r_A(P_A)} \qquad (12)$$

$$-r_A = -\frac{1}{V_L} \frac{dN_A}{dt} = K_2 B A_i = K_2 B\, P_A/H \qquad (13)$$

Substitution of (13) into (12) and integration yields

$$h = \frac{G'H}{\pi f K_2 B} \ln \frac{P_{A_1}}{P_{A_2}}$$

$$= \frac{972.9 \frac{\text{lb-moles}}{\text{hr-ft}^2} \times \frac{404 \text{ l-atm}}{\text{g-mole}} \times \frac{454 \text{ g}}{\text{lb}} \times \frac{\text{ft}^3}{28.3 \text{ l}} \times \ln\frac{800}{400}}{\frac{2000}{14.7} \text{ atm} \times 0.09 \times \frac{0.0555}{\text{sec}} \times 3600 \frac{\text{sec}}{\text{hr}}}$$

$$= 164 \text{ ft}$$

The above calculation assumed a rate constant of 0.0555/sec. Table 6 summarizes the results of calculations for various assumed rate constants.

Comparison with Ideal Separations

I. Ideal vs. Cryogenic Process for H_2/CH_4 Separation

The minimum energy for the separation of a 60/40 H_2/CH_4 mixture into the product and recycle streams shown in Figure 2 is calculated (see Progress Report No. 1, p. 20, Eq. 14) to be

$$\Delta G_{min} = 271 \text{ cal/mole feed}$$
$$= 766 \text{ cal/mole } CH_4 \text{ separated}$$

The actual energy for a cryogenic separation utilizing partial liquefaction was calculated to be about 4427 cal/mole CH_4. The process efficiency is given by

$$\eta = \frac{766}{4427} = 0.173$$

which is at the high end for cryogenic efficiencies.

II. Ideal vs. Clathrate (Gas Hydrate) Process for H_2/CH_4 and $H_2/CH_4/CO$ Separation

The minimum energy required for the separation of a 60/40 (H_2 and CO)/CH_4 mixture into the product and recycle streams shown in Figure 11 is calculated to be 705 cal/mole CH_4 separated. The streams compositions coincide with those employed for the gas hydrate process outlined previously. The CO levels will probably not amount to more than 20% in the feed stream. R and P are recycle and product streams.

The total power requirements for the process are summarized in Table 4. Converting this number to cal/mole CH_4 separated yields the following

$$133085 \text{ hp} \times \frac{1}{250\text{x}10^6 \text{ scf/day } CH_4} \times 379 \text{ scf/lb-mole} \times 24 \text{ hrs/day} \times 3600 \text{ sec/hr}$$
$$\times \frac{550 \text{ ft-lb/sec}}{\text{hp}} \times \frac{\text{Btu}}{778 \text{ ft-lb}} \times \frac{\text{cal/g-mole}}{1.8 \text{ Btu/lb-mole}}$$
$$= 6849 \text{ cal/mole } CH_4 \text{ separated}$$

The efficiency is

$$\eta = \frac{705}{6846} = 0.103$$

Table 6

K_2 $\frac{\text{liters}}{\text{mole-sec}}$	$K_1 = K_2B$ sec^{-1}	$\phi = \frac{K_2BD_A}{K_L^o}$	$E = K_L/K_L^o$ α=4000	α=10000	Tower Height* (feet)
1000	55,500	11.5	11.5	11.5	6.4
100	5,550	3.6	3.6	3.6	20.6
10	555	1.1	1.3	1.3	57
5	277.5	0.8	1.1	1.1	67
1	55.5	0.36	1.0	1.0	74
0.1	5.55	0.11	0.98	0.99	76
0.01	0.555	0.036	0.84	0.93	88
0.001	0.0555	0.0114	0.34	0.56	164
0.0001	0.00555	3.62×10^{-3}	0.05	0.16	1640

$D_A = 0.85 \times 10^{-5}$ cm^2/sec $\quad$ $K_L^o = 0.06$ cm/sec

$K_L^o a = 432\ hr^{-1}$ $\quad$ Diameter of Tower = 113 ft^2

$a = 2.0\ cm^{-1}$ $\quad$ *Does not include disengagement space.

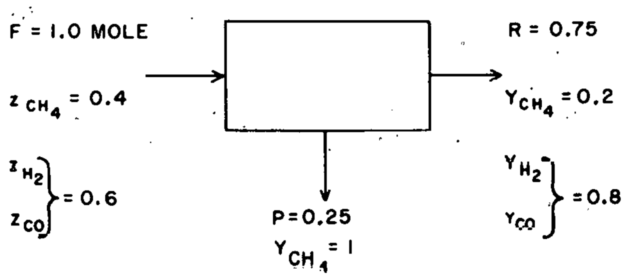


Figure 11.

Conclusions

A comparison of the gas hydrate process with a cryogenic separation of H_2/CH_4 indicates that the cryogenic system is less energy intensive and probably superior. However, this is based on a 500 psia incoming stream. If the process operates at substantially higher pressures (1000 to 1500 psia), then considerable compression cost savings could be realized making the process more competitive. For the separation of $H_2/CO/CH_4$ mixtures, the gas hydrate energetics are roughly the same whereas a cryogenic system would probably require a distillation column to ensure CO removal from the product stream. CO does not form a gas hydrate.

One major problem of the process as outlined is the reduction of the CH_4 concentration to 20% in the recycle stream. This is probably unacceptably high. To reduce this to a level of say 9 to 15% would require an increase in the total process pressure so that the methane partial pressure is above the decomposition pressure ($\sim$ 400 psia). It also might be possible to utilize substantial quantities of propane in the process to lower the pressure by trapping methane in the Structure II lattice formed by propane as discussed in this report. This would require a propane recovery system.

Finally, the most important unknown is the kinetics of hydrate formation. A look at Table 6 shows that there is a probable cut off of process feasibility at the value of $K_1 = 0.0555\ sec^{-1}$. An order of magnitude lower would require over 1000 feet of reactor.

References

1. King, C. J., Separation Processes, McGraw-Hill, N.Y., 1971, p. 636-7.

2. Dodge, B. F., Chemical Engineering Thermodynamics, McGraw-Hill, N.Y., 1944, p. 436.

3. Hagen, M., Clathrate Inclusion Compounds, Rheinhold Publishing Co., 1962.

4. Jeffrey, G. A. and McMullan, R. K., The Clathrate Hydrates, in Progress in Inorganic Chemistry, Vol. 8, Interscience Publishers, N.Y., 1967, p. 81.

5. Ibid, p. 83.

6. van der Waals, J. H. and Platteeuw, I. C., Clathrate Solutions, in Advances in Chemical Physics, I. Prigogine (Editor), Interscience Publishers, N.Y., 1959, p. 8.

7. McCain, W. D., The Properties of Petroleum Fluids, Petroleum Publishing Co., Tulsa, OK, 1973, p. 294.

8. Ibid, p. 295.

9. van der Waals and Platteeuw, Op. Cit., p. 32.

10. Ibid, p. 45.

11. Glew, D. N., Aqueous Solubility and the Gas Hydrates. The Methane-Water System, Trans. Far. Soc., 66, p. 605-9 (1962).

12. van der Waals and Platteeuw, op. cit.

13. Danckwerts, P. V., Gas-Liquid Reactions, McGraw-Hill, New York, 1970.

14. van Krevelen, D. W., Hoftijzer, P., and van Hooren, C. J., Rev. Trav. Chim., 67, 563-87 (1948).

15. Bridgewater, J. and Carberry, J. J., British Chemical Engineering, 12, 58-64 (1967).

16. Kramers, H. and Westerterp, K. R., Elements of Chemical Reactor Design and Operations, Netherlands University Press, Amsterdam, 1963.

17. Chemical Engineers Handbook, edited by Perry and Chilton, 5th Edition, 18-81, Fig. 18-132 and Eq. 18-146.

18. Levenspiel, O., Chemical Reaction Engineering, Wiley, 1972, p. 425-41.

19. Ibid, p. 419.

20. Ibid, p. 439.

Appendix

I. Feed Gas Compression

$x_{CH_4} = 0.4 \qquad x_{H_2} = 0.6$

π = 500 psia

T = 100°F

Feed rate = 1.0×10^9 SCFD = 1.832×10^3 lb-moles/min

The gas is to be compressed from 500 to 2000 psia. The required number of stages n is given by the condition

$$\sqrt[n]{\frac{P_f}{P_i}} = 4$$

where P_f is the final pressure and P_i the initial pressure. Assuming an efficiency η of 0.8, adiabatic compression, and using γ = 1.41 (for H_2), the horespower is given by

$$h_p = \frac{(0.0643)\ T_i\ \gamma\ q_o}{520(\gamma-1)\eta}\left[\left(\frac{P_f}{P_i}\right)^{\frac{\gamma-1}{\gamma}} -1\right]$$

$$= \frac{(0.0643)(560)(1.41)\ \frac{1.0\times10^9}{24\times60}}{(520)(0.41)(0.80)}\left[4^{0.41/1.41} -1\right]$$

$$= 102629$$

where q_o is the volumetric flow rate in standard cubic feet per minute and T_i inlet temperature. The requirement for ideal isothermal compression at 100% efficiency is 66,596.

The temperature of the gas leaving the compressor is calculated from

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} = (4)^{(0.41/1.41)} = 1.496$$

so that

$$T_2 = (1.496)(560) = 838°R = 378°F$$

II. Feed Gas Cooling

$$C_{P_1 \text{mean}}^{CH_4} = 8.38 \qquad C_{P_1 \text{ mean}}^{H_2} = 6.88$$

$$C_P^{mix} = (0.4)(8.38) + (0.6)(6.88) = 7.48 \text{ Btu/lb-mole } ^oF$$

The required rate of heat removal for reducing the temperature from 100° to 32°F is

$$Q = M\ C_p \Delta T = (1.832 \times 10^3)(7.48)(100-32)$$
$$= 9.32 \times 10^5 \text{ Btu/min}$$

The refrigeration load is calculated using a Carnot cycle operating at 40% efficiency.

$$W = \frac{Q}{\eta}\ \frac{T_h - T_1}{T_1}$$

$$= \frac{9.32 \times 10^5}{0.40}\ \frac{560-492}{492} = 3.22 \times 10^5 \text{ Btu/min}$$

$$= 7593 \text{ hp}$$

(Note: 1 Btu/min = 2.358×10^{-2} hp)

III. Heat Pump Between Reactor and Decomposer

The heat of reaction for gas hydrate formation from methane gas and water is -12,830 cal/mole.

$$nH_2O(l) + CH_4(g) = CH_4 \cdot nH_2O(h) \qquad n = 5.75$$

The total heat evolved is

$$5.49 \times 10^4 \text{ lbs hydrate/min} \times \frac{\text{lb mole}}{119.8 \text{ lbs}} \times \frac{1.8 \text{ Btu/lb-mole}}{\text{cal/g-mole}} \times (-12830)\frac{\text{cal}}{\text{g-mole}}$$

$$= -1.06 \times 10^7 \text{ Btu/min}$$

The same amount of heat is required for decomposition. If a heat pump is used to transfer the heat of reaction to the decomposer, the work required at 40% efficiency is given by

$$W = \frac{Q}{n} \quad \frac{T_{decomp} - T_{reactor}}{T_{reactor}}$$

$$= \frac{1.06 \times 10^7}{0.40} \qquad \frac{520 - 492}{492}$$

$$= 1.508 \times 10^5 \text{ Btu/min} = 35,559 \text{ hp}$$

IV. Power Recovery (Product Stream)

The decomposer pressure is 2000 psia at 60°F. It is desired to adjust this stream to a final pressure of 1000 psia and a final temperature of 100°F, using a turbo-expander. The work, W_s, recovered is obtained from a pressure-enthalpy diagram for methane. In order to achieve a final temperature of 100°F, it is necessary to heat the incoming stream from 60°F to 205°F (see next section). The recovered work at 75% efficiency is given by

$$W_s = - \Delta H = -256 + 304$$

$$= (-256 + 304) \text{Btu/lb} \times 16 \text{ lb/lb-mole} \times 27487 \text{ lb-mole/hr} \times \text{hr/60 min.} \times 0.75$$

$$= 2.64 \times 10^5 \text{ Btu/min}$$

$$= 6222 \text{ hp}$$

V. Product Stream Heating

The heating requirement for raising the product streams from 60°F to 205°F is

$$q = 27487 \text{ lb-moles/hr} \times \text{hr/60 min} \times 7.48 \text{ Btu/lb-mole } ^\circ\text{F} \times (205-60)^\circ\text{F}$$

$$= 4.97 \times 10^5 \text{ Btu/min}$$

The work lost is that work which could be derived from a reversible heat engine operating between ambient temperature and 205°F.

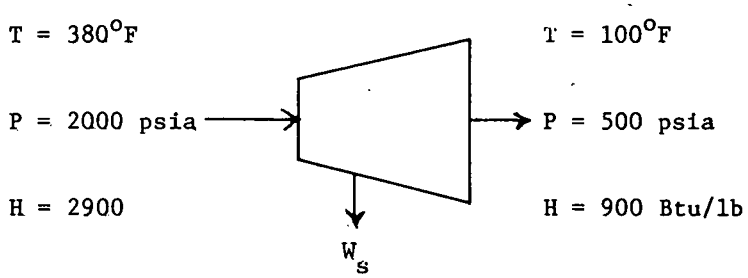
$$W = Q \frac{T_H - T_O}{T_H}$$

$$= (4.97 \times 10^5) \left(\frac{665-520}{665}\right)$$

$$= 1.08 \times 10^5 \text{ Btu/min} = 2555 \text{ hp}$$

VI. Power Recovery (Recycle Stream)

The recycle stream is sent back to process at 500 psia and therefore must be reduced in pressure from 2000 psia to the process pressure.



$$W_s = (2900 - 1900)\ \text{Btu/lb} \times 2\ \text{lb/mole} \times 82451/60\ \text{mole/min} \times 0.75$$
$$= 2.06 \times 10^6\ \text{Btu/min} = 48{,}633\ \text{hp}$$

The above calculation assumes a 100% hydrogen stream and 75% recovery efficiency.

VII. Recycle Stream Heating

The heating requirement to heat the recycle stream from 32°F to 380°F is

$$Q = \frac{82{,}451}{60}\ \frac{\text{lb moles}}{\text{min}} \times 7.28\ \text{Btu/lb-mole}\ {}^{\circ}\text{F} \times (380 \times 32)$$

$$= 3.48 \times 10^6\ \text{Btu/min}$$

Operation of a heat engine between 380°F and ambient gives a measure of the lost work.

$$W = Q\,\frac{T_h - T_o}{T_h}$$

$$= 3.48 \times 10^6\ \frac{840-520}{840}$$

$$= 1.32 \times 10^6\ \text{Btu/min} = 31{,}260\ \text{hp}$$

VIII. Water Pumping

The power requirements for pumping the large quantities of brine between the reactor and the decomposer are calculated by assuming a pressure drop across the pump of 100 psia and another 100 psia due to hydrostatic head and friction losses.

$$\Delta h = 200\ lb_f/in^2 \times 144\ in^2/ft^2 \times ft^3/62.4\ lb_m$$

$$= 461.5\ ft\text{-}lb_f/lb_m$$

The horsepower, assuming an efficiency $\eta = 0.6$, is

$$hp = \frac{\dot{m}\ \Delta h}{\eta}$$

$$= \left(\frac{3.58 \times 10^5}{60}\ \frac{lb_m}{sec}\right)\left(461.5\ \frac{ft\text{-}lb_f}{lb_m}\right)\left(\frac{hp}{550\ \frac{ft\text{-}lb_f}{sec}}\right)\left(\frac{1}{0.6}\right)$$

$$= 8344$$

This is the horsepower required for pumping all the water which includes recycle from the reactor and water from the decomposer. In practice two pumps will be required to generate this power.

Distribution List

L. Naphtali, DOE
K. Woodcock, DOE
E. Schmetz, DOE
H. Podall, DOE
R. Fisher, DOE
W. E. Winsche, BNL
D. Gurinsky, BNL
M. Steinberg, BNL
A. Albanese, BNL
V. Dang, BNL
J. E. Gallgher, Exxon
J. C. Tao, Air Products

☆ U.S. GOVERNMENT PRINTING OFFICE: 1980—614-090/16