231
8-15-79 BNL 51011

LQ. 3002

MASTER

ALTERNATIVE PROCESS SCHEMES FOR COAL CONVERSION

PROGRESS REPORT NO. 1
OCTOBER 1, 1978 - JANUARY 31, 1979

February 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 51011
UC-90
(Coal Conversion and Utilization -
TID-4500)

ALTERNATIVE PROCESS SCHEMES FOR COAL CONVERSION

PROGRESS REPORT NO. 1
OCTOBER 1, 1978 - JANUARY 31, 1979

Principal Investigator: MICHAEL J. SANSONE

Contributors:
Anthony S. Albanese
Meyer Steinberg

February 1979

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

M. 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
Price: Printed Copy $4.50; Microfiche $3.00

May 1979 340 copies

Table of Contents

Summary

On the basis of simple, first approximation calculations, it has been shown that catalytic gasification and hydrogasification are inherently superior to conventional gasification with respect to carbon utilization and thermal efficiency. However, most processes which are directed toward the production of substitute natural gas (SNG) by direct combination of coal with steam at low temperatures (catalytic processes) or with hydrogen (hydrogasification) will require a step for separation of product SNG from a recycle stream. The success or failure of the process could well depend upon the economics of this separation scheme.

The energetics for the separation of mixtures of ideal gases has been considered in some detail. Minimum energies for complete separation of representative effluent mixtures have been calculated as well as energies for separation into product and recycle streams. The gas mixtures include binary systems of H_2 and CH_4 and ternary mixtures of H_2, CH_4, and CO.

A brief summary of a number of different real separation schemes has also been included. We have arbitrarily divided these into five categories: liquefaction, absorption, adsorption, chemical, and diffusional methods. These separation methods will be screened and the more promising methods examined in more detail in later reports. Finally, a brief mention of alternative coal conversion processes concludes this report.

Introduction

The purpose of this program is to suggest improvements to existing and developing gasification processes and to identify and initiate studies on potentially attractive new gasification concepts.

A central step in the conversion of coal to gaseous and/or liquid hydrocarbon products is the gasification reaction wherein coal is contacted with steam in a fixed, fluid, or entrained bed reactor generating a mixture of CO and H_2 called water gas.

$$C + H_2O = CO + H_2 \qquad \Delta H^o_{298} = 42 \text{ kcal/mol} \qquad (1)$$

The heat required to drive the above reaction is either supplied via an external source or by combustion of some of the coal in the gasifier by supplying air or oxygen to the reactor.

$$C + O_2 = CO_2 \qquad \Delta H^o_{298} = -94 \text{ kcal/mol} \qquad (2)$$

If air is used, the resulting gas has a low Btu (100 to 250 Btu/scf) rating due to the high nitrogen content. Use of oxygen results in a medium Btu gas (250 to 500 Btu/scf). The low or medium Btu synthesis gas thus produced can be subsequently converted to methane (after adjusting the CO/H_2 ratio via the water gas shift reaction) according to

$$CO + 3H_2 = CH_4 + H_2O \qquad \Delta H^o_{298} = -60 \text{ kcal/mol} \qquad (3)$$

The resulting high Btu gas (1000 Btu/scf) is designated SNG (substitute natural gas) and can be economically transported by pipeline.

Alternatively, the synthesis gas can be converted to methanol via the catalytic reaction

$$CO + 2H_2 = CH_3OH \qquad \Delta H^o_{298} = -22 \text{ kcal/mol} \qquad (4)$$

This reaction utilizes hydrogen most efficiently since there is no water produced. The Mobil process can convert this methanol to gasoline by means of a dehydration reaction over a zeolite catalyst.

$$nCH_3OH = (CH_2)_n + nH_2O \qquad (5)$$

The conversion of synthesis gas to liquid hydrocarbon products (indirect liquefaction) via the Fisher-Tropsch reaction

$$nCO + 2nH_2 = C_nH_{2n} + nH_2O \qquad (6)$$

$$nCO + (2n + 1)\ H_2 = C_nH_{2n+2} + nH_2O \qquad (7)$$

and to oxygenated compounds

$$nCO + 2nH_2 = C_nH_{2n+1}OH + (n-1)H_2O \qquad (8)$$

has been practiced on a commercial scale at Sasolburg, South Africa for many years. A disadvantage of this reaction is that the resulting process is non-specific and produces a variety of hydrocarbon and oxygenated products.

The reaction of coal and steam to methane and CO_2 competes with (1).

$$C + H_2O = 1/2CH_4 + 1/2CO_2 \quad \Delta H^o_{298} = +12\ \text{kcal/mol} \qquad (9)$$

This reaction is practically thermally neutral between steam and coal at reactor conditions and highly desirable since it yields SNG in combination with an easily removed byproduct. However, gasification rates are low in the temperature range (650° to 750°C) where appreciable concentrations of methane are thermodynamically stable with respect to CO and H_2 formation. Thus, the introduction of a catalyst to achieve the requisite rates at low gasification temperatures is required. The Exxon catalytic process uses an alkali metal carbonate catalyst and a cryogenic separation of methane from the CO and H_2 which are recycled to the gasifier.

Coal can also be gasified directly with hydrogen (hydrogasification) at 800° to 900°C and 1500 to 2500 psi.

$$C + 2H_2 = CH_4 \qquad \Delta H^o_{298} = -18 \text{ kcal/mole} \qquad (10)$$

The products of direct reaction with hydrogen range from primarily liquid to primarily gaseous depending on operating conditions.

Thus, depending on the type of gasifier and the reaction conditions, the gasifier stream contains most of the following components in various proportions: CO, H_2, CH_4, CO_2, H_2O, H_2S, NH_3, COS, N_2. Separation of the various species as well as environmental control problems are important factors in the selection and design of acceptable processes.

Essentially the purpose of the coal conversion process is to upgrade the H/C ratio from approximately 0.8 to over 1 and as high as 4 for the production of SNG. The hydrogen deficiency is made up by the reduction of water with carbon in the gasifier. Thermal efficiencies can be improved by low temperature gasification and by direct hydrogenation.

Hydropyrolysis of Coal

The direct reaction of coal with hydrogen in the gas phase is called hydropyrolysis. Depending upon the reaction conditions and reactor configuration, a slate of hydrocarbon products ranging from primarily liquid to primarily gaseous can be obtained. There are currently a number of processes under development. Three are briefly outlined in the following paragraphs.

Hydrane(1) - US Bureau of Mines, Pittsburgh Energy Technology Center

Crushed coal is fed into a two zone hydrogenator operated at 900°C and 1000 psi. The coal falls through the top zone where about 20% of the carbon is converted to methane leaving a char which drops into the second zone where further reaction with hydrogen converts another 35% of the carbon values to CH_4. The residual char is gasified to provide the hydrogen needed for the process. The off-gases are passed through a methanator where the 2 to 5% CO is converted to methane. No gas separation is required for this process. A flowsheet is shown in Figure 1.

Flash Hydropyrolysis (FHP)(2) - Brookhaven National Laboratory

Pulverized coal is contacted with heated hydrogen at elevated pressures in a down-flow entrained bed tubular reactor. Temperatures range from 700° to 900°C with pressures of 1500 to 4000 psi H_2. The coal is rapidly heated causing rapid devolatilization and thermally induced depolymerization. The free radical ends generated readily add hydrogen forming aromatic hydrocarbons (benzene, toluene, xylene-BTX). Rapid quenching at this point prevents further reaction leading ultimately to formation of gaseous products, principally CH_4. The coal residence time ranges from 1 to 10 seconds. By operating at 750°C and 2000 psi, up to 20% of the carbon in lignite fed forms benzene and aromatic liquid and about 40% forms methane and ethane. By raising the temperature to 875°C and 2500 psi, no liquid forms and up to 90% of carbon fed is converted to methane for SNG. The process will require separation of recycle H_2 from the product methane.

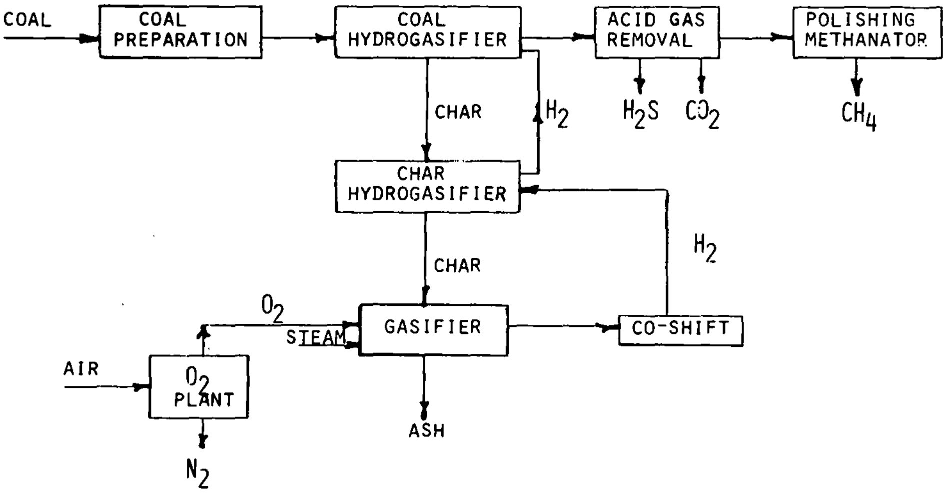


Figure 1. Hydrane process.

Flash Hydropyrolysis(3) - Rocketdyne Division, Rockwell International

This process is based on the same principles as the BNL system. The reactor utilizes rocket engine techniques to achieve rapid mixing of coal and hydrogen and controlled short residence times (30 to 700 msec). Liquids are formed initially but these react to form gases if not quenched. Dense phase transport of coal is used to minimize the gas requirement for feeding and heating the coal.

Catalytic Gasification (Exxon)(4)

The kinetics of coal gasification are acceptable at temperatures of 950°C and higher. At this temperature, 50 atm pressure and H/O = 2, the equilibrium gas composition is about 12% H_2O, 8% CO_2, 8% CH_4, 36% H_2, and 36% CO. The reaction is also highly endothermic requiring large amounts of heat. Lower temperature favors the formation of methane.

At lower temperatures, the lowered reaction rate must be catalyzed. The Exxon process utilizes the well-known ability of alkali metal salts to catalyze the gasification reaction. At 700°C, 50 atms, and H/O = 2, the equilibrium gas composition is shifted to higher methane: 37% H_2O, 24% CO_2, 19% CH_4, 15% H_2, and 5% CO. The use of the alkali metal catalysts also prevents swelling and agglomeration in caking coals and it is claimed that the methanation equilibrium is promoted. The equilibrium amount of methane in the gasifier effluent is further enhanced because of the high H_2 content in the gasifier recycle stream (see below). The gasifier effluent is cooled and scrubbed to knock out water and remove ammonia followed by acid gas removal. The stream, now consisting of about 45% H_2, 42% CH_4, and 13% CO, is cryogenically separated to a pure methane fraction (∿ 34%) and a recycle stream (∿ 66%) of composition 70% H_2, 19% CO, and

11% CH_4. The overall reaction for the process is

$$C + H_2O = 1/2CH_4 + 1/2CO_2 \qquad (11)$$

which as mentioned is almost thermally neutral under reaction conditions.

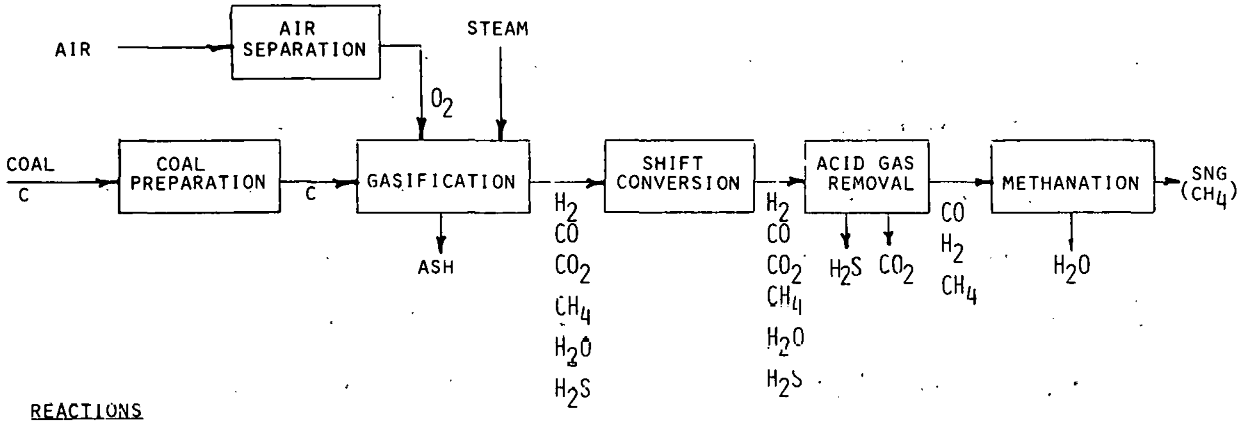
Thermal Efficiency and Coal Utilization for Gasification Processes

For purposes of indicating overall efficiency, a basic thermodynamic and carbon mass balance analysis of four major methods for converting coal to pipeline gas (CH_4) has been made and is summarized below. For direct comparison, the systems have been idealized by assuming no material or thermal losses.

1. Coal Gasification Reference Process

The standard procedure for making SNG consists of the following four basic steps: (1) water gas reaction, (2) carbon oxidation (to supply heat for step(1) which is endothermic), (3) water gas shift, and (4) methanation. A schematic flowsheet for the process is shown in Figure 2. The standard heat of reaction for each of the reactions (higher heating values are used) and carbon and thermal efficiencies are given below.

		ΔH^o_{298} (kcal/mole)
(1)	$2C + 2H_2O = 2CO + 2H_2$	
	0 −136 −52 0	+84
(2)	$0.894C + 0.894O_2 = 0.894CO_2$	
	0 0 (0.894)(−94)	−84
(3)	$CO + H_2O = CO_2 + H_2$	
	−26 −68 −94 0	0
(4)	$CO + 3H_2 = CH_4 + H_2O$	
	−26 0 −18 −68	−60



REACTIONS

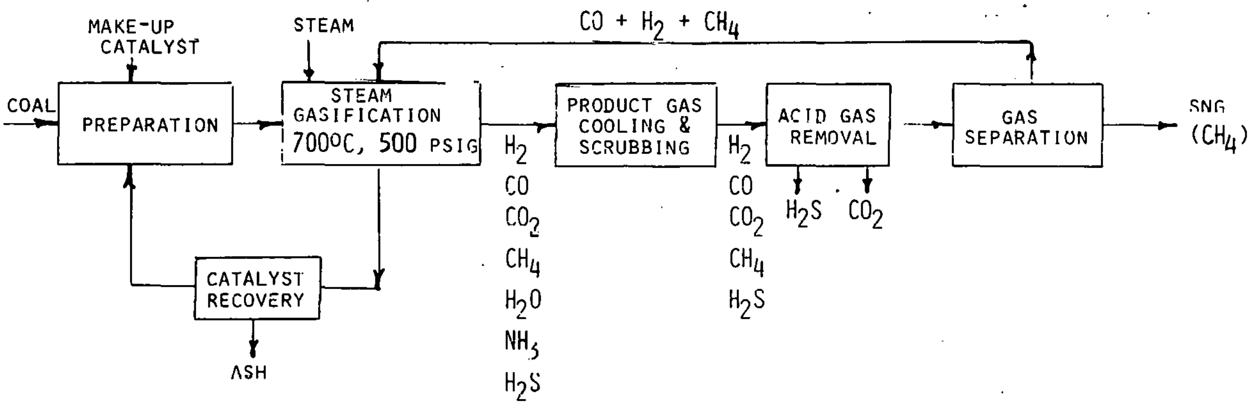
WATER GAS: $C + H_2O = H_2 + CO$

OXIDATION: $C + O_2 = CO_2$

WATER GAS SHIFT: $CO + H_2O = H_2 + CO_2$

METHANATION: $CO + 3H_2 = CH_4 + H_2O$

Figure 2. Gasification-reference system (oxygen-gasification-shift-methanation).



REACTIONS

WATER GAS: $C + H_2O = CO + H_2$

WATER GAS SHIFT: $CO + H_2O = CO_2 + H_2$

HYDROGENATION: $C + 2H_2 = CH_4$

NET GASIFIER RUN: $2C + 2H_2O = CH_4 + CO_2$

Figure 3. Low temperature catalytic gasification (Exxon).

In addition, coal is needed to produce 0.894 mole O_2. This amounts to 0.254 moles carbon/mole CH_4 assuming 300 kwh(e)/ton O_2 and 34% power cycle efficiency. The heat of coal combustion in the gasifier supplies the endothermic heat of the water gas reaction. The methanation reaction is highly endothermic but produces essentially waste heat.

One of the main drawbacks to this scheme is the fact that reactions (1), (3), and (4) are conducted in separate vessels with cooling of the product gas for removal of undesirable components at each stage. This leads to increased thermal inefficiency and the extra reaction vessels lead to higher capital investment. A one vessel direct conversion system would be a significant advance in gasification technology.

As a first approximation, the carbon conversion efficiency ξ will be defined as the ratio of moles of methane produced to the moles of carbon consumed and the energy efficiency η as the ratio of the heat of combustion of the product methane to the heat of combustion of the carbon consumed.

$$\xi = \frac{\text{moles methane}}{\text{g-atom carbon}} = \frac{1}{2+0.894+0.254} = 0.318$$

$$\eta = \frac{\Delta H_c \text{ methane}}{\Delta H_c \text{ carbon}} = \frac{212}{(3.148)(94)} \approx 0.716$$

2. Catalytic Gasification (Exxon)

The process essentially involves lowering the temperature of gasification through the use of an alkali metal carbonate catalyst preferably K_2CO_3. At these lower temperatures, the formation of methane is thermodynamically more favored so that a significant proportion of the gasifier effluent (∿ 22%) is CH_4. The CH_4 is separated from the CO and H_2 which are recycled to the gasifier. The simplified flowsheet is shown in Figure 3. The net reaction is

$$C + H_2O = 1/2CH_4 + 1/2CO_2 \qquad \Delta H^o_{298}$$

$$0 \quad -68 \quad -1/2(18) \quad -1/2(94) \qquad 12$$

Although the system is almost thermally neutral, heat is required to produce steam. The moles of carbon required to supply the heat of reaction are 12/94 = 0.128 so that the carbon utilization is

$$\xi = \frac{0.5}{1+0.128} = 0.443$$

and the thermal efficiency

$$\eta = \frac{(0.5)(212)}{(94)(1.128)} = 1.000$$

3. Hydrogasification (Flash Hydropyrolysis, Hydrane, etc.)

This process involves the direct hydrogenation of coal with the hydrogen being produced by other means such as coal gasification plus water gas shift. Figure 4 presents a flowsheet for such a process scheme.

$$\Delta H^o_{298}$$

$$C + 2H_2 = CH_4$$

$$0 \quad 0 \quad -18 \qquad -18$$

$$C + H_2O = CO + H_2$$

$$0 \quad -68 \quad -26 \quad 0 \qquad +42$$

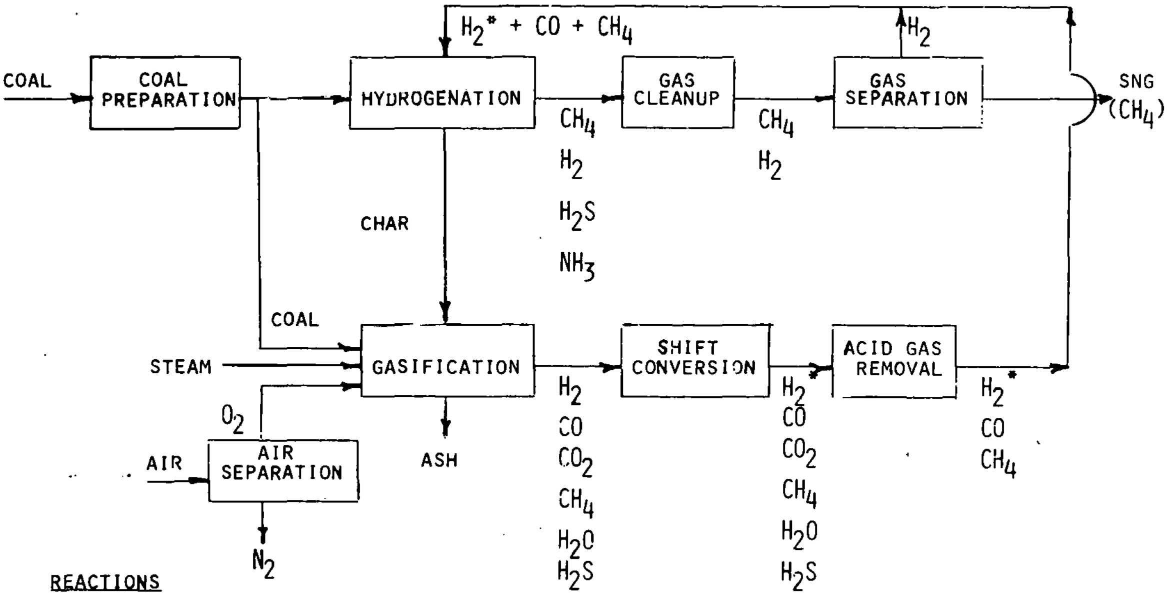
$$0.447C + 0.447O_2 = 0.447CO_2$$

$$0 \quad 0 \quad (0.477)(-94) \qquad -42$$

$$CO + H_2O = CO_2 + H_2$$

$$-26 \quad -68 \quad 94 \quad 0 \qquad 0$$

The coal required for the production of O_2 is 0.127 which is half that required for process 1. The carbon utilization is



REACTIONS

HYDROGENATION: $C + 2H_2 = CH_4$

WATER GAS: $C + H_2O = CO + H_2$

OXIDATION: $C + O_2 = CO_2$

CO SHIFT: $CO + H_2O = CO_2 + H_2$

* MAJOR COMPONENT

Figure 4. Hydrogenation - H_2 supply by gasification.

$$\xi = \frac{1}{2 + 0.447 + 0.127} = 0.388$$

and the thermal efficiency is

$$\eta = \frac{(212)}{(94)(2.574)} = 0.876$$

4. CO_2 Acceptor Process(5)

In this process, lime is added to the gasifier both to remove CO_2 and to provide the heat of reaction for the gasification reaction, thus eliminating the need for an oxygen plant. The removal of CO_2 enhances the water gas shift reaction while the crude effluent gas has a high methane content (∿ 12%) and a three to one ratio of H_2/CO, thus eliminating the need for a separate water gas shift. The calcium carbonate is regenerated (calcined) by using the heat of combustion of coal. The flowsheet for this system is shown in Figure 5.

The gasifier reactions are:

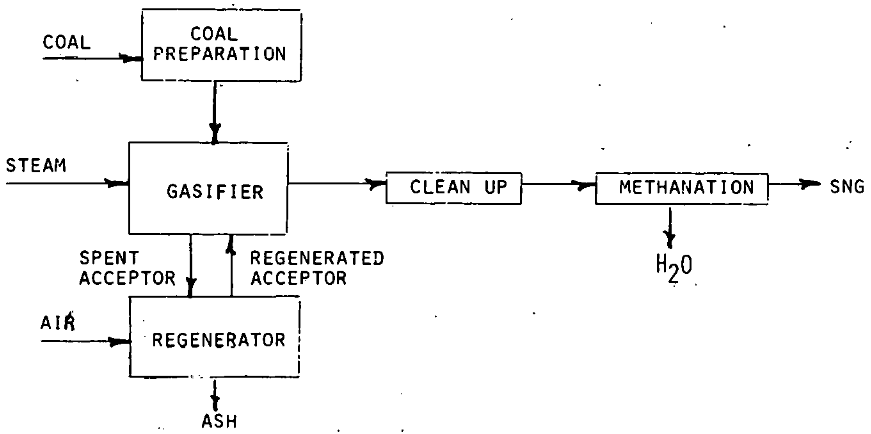
	ΔH^o_{298}
$C + H_2O = 1/2CH_4 + 1/2CO_2$	12
$C + H_2O = CO + H_2$	42
$1/2CO + 1/2H_2O = 1/2CO_2 + 1/2H_2$	0
$CaO + CO_2 = CaCO_3$	-42.5
$2C + 5/2H_2O + CaO = 1/2CH_4 + 3/2H_2 + 1/2CO + CaCO_3$	11.5

Regeneration is given by

$$CaCO_3 = CaO + CO_2 \qquad 42.5$$

while methanation requires

$$3/2H_2 + 1/2CO = 1/2CH_4 + 1/2H_2O \qquad -30$$



REACTIONS

GASIFICATION: $C + H_2O = 1/2CH_4 + 1/2CO_2$

$C + H_2O = CO + H_2$

WATER GAS SHIFT: $CO + H_2O = CO_2 + H_2O$

ACCEPTOR: $CaO + CO_2 = CaCO_3$

REGENERATION: $CaCO_3 = CaO + CO_2$

METHANATION: $3H_2 + CO = CH_4 + H_2O$

Figure 5. Medium temperature gasification with lime (CO_2 acceptor process).

Regeneration requires (42.5 + 11.5)/94 = 0.574 g/moles carbon. The carbon efficiency is thus given by

$$\xi = \frac{1}{2 + 0.574} = 0.388$$

and the thermal efficiency is

$$\eta = \frac{212}{(2.574)(94)} = 0.876.$$

A summary of the calculated ideal efficiencies for the four gasification processes is given in Table 1.

Table 1

Efficiencies of Coal Gasification Processes
for Production of SNG (CH_4)

Process	Coal Utilization Efficiency - %	Thermal Efficiency - %
1) Coal Gasification Reference	31.8	71.6
2) Catalytic Gasification	44.3	100.0
3) Hydrogasification	38.8	87.6
4) CO_2 Acceptor	38.8	87.6

For production of SNG, the highest utilization and thermal efficiency is the catalytic gasification process. The hydrogasification and CO_2 acceptor processes are roughly equivalent while the standard coal gasification reference process is clearly the least efficient. The CO_2 acceptor process suffers from the costly problem of handling large quantities of high temperature solids (lime and limestone). The catalytic gasification and hydrogasification processes have been selected for further study since in addition to their high efficiency

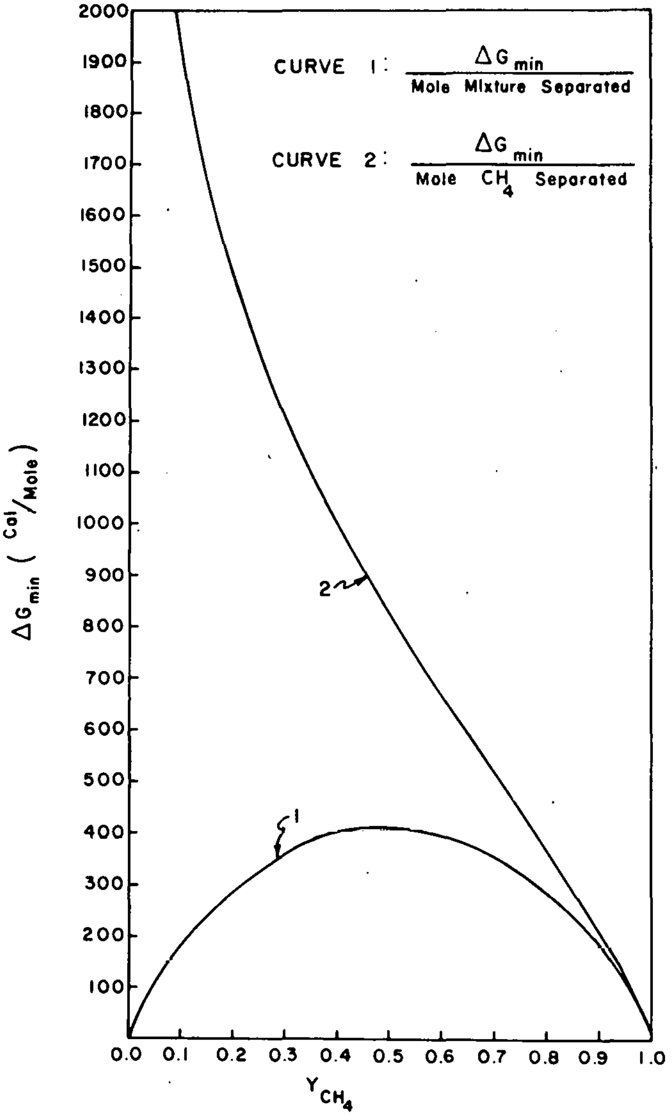


Figure 6.

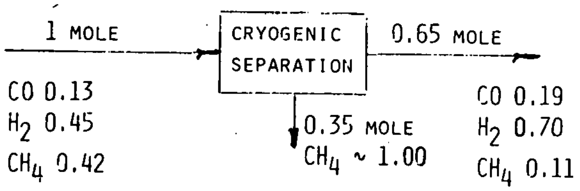


Figure 7.

compared with standard gasification, they both involve effluent streams which must be separated into product (CH_4) and recycle streams. The assessment of various gas separation schemes will be a major task of this program.

Gas Separation

Although the coal gasification (water gas or hydrogenation) is a central step in the coal conversion process, it has become known that the downstream or product separation steps make up a major fraction of the cost of the process. Thus product gas separation is worthy of study for possible improvements.

The gasification of coal (considered as carbon) leads to systems containing the following six components: C, CO, CO_2, H_2, H_2O, and CH_4. Three independent chemical reactions can be written for this system.

$$C + H_2O = CO + H_2 \qquad \text{Water Gas Reaction}$$

$$CO + H_2O = CO_2 + H_2 \qquad \text{CO-Shift}$$

$$C + 2H_2 = CH_4 \qquad \text{Hydrogenation}$$

From the above reactions, a number of important dependent reactions are readily derived. Among these are the following:

$$C + H_2O = 1/2CH_4 + 1/2CO_2$$

$$CO + 3H_2 = CH_4 + H_2O \qquad \text{Methanation}$$

$$CO + CO_2 = 2CO \qquad \text{Boudouard Reaction}$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O \qquad CO_2\text{-Methanation}$$

If the gasifier is oxygen-blown, one additional equation is required, e.g.

$$C + O_2 = CO_2$$

Thus, the species in the gasifier effluent will consist of five major gases CO, CO_2, H_2, H_2O, and CH_4 and some minor components such as NH_3,

H_2S, COS, etc. which derive from the heteroatoms in the coal. Ammonia and water are removed in a condensation step while CO_2, H_2S, and COS are acid gases which can be removed by a number of solvent absorption processes such as Purisol, Recitsol, etc. Thus, the focus of attention for gas separation will be the separation of mixtures of CO, H_2, and CH_4.

Separations of Ideal Gas Mixtures

As a first approximation, the minimum energy for complete separation of representative mixtures is calculated as the negative of the entropy of mixing for ideal gases multiplied by the temperature.

$$-\Delta G = W_{min} = T\Delta S_{mix} = RT\sum_i y_i \ln y_i \qquad (12)$$

R = gas constant = 1.987 cal/g-mole-°K

T = 298°K

y_i = mole fraction species i in the gas mixture

W_{min} = ideal minimum work required for separation into components with each component at the same volume as the initial mixture (cal/g-mole)

The results of the calculation are given in Table 2 for a range of gas mixtures of interest in FHP and catalytic gasification.

Table 2

Minimum Energies of Separation for Some Representative Mixtures

	FHP			Catalytic Gasification	
H_2	0.90	0.70	0.5	0.34	0.45
CH_4	0.10	0.30	0.5	0.33	0.40
CO	0.0	0.0	0.0	0.33	0.15
W_{min} / mole mixture	192	362	410	650.5	598
W_{min} / mole methane separated	1920	1207	820	1971	1495
W(20%) / mole methane	9600	6035	4100	9855	7475

The quantity W(20%) represents the minimum energy required for separation at an efficiency of 20% which is typical of the maximum efficiency for a cryogenic separation obtained, for example, from the large-scale separation of oxygen from air. It can be readily shown (see Appendix A) that the minimum energy required for total separation is a maximum for equimolar mixtures and is given by the equation

$$W_{min}^{max} = RT\ln N \tag{13}$$

where N is the total number of components and $x_i = 1/N$. Figure 6 is a plot of separation energy vs. mole fraction for an ideal binary system for complete separation.

In general, complete separations are not physically or economically feasible so that minimum energies for partial separations are quantities of interest. For example, the Exxon catalytic gasification process cryogenically separates CO, H_2, and CH_4 into a stream of almost pure methane and a recycle stream with roughly 11% CH_4, 70% H_2, and 19% CO (see Figure 7).

The minimum energy required for separation of the inlet stream into the above product and recycle stream into the above product and recycle streams is given by

$$W_{min} = RT\sum_j n_j \sum_i y_i \ln y_i \tag{14}$$

where the first sum is over all streams (+ for in, - for out). Thus

$$\begin{aligned} W_{min} &= -(1.987)(298)[0.13\ln 0.13 + 0.45\ln 0.45 + 0.42\ln 0.42] \\ &\quad + (0.6467)(1.987)(298)[0.19\ln 0.19 + 0.70\ln 0.70 + 0.11\ln 0.11] \\ &\quad + (0.3533)(1.987)(298)[0] \\ &= 276 \text{ cal/mole mixture} \end{aligned}$$

$$\Delta G_{min} = 781 \text{ cal/mole } CH_4 \text{ separated}$$

$$\Delta G(20\%) = 3906 \text{ cal/mole } CH_4 \text{ separated}$$

It is also of interest to calculate the separation energy for binary mixtures into two streams, a pure product stream and a recycle stream containing both components as shown in Figure 8. The following equation is derived from that figure:

$$\frac{\Delta G}{RT} = y_A \ln y_A + y_B \ln y_B - a(y_A' \ln y_A' + y_B' \ln y_B') - b(y_A'' \ln y_A'' + y_B'' \ln y_B'') \tag{15}$$

Using the fact that $y_A + y_B = y_A' + y_B' = 1$ and $y_A = ay_A'$ allows the above equation to be rewritten in terms of y_A and a. (Note that the term b(...) on the right hand side of (15) is zero.)

$$\frac{\Delta G}{RT} = (1 - y_A)\ln(1 - y_A) - (a - y_A)\ln(a - y_A) + a \ln a \tag{16}$$

Division of ΔG by 1 - a = b gives the free energy per mole of B separated. Figure 9 is a graph of ΔG vs. y_{CH_4} with the quantity b as parameter. The dotted curve gives the energy for complete separation per mole of methane. For example, if the inlet stream contains 40% CH_4 and the pure product methane stream is 0.3 moles CH_4 per mole of feed, then the minimum energy required is about 760 cal which is 46% of the energy required for complete separation. The same data is given in Figure 10 with ΔG vs. b and y_{CH_4} as parameter. The dotted curve is again the energy required for complete separation. It should be noted that these curves approach a limiting value as b → 0. It can be shown (see Appendix B) that the limiting value of equation 16 as b → 0 is given by

$$\Delta G = RT\ln(1 - y_A)$$

$$= RT\ln y_{CH_4}$$

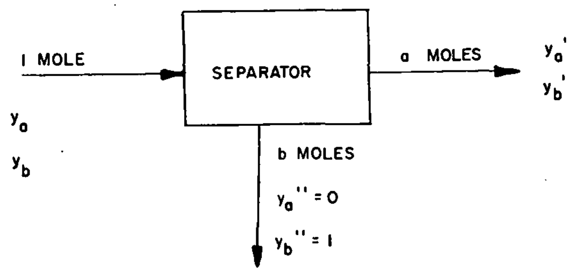


Figure 8.

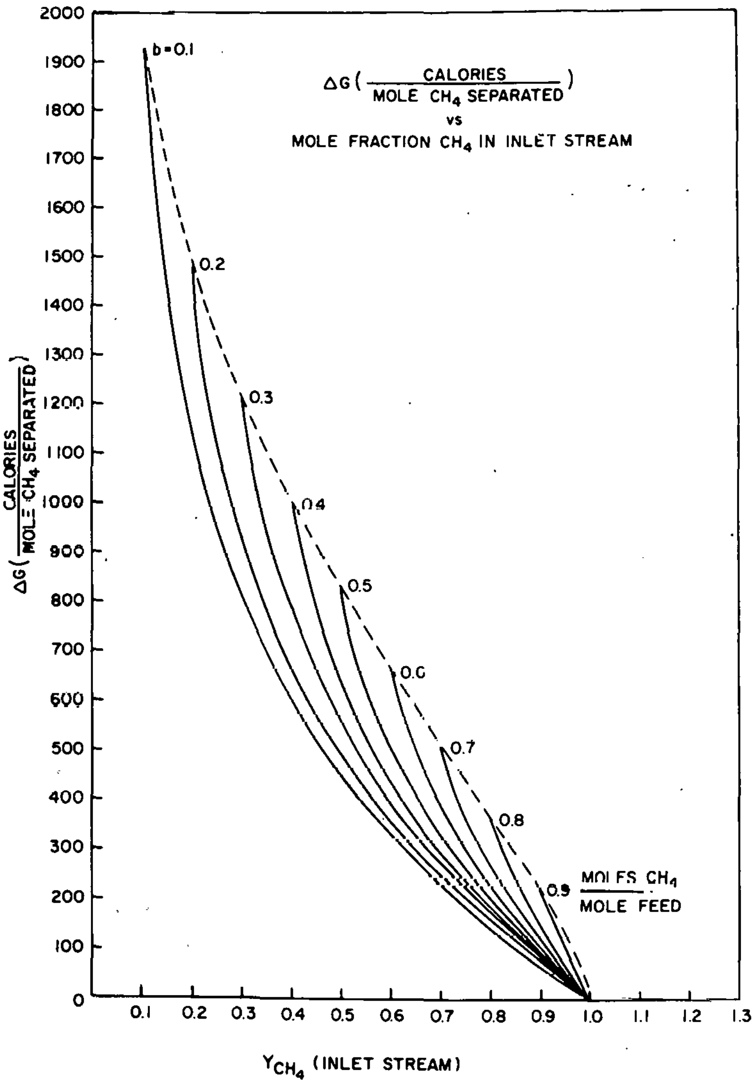


Figure 9.

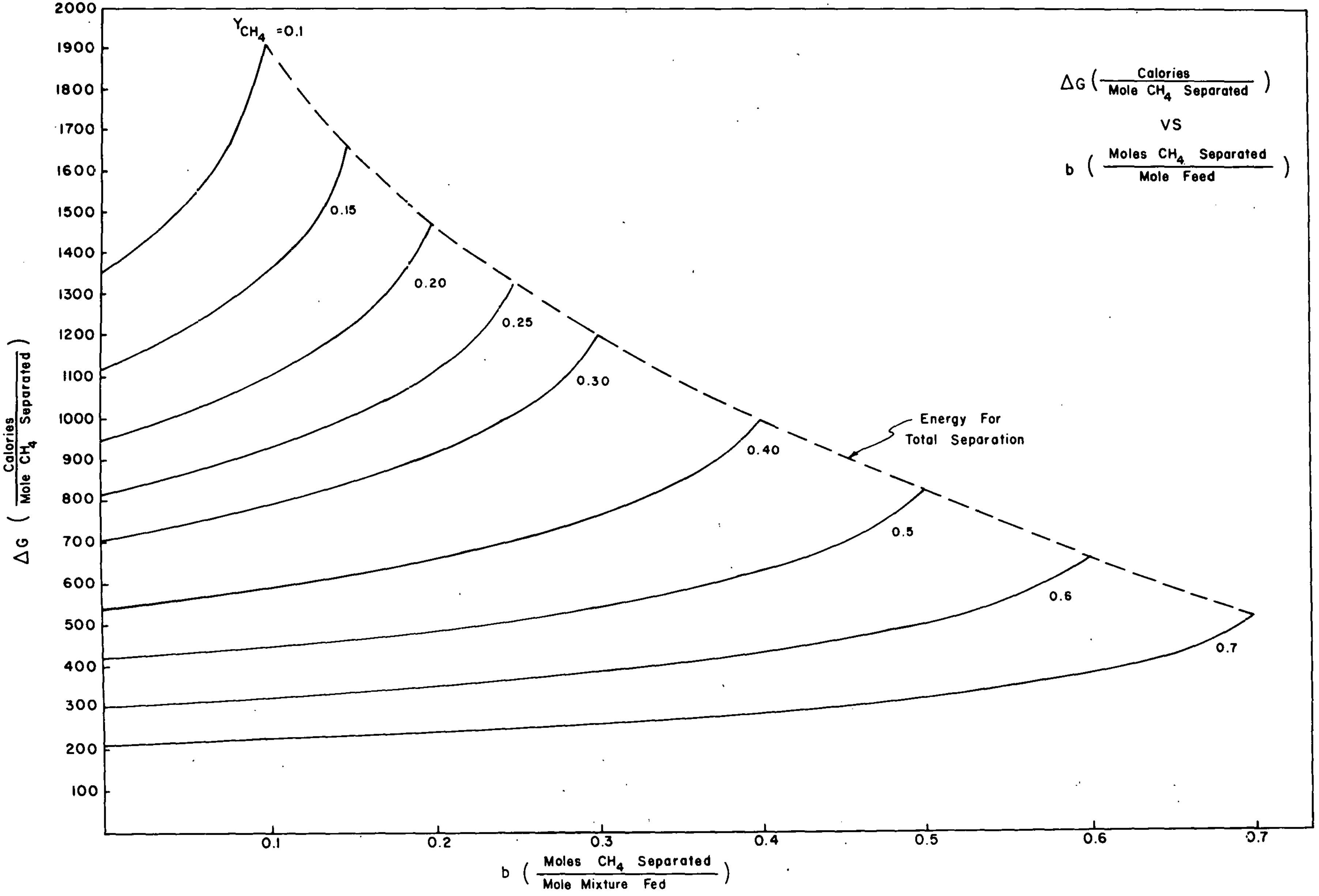

ΔG (Calories / Mole CH_4 Separated)
VS
b (Moles CH_4 Separated / Mole Feed)
Y_{CH_4} =0.1
0.15
0.20
0.25
0.30
0.40
0.5
0.6
0.7
Energy For Total Separation
ΔG (Calories / Mole CH_4 Separated)
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0.1
0.2
0.3
0.4
0.5
0.6
0.7
b (Moles CH_4 Separated / Mole Mixture Fed)

Figure 10.

Separation Methods

Having discussed the minimum energy for separation of ideal gases, it is appropriate at this point to consider some separation schemes which will be reviewed and evaluated in the near future. A somewhat arbitrary division into five categories has been made. These are: (1) liquefaction, (2) adsorption, (3) absorption, (4) chemical, and (5) diffusional methods.

1) Liquefaction - Since all gases are completely miscible, any separation method which depends upon phase equilibrium will require the generation of an additional phase. One such method entails liquefaction of at least part of the gas. Since this is possible only below the critical temperature which is below room temperature for most gases, refrigeration is required. The degree of difficulty of the separation depends upon the relative volatilities of the components and fractional distillation of the liquefied gases is frequently required. Since cryogenic distillation is well established technology, it will serve as the base case against which other separation techniques will be measured.

2) Adsorption - The selective adsorption of one or more of the constituents of the gaseous mixture (CO, H_2, CH_4) on various solid sorbents will also be considered. Adsorbents may be naturally occurring or synthetic materials (e.g. molecular sieves) whose internal pore surfaces are accessible for selective combination of solute and solid. In the case of physical adsorption (e.g. adsorption on activated carbon), the attractive forces between solute and sorbent are relatively weak and less specific than those of chemical bonds. If adsorption occurs through chemical bonding, it is termed chemisorption.

In a preliminary evaluation of methods of separating methane from synthesis gas, Dravo Corporation concluded that adsorption on activated carbon was more attractive than cryogenic separation for the following reasons: (1) the adsorption process produces a pure methane product (less than 0.1% CO), (2) it provides for nearly quantitative recovery of methane and hydrogen, (3) it is a flexible process with regard to the number of streams that can be produced, (4) it is mechanically simpler than a cryogenic system, and (5) "breakthrough" of high boiling components is readily accommodated by the activated carbon system - freezing could occur in the cryogenic system, seriously affecting operations.

3) Absorption - This method of separation involves selectively dissolving one or more components of the gaseous mixture (preferably CH_4 in our case) in a solvent. The absorbed material may dissolve physically in the liquid or react chemically. Solute would be desorbed by stripping or distillation and the solvent returned to the absorption step for reuse. Absorption is used extensively in the chemical process industries for removing impurities from gaseous product streams and for removing potential pollutants from gaseous process effluents. For example, the byproduct gas from coke ovens is washed with water or sulfuric acid to remove ammonia and again with an oil to remove benzene and toluene vapors. Hydrogen sulfide and carbon dioxide can be removed

from synthesis gas by scrubbing with alkaline solutions or amines. The captured benzene and toluene mentioned above are normally removed from the oil by injecting live steam (steam stripping) into the solute laden oil, whereupon the vapors enter the gas steam and are carried away. The regenerated oil may be recycled for reuse. Tables 3 and 4 list more solute/solvent systems amenable to the gas-absorption process.

In addition to the relative solubilities of the constituents of the gaseous mixture with respect to a particular solvent, several other factors effect the economic viability of the absorption process, such as solvent pumping energy, the energy required to desorb the captured gas(es) and regenerate the solvent, and the volatility and cost of the solvent. All of these factors must be taken into account when designing a commercial gas absorption system.

4) Chemical - The use of clathrate compounds for the separation of gas mixtures will be investigated. Clathrates are cage-like compounds in which a guest molecule (or atom) is enclosed by a structure composed of host molecules. The host molecules are usually hydrogen bonded and there are no chemical bonds between host and guest. For example, hydroquinone clathrates have the general formula $3C_6H_4(OH)\cdot X$ where X can be CH_4, CO, CH_3OH, and others. The gas hydrates are another important class of clathrates. They are formed when water is solidified in the presence of certain gases including CH_4, C_2H_6, C_3H_8, and others. In fact, they are claimed to occur in nature and are known to form in gas transmission lines in the presence of water vapor. The formation of methane hydrates as a method of gas separation in effect raises the condensation temperature of methane which might compete with cryogenic separation methods.

Table 3

Gas-Absorption Systems of Commercial Importance*

Solute	Solvent	Reagent	Degree of Commercial Importance		
			High	Moderate	Low
CO_2, H_2S	Water	--	X		
CO_2, H_2S	Water	Monoethanolamine	X		
CO_2, H_2S	Water	Diethanolamine	X		
CO_2, H_2S	Water	Triethanolamine	--	--	X
CO_2, H_2S	Water	Diaminoisopropanol	--	--	X
CO_2, H_2S	Water	Methyl diethanolamine	--	--	X
CO_2, H_2S	Water	K_2CO_3, Na_2CO_3	X		
CO_2, H_2S	Water	NH_3	--	X	
CO_2, H_2S	Water	NaOH, KOH	--	X	
CO_2, H_2S	Water	K_3PO_4	--	X	
CO_2	Propylene carbonate	--	--	X	
CO_2	Glycerol triacetate	--	--	X	
CO_2	Butoxy diethylene glycol acetate	--	--	X	
CO_2	Methoxy triethylene glycol acetate	--	--	X	
HCl, HF	Water	--	X		
HCl, HF	Water	NaOH	X		
Cl_2	Water	--	X		
SO_2	Water	--	--	--	X
SO_2	Water	NH_3	--	X	
SO_2	Water	Xylidine	--	X	
SO_2	Water	Dimethyl aniline	--	X	
SO_2	Water	$Ca(OH)_2$, oxygen	--	--	X
SO_2	Water	Aluminum hydroxide-sulfate	--	X	
NH_3	Water	--	X		
NO_2	Water	--	X		
HCN	Water	NaOH	X		
CO	Water	Copper ammonium salts	X		

---

*Kohl and Reisenfeld, Chem. Eng., 66 (12), 127 (1959); Sherwood and Pigford, "Absorption and Extraction," McGraw-Hill, New York, 1952.

Table 4

Solutes and Non-Aqueous Solvents for Gas Absorption*

Solutes	Solvents
Acetylene, C_2H_2	Acetic acid (glacial), $C_2H_4O_2$
Air	Acetic anhydride, $C_4H_6O_3$
Ammonia, NH_3	Acetone, C_3H_6O
Bromine, Br_2	Amyl alcohol, $C_5H_{12}O$
Carbon dioxide, CO_2	Aniline, C_6H_7N
Carbon monoxide, CO	Benzene, C_6H_6
Chlorine, Cl_2	Bromobenzene, C_6H_5Br
Ethane, C_2H_6	Carbon disulfide, CS_2
Ethylene, C_2H_4	Carbon tetrachloride, CCl_4
Hydrogen, H_2	Chlorobenzene, C_6H_5Cl
Hydrogen chloride, HCl	Chloroform, $CHCl_3$
Hydrogen sulfide, H_2S	Ethyl acetate, $C_4H_3O_2$
Methane, CH_4	Ethyl alcohol, C_2H_6O
Methyl chloride, CH_3Cl	Ethylene chloride, C_2H_4Cl
Nitric oxide, NO	Ethyl ether, $C_4H_{10}O$
Nitrogen, N_2	Methyl acetate, $C_3H_6O_2$
Nitrous oxide, N_2O	Methyl alcohol, CH_4O
Oxygen, O_2	Nitrobenzene, $C_6H_5NO_2$
Sulfur dioxide, SO_2	Propyl alcohol, C_3H_8O
Etc.	Propylene, C_3H_6
	Toluene, C_7H_8
	Etc.

---

*Perry's Chemical Engineers Handbook, 5th Ed.

Another potentially useful chemical system would remove hydrogen via metal hydride formation.[7] For example, the intermetallic compound FeTi reacts reversibly with molecular hydrogen to form iron titanium hydride according to the following scheme:

$$2.13\ FeTiH_{0.10} + H_2 = 2.13\ FeTiH_{1.04}$$

$$2.20\ FeTi\ H_{1.04} + H_2 = 2.20\ FeTiH_{1.95}$$

In order to remove hydrogen, the temperature of the system is raised. Figure 11 shows the pressure-composition isotherms for the iron-titanium system. A number of other metal hydrides will also be considered.

5) Diffusional - Such processes would achieve separation by diffusion of the components of the gas through a membrane or barrier at different rates. Ideally, the membrane will be highly selective permitting the passage of only one component. The metal palladium is highly selective to hydrogen which is associatively adsorbed on the high pressure side, passes through the metal as hydrogen atoms, and recombines at the low pressure side to reform H_2 gas. R. J. Teitel Associates[8] has developed a microcavity system consisting of hollow glass microspheres which allow diffusion of hydrogen and helium only. The potential for use in a hydrogen separation process will be examined. Finally, other membrane processes such as that under development by DuPont will be examined.

Alternative Coal Conversion Processes

Some study is being given to seeking alternate coal conversion processes with the objective of finding potentially attractive new gasification and/or liquefaction concepts. The current concepts are listed below by subject only and will be expanded upon in future reports.

1. Thermal formation of metal carbides which can be hydrolyzed to hydrocarbon products.
2. The flame hydropyrolysis of coal.
3. Formic acid and formaldehyde treatment of coal for hydrocarbon formation.
4. A moving bed hydropyrolysis reactor.

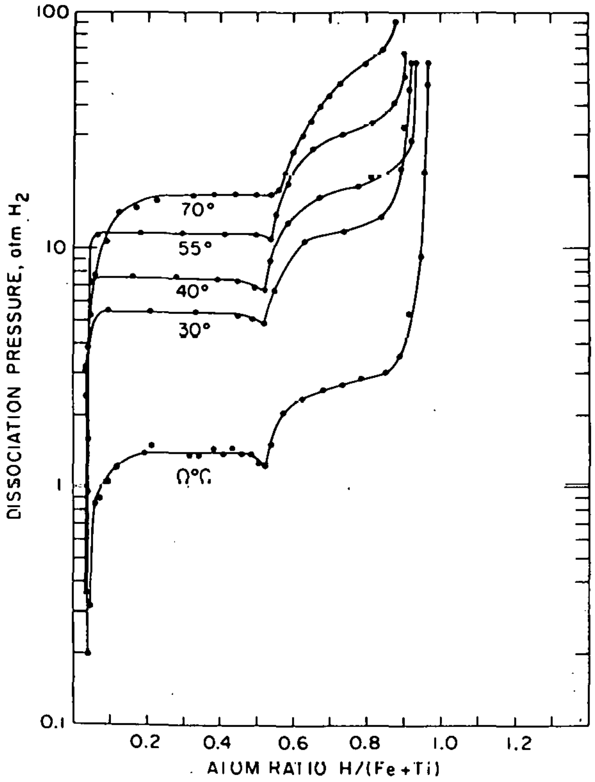


Figure 11. Pressure-composition isotherms for the Fe-Ti-H system.

References

1. Howard-Smith, I. and Werner, G. J., Coal Conversion Technology, Noyes Data Corp., New Jersey (1976) p. 47, 119.

2. Steinberg, M., Fallon, P., Dang, V., Bhatt, B., Zeigler, E., and Lee, Q., Reaction Process and Cost Engineering for the Flash Hydropyrolysis of Coal, BNL 25232; Proceedings of the 71st AIChE Meeting, Nov. 1978, Miami Beach, Florida.

3. Oberg, C. L., Falk, A. Y., and Silverman, J., Flash Hydropyrolysis of Coal Using Rockwell Short-Residence Time Reactors, Proceedings of 71st AIChE Meeting, Nov. 1978, Miami Beach, Florida.

4. Vadovic, C. J. and Eakman, J. M., Kinetics of Potassium Catalyzed Gasification, DOE Contract #(49-18)-2369.

5. Howard-Smith, I. and Werner, G. J., Op. Cit. p. 42, 117.

6. Dravo Corporation Report, Hydrogasification Gas Processing Studies, Contract CPD-7029.

6. Reilly, J., Hoffman, K. C., Strickland, J., Wiswall, R., Iron Titanium Hydride as a Source of Hydrogen Fuel for Stationary and Automotive Applications, 26th Annual Proceedings Power Sources Conference, May 1974.

8. R. J. Teitel Associates, Microcavity Systems (MCS) for Hydrogen Storage and Separation, Report No. 780001005V.

Appendix A

Calculation of the maximum minimum energy of separation for ideal gas mixtures.

Let $f = \frac{W}{RT} = \sum_i y_i \ln y_i .$

It is desired to maximize the above equation subject to the constraint

$$\sum_i y_i = 1$$

Using the method of Lagrange multipliers gives the following expression:

$$\delta f = \sum_i (1 + \ln y_i) \delta y_i$$

$$\lambda \delta g = \lambda \sum_i \delta y_i$$

$$\delta f + \lambda \delta g = \sum_i (1 + \ln y_i + \lambda) \delta y_i = 0$$

λ is the Lagrange multiplier. Since $\delta y_i \neq 0$, the above expression requires that

$$1 + \ln y_i + \lambda = 0.$$

Therefore

$$y_i = e^{-(1 + \lambda)}.$$

Now

$$\sum_i y_i = \sum_{i=1}^{N} e^{-(1 + \lambda)} = Ne^{-(1 + \lambda)} = 1.$$

We conclude that

$$1 + \lambda = \ln N$$

where N is the number of components in the mixture. Substitution back into the equation for f yields

$$f = \frac{W}{RT} = -\sum_{i=1}^{n}(1 + \lambda)e^{-(1 + \lambda)} = \sum_{i=1} \ln N e^{-\ln N} = \ln N.$$

Therefore,

$$W_{\min}^{\max} = RT\ln N$$

with

$$y_i = 1/N$$

Appendix B

<u>Calculation of limiting value for energy of separation of ideal binary gas mixtures.</u>

It is desired to calculate the limit as b(=1 - a) → 0 for the expression

$$\Delta G\left(\frac{\text{cal}}{\text{mole B separated}}\right) = \frac{RT}{b}\left[(1-y_A)\ln(1-y_A)-(a-y_A)\ln(a-y_A) + a\ln a\right]$$

(See Figure 8 in text for diagram of the process and definition of symbols.) Let $x = 1 - y_A$ and substitute $b = 1 - a$ into the bracketed part of the above equation.

$$\begin{aligned}[\,] &= x\ln x - (x-b)\ln(x-b) + (1-b)\ln(1-b)\\ &= x\ln x - (x-b)\ln x(1-b/x) + (1-b)\ln(1-b)\\ &= x\ln x - (x-b)\ln x - (x-b)\ln(1-b/x) + (1-b)\ln(1-b)\end{aligned}$$

Expanding $\ln(1-x) \doteq -x$ yields

$$\begin{aligned}[\,] &\doteq x\ln x - x\ln x - b\ln x - (x-b)(-b/x) + (1-b)(-b)\\ &\doteq b\ln x + b^2 - \frac{b^2}{x}\end{aligned}$$

Now

$$\Delta G \doteq \frac{RT}{b} (b\ln x + b^2 - \frac{b^2}{x})$$

for small b. In the limit as b → 0, we have

$$\Delta G \doteq RT\ln x = RT\ln(1 - y_A)$$