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THE MANUFACTURE OF HIGH BTU GAS FROM COAL

Ralph H. Schatz

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I. INTRODUCTION

Increasingly larger quantities of fuel gas are being used yearly in the United States for both domestic and industrial heating by consumers who prefer the convenience, low cost, and cleanliness of gas to other sources of energy. Natural gas from gas wells located primarily in the Southwest accounts for over ninety percent of the fuel gas consumed yearly, and this percentage is increasing with each succeeding year. Like most natural resources, natural gas is not an inexhaustible commodity, and the gas industry has a vital interest in having a substitute for natural gas available if the need should arise. While the existence of large known reserves of natural gas and the continual discovery of new reserves insures the availability of this source of energy for many years, nevertheless, the dedication of large portions of these reserves to existing inter-state pipe lines and to large volume users at the point of production may in the near future make natural gas unavailable or in short supply in many areas of the country not served directly by pipe lines. It is becoming increasingly apparent that the possibility of obtaining fuel gas from other sources should be considered long before the day when natural gas reserves actually near exhaustion.

The existence of extensive known coal reserves in the United States makes coal a logical choice as the raw material for fuel gas manufacture. Combustible gas mixtures can be manufactured by gasifying coal with air or oxygen and steam, using any one of several processes. The gas mixtures produced, however, are of low

heating value. At present there is not a one-step gasification process known which can deliver a gas with a heating value greater than about 500 BTU/SCF. Long distance transmission lines and utility equipment in use today have, for the most part, been designed for natural gas which has a heating value of about 1000 BTU/SCF. Because the transmissions of low BTU gas and also the conversion of utility equipment to accommodate a 450 to 500 BTU gas may be prohibitively expensive, low BTU fuel gas manufactured from coal must be upgraded to a high BTU gas comparable to natural gas if it is to serve as an attractive substitute. Upgrading can be accomplished by catalytically converting the hydrogen and carbon monoxide present in the gaseous products from coal gasification to methane. Processes and catalysts for methane synthesis have been studied extensively.

An overall process for the conversion of coal to high BTU fuel gas would require five steps: (1) gasification of coal with steam and oxygen to produce synthesis gas; (2) removal of carbon dioxide and sulfur compounds from this synthesis gas; (3) catalytic conversion of synthesis gas to methane; (4) removal of carbon dioxide from the gas produced; and (5) compression of the purified high BTU gas to transmission pipe line pressure. It is the purpose of this report to review briefly the processes which may be used for gasifying coal and for purifying synthesis gas, to discuss in detail the catalysts which have been investigated and developed for the methanation reaction, and to present economics for the overall process of making high BTU gas from coal in the light of present-day costs.

II. GASIFICATION

Because there is not a one-step process known which will convert coal or other solid fuel to a fuel gas with a heating value greater than about 500 BTU/SCF, any process to manufacture high BTU gas of 850 to 1000 BTU/SCF from coal must necessarily consist of a number of sub-processes. Gasification of the solid fuel to produce a mixture of CO and H_2, generally referred to as "synthesis gas," is the first step of an integrated process (which includes purification and methanation steps) to produce high BTU gas. The relative importance of the gasification step compared to the subsequent processing steps is illustrated by Table I which shows the share which each sub-process contributes to the overall cost of manufacturing high BTU gas from coal.

TABLE I.   RELATIVE COST OF THE VARIOUS STEPS IN
           MANUFACTURING HIGH BTU GAS FROM COAL
           AS A PERCENTAGE OF THE TOTAL COST

Gasification (including raw materials cost)	70.0%
Initial Purification	11.4
Methanation	4.1
Final Purification	2.4
Final Compression	2.2
Auxiliaries	9.9
Total	100.0%
Fuel Cost (coal)	29.2%
Raw Material Cost	60.5%

The data of Table I are developed and discussed in greater detail

in a later section on the Economics of High BTU Gas Manufacture,

but serve at this point to show that gasification of the solid fuel

plus purification of the synthesis gas prior to upgrading comprise

about 80% of the total cost of producing high BTU gas. The need

for developing efficient and inexpensive methods of gasification,

as well as improved methods for mining coal, are obvious. A great

deal of research is justified to devise means by which the cheapest

of fuels can be converted to synthesis gas in large units with a

minimum of operating expense.

Gasification of coal is by no means a new development.
There are numerous references in the literature to gasification

processes, including foreign developments. A historical review of

gasification developments will not be attempted, but rather this

section will be devoted to discussing those processes which appear

particularly promising for production of synthesis gas from American

coals. These, to a large degree, are of the coking variety, and there-

fore, gasification units which may ultimately be developed for process-

ing American coals are likely to differ from those developed in

Europe where non-coking coals are available in great quantity.

The reactions which take place and the products formed

when solid carbonaceous fuel is gasified by oxygen and steam may be

described by the following equations:

$$C + H_2O \rightleftarrows CO + H_2, \qquad \Delta H = 58,340 \text{ Btu/lb mol C at } 1300° \text{ K.} \qquad (1)$$

$$C + 2H_2O \rightleftarrows CO_2 + 2H_2, \qquad \Delta H = 44,635 \text{ Btu/lb mol C at } 1300° \text{ K.} \qquad (2)$$

$$C + 1/2\ O_2 \rightleftarrows CO, \qquad \Delta H = -48,982\ Btu/lb\ mol\ C \\ at\ 1300°\ K. \qquad (3)$$

$$C + O_2 \rightleftarrows CO_2, \qquad \Delta H = -170,021\ Btu/lb\ mol\ C \\ at\ 1300°\ K. \qquad (4)$$
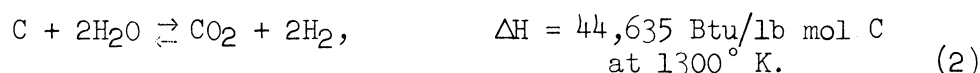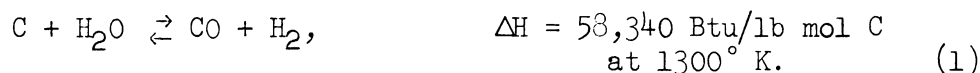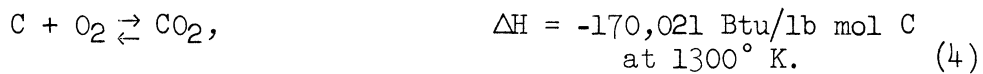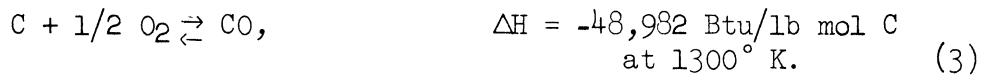
The formation of CO, CO_2 and H_2 according to equations (1) and (2) requires a high reaction temperature. Moreover, the two reactions are endothermic in nature, making it difficult to maintain the required temperature. Early practice in water-gas manufacture was to blow a fixed-bed of fuel with air [equations (3) and (4)] in order to raise the temperature of the bed to a desired level and then to pass steam through the hot bed to produce a mixture of H_2 and CO [equation (1)]. This type of operation was necessarily cyclic in nature, because the fuel bed was continuously cooled during the endothermic water-gas step and periodically had to be reheated by air-blowing. The gas produced during the water-gas operation had a gross heating value in the range of 250 to 350 BTU SCF after H_2O and CO_2 were removed. It was not economical practice to combine the pre-heating step with the water-gas step by simultaneously passing air and steam through the fuel bed, because the inert nitrogen present in the blast air ended up in the product, reducing its heating value. Synthesis gas which has been produced by gasification of coal with air and steam cannot be upgraded to high BTU gas by methane synthesis, if by high BTU gas we mean a product with a heating value above 350 BTU SCF, because of the presence of inert nitrogen which is introduced with the air blast and acts to dilute the heating value of the product.

The development of economical processes to produce large
quantities of relatively pure oxygen, e.g., the Linde-Frankel proc-
ess, eliminated the need for cyclic operation in water-gas manufacture.
Oxygen and steam could be simultaneously introduced to produce a
product containing CO, H_2, CO_2, H_2O with only a small amount of
inert nitrogen. The availability of pure oxygen is of fundamental
importance, for without oxygen the production of high BTU gas is
virtually impossible. The subject of oxygen production will not
be discussed other than to say that commercially proven processes,
which are based upon low temperature distillation of liquid air,
are available. Unfortunately, however, oxygen is expensive; the
cost of oxygen used in gasification accounts for better than 10%
of the cost of the final high-BTU product. Any economies which
can be made in oxygen production will, therefore, be a primary
factor in reducing the cost of producing high BTU gas.

The American Gas Association has sponsored research in
which the effect of gasification temperature and pressure on the
equilibrium composition of the products from gasification of char
have been determined.[1] These calculations show that an increase
of reaction temperature brought about by increasing the oxygen
to steam ratio of the blast gas decreases the H_2 to CO ratio of the
product gas. Oxygen consumption is increased and steam consumption
is reduced. Total gas yield of net combustibles ($CO + H_2 + CH_4$)
is virtually unchanged.

Increasing the gasification pressure greatly reduces
oxygen consumption at a given gasification temperature. The yield
of net combustibles (CO, H_2 and CH_4) falls off slightly with

higher pressure, but the yield of methane increases appreciably. Increased pressure results in an increase in the product H_2 to CO ratio, as shown by the following tabulation.

GASIFICATION OF CHAR

H_2/CO Ratio at 700°C and Various Pressures[1]

Pressure, atm.	H_2/CO ratio
1	1.2
5	1.97
10	2.38
20	2.78
85	3.52

At pressures above 10 atm. the gas composition has reached the point where the H_2 to CO ratio is out of the range for complete stoichiometric reaction, and the gas becomes more and more unsuitable for upgrading. Raising the operating temperature will remedy this situation, however, since higher temperatures decrease the H_2 to CO ratio of the product gas. The calculated results of gasification of char at 85 atm. and 800°C are shown in Table II. At temperatures in the region of 800°C and above, ash formed by gasification can be above its softening point. In this event, ash must be removed from gasification reactors in the form of liquid slag. Another method of adjusting H_2 to CO ratios of product gas to desired values can be utilized at temperatures below the ash softening point. Carbon dioxide can be recycled to the gasification reactors, thus shifting the equilibrium described by the equation

$$H_2 + CO_2 \rightleftarrows CO + H_2O \tag{5}$$

to form more CO. Theoretically, gas with a suitable H_2 to CO ratio

for upgrading can be produced at any pressure and suitable gasifica-

tion temperature by using proper ratios of oxygen to steam in the

blast gas, and if necessary by recycling carbon dioxide.

TABLE II. CALCULATED RESULTS OF GASIFICATION OF CHAR
AT ELEVATED PRESSURES AND TEMPERATURES[1]

Pressure, atm.	85	
Temperature, °C	800	
Blast Gas Composition, vol. %		
H_2O	91.3	
O_2	8.3	
N_2	0.4	
Product Gas Composition, %	As produced	$H_2O + CO_2$ free
CO	12.6	25.8
CO_2	17.8	--
H_2	24.7	50.5
H_2O	33.3	--
CH_4	10.7	21.9
H_2S	0.2	0.4
N_2	0.7	1.4
	100.0	100.0
H_2/CO ratio	1.96	
Gas Yield SCF/lb. fuel		
Total	65.3	
Net Combustible (CO + H_2 + CH_4)	31.4	

Three main principles of gasification have shown promising

results. These are:

    1. Fixed-bed countercurrent gasification operating at

either elevated or atmospheric pressure and employing oxygen-steam

blast.

    2. Down-draft gasification; e.g., the Flesh-DEMAG process.

    3. Gasification in suspension.

Any of the above could serve as the basis for a process to manufacture synthesis gas from American coking coals. A short discussion citing the advantages, disadvantages and future potentialities of each follows.

A. Fixed-Bed Countercurrent Gasification

The upward flow of blast gas (oxygen and steam) and the slow downward movement of the fuel bed are characteristic of the countercurrent gasification process. Countercurrent reactors have deep fuel beds with a large excess of carbon present. A sequence of zones exist in the fuel bed. In the direction of gas flow these are the ash zone, the oxidation zone, the reduction zone, and the preheating zone. Countercurrent processes, which are fed by gravity flow of the fuel, require a uniformly sized, non-agglomerating fuel with a minimum of fines to insure uniformity of flow. Classical gasification fuels are lump coke, double-screened anthracite, non-caking bituminous coals, and briquetted brown coal or lignite. Countercurrent processes have been operated at pressures from atmospheric up to 25 atmospheres. Gasification at higher pressures, i.e., in the range of pipe line pressures, may prove possible and desirable. The advantages of both high pressure and atmospheric pressure gasification are discussed below.

1. High Pressure

High pressure fixed-bed gasification as exemplified by the Lurgi process appears at present to be one of the most promising methods for producing synthesis gas from coal. The fixed bed countercurrent system is high in efficiency. Furthermore, high pressure gasification increases the throughput of fuel and blast gas

considerably. The synthesis gas produced is at high pressure

which aids in subsequent purification and methanation operations

and also reduces gas compression load. If fixed-bed gasification

pressures can ultimately be raised to a level comparable to long-

distance pipe line pressures, which range from 800 to 1200 psig,

the final product gas compression step can be eliminated entirely.

Elimination of the compression step would reduce the cost of pro-

ducing high BTU gas by about 2% as shown by the information of

Table I, and decrease the required plant investment by about

$1,000,000.

Gasification of non-caking fuels utilizing solid ash dis-

charge has been proven in practice at medium pressures, i.e., around

300 to 350 psi, using Lurgi gas generators. The Lurgi generator

reached a commercial state of development between 1930 and 1932.

The first installation, which manufactured city gas from lignite,

was built in 1936 at Hirshfelde, Saxony, to supply the town of Zittau.

Since that time, there has been a great deal of information reported

about the Lurgi gasification process. A recent bibliography cites

many of the published reports.[2] Essentially, the high-pressure Lurgi

gasification process consists of continuously blowing a hot bed of

solid fuel with a mixture of 95% purity oxygen and superheated steam.

Oxygen is mixed with steam to give about 10 vol % of oxygen in the

blast mixture entering the fuel bed. The temperature of the bed is

controlled by the proportion of oxygen used, and is maintained above

1900°F but below the softening point of the ash formed. Reactor

pressures range from 20 to 25 atmospheres. Raising the gasification

pressure increases the heating value of the synthesis gas produced and reduces oxygen consumption; however, heretofore on the basis of economic and structural considerations the maximum reactor pressure has been considered to be about 30 atm.

The Lurgi reactor itself is a cylindrical vessel which is refractory-lined and water-jacketed. Blaw-Knox Construction Company has reported that the optimum size is the maximum which can be shipped in one piece, i.e., a reactor with an I.D. of 11.8 feet.[1] Fuel is supplied to the fuel bed by gravity flow from a hopper positioned above the reactor at a rate corresponding to the rate of descent of the fuel bed. In operation, the blast of oxygen and steam results in an intense reaction zone at the bottom of the fuel bed. Below this zone, fine ash collects. The ash is supported on a mush-room-shaped grate which is rotated by a hollow shaft that extends through the bottom of the reactor and further serves to supply the steam-oxygen mixture to orifices positioned below the ash grate. The slow rotation of the grate moves the ash to the periphery, and plow blades underneath the bottom side of the mushroom head move the ash into an opening at the bottom of the reactor. The ash falls through an ash pipe and into a pressure vessel below the reactor. When the ash hopper becomes filled, a valve between the hopper and the reactor is closed, the hopper pressure is reduced, and the ash is dumped without interrupting the gasification operation in the reactor. Product gas is removed through the top of the generator. A water jacket surrounding the reactor serves to cool the shell of the re-action vessel. Sufficient steam is formed to maintain a pressure

on the outside of the reactor shell equivalent to the gasification

pressure, and thus, eliminate the structural problem of containing

a gaseous mixture at 2000°F and 20 atm. in a steel vessel.

Synthesis gas produced at high pressure in Lurgi generators

contains from 5 to 15 percent methane, and has a heating value ranging

from 350 to 500 BTU/SCF. A typical analysis of a gas produced from

German "Braunkohle" and coke briquet is presented in Table III.

TABLE III. TYPICAL COMPOSITION OF SYNTHESIS GAS
PRODUCED IN LURGI GASIFICATION UNITS[3]

Component	Volume %	
	Raw Gas	Purified Gas
CH_4	14.9	20.6
H_2	35.6	52.2
CO	12.9	18.3
C_nH_{2n+2}	0.8	0.7
H_2S	2.0	--
CO_2	32.1	6.8
O_2	0.2	0.2
N_2	1.5	1.2
	100.0	100.0
Heating Value, BTU/SCF	342	475

Before upgrading the crude synthesis gas by methanation, a purifi-

cation step to remove CO_2, H_2S and any other organic sulfur com-

pounds is required. A typical composition of purified raw gas is

shown in the second column of Table III.

In the past, the Lurgi process has primarily used pre-dried lignite for solid fuel, but runs have also been made with coke, char from bituminous coal, semi-anthracite and bituminous coal. These all fall in the non-caking or only weakly agglomerating class. While successful operation in pilot plant scale equipment has been reported[4,5] with caking bituminous coals by using a mechanical stirrer, successful operation with caking coals has yet to be demonstrated in commercial-size Lurgi generators.

In summary, the advantages of high pressure gasification may be listed as:

(a) High fuel rates.

(b) Lower oxygen consumption.

(c) Increased methane content in the product gas.

(d) Lower gas compression requirements.

Disadvantages are:

(a) Inaccessability to equipment because of high pressure.

(b) The need for mechanical agitation when processing caking coals.

2. Atmospheric Pressure

While high pressure and medium pressure gasification processes have the advantages of large capacities, lower oxygen consumption, and the need for less gas compression in subsequent processing steps, there are advantages of atmospheric pressure gasification which should not be disregarded. The most important of these is the availability of suitable gas generators which have proven by years of commercial operation to be dependable. Moreover, atmospheric

pressure gasification permits greater accessibility to gasification equipment. Direct observation of the fuel bed is possible and corrective measures can be taken if visual observation indicates that gasification is not proceeding in the desired manner. Slag-tapping operation, by which ash is drawn off from tne reactor in the form of liquid slag, is easily applied to atmospheric pressure gasification units.

The fuel beds of updraft gasification processes are usually supported by grates. Rotating grates or fixed grates with rotating stirrers serve to continuously remove the ash produced during gasi-fication. Such mechanical grates impose limits on the size of reactors to diameters of 10 to 12 feet. However, by raising the temperature of gasification so that the ash produced is above its melting point, it is possible to remove ash from gasifiers by tapping it off in the form of a liquid slag. The need for rotating grates or stirrers is, thus, eliminated, avoiding the high maintenance costs associated with such equipment. Basically, slagging ash gasifiers are simple in design and can be built in large units. A unit has been built and operated which can gasify 300 tons of coke per day.[6] Moreover, based on experience with blast furnaces, which closely re-semble slagging ash gasifiers but are several times larger, higher capacity units should be possible.

The yield of methane from atmospheric-pressure gasifiers is considerably lower than that obtained from high pressure gasifi-cation. As a result, more oxygen is required to gasify coal at

atmospheric pressure since the solid carbon is converted to gas

primarily by reaction with oxygen and to a lesser extent by combi-

nation with hydrogen to form methane.

To summarize, atmospheric pressure countercurrent gasifiers

are of two major types: rotary-grate generators .and slagging ash

generators. While atmospheric pressure rotary-grate generators are

now available, they do not appear promising for future use in processes

to manufacture high BTU gas particularly because of high maintenance

costs and size limitations. Slagging ash gasifiers, however, are

worthy of further consideration for they possess a number of de-

sirable characteristics:

(a) They can be built in large units of high capacity.

(b) Operation at atmospheric pressure eliminates problems

associated with operating and maintaining high pressure

equipment.

(c) Low-grade, high-ash caking coals can be gasified,

and valuable by-products, mainly pig iron and slag

for building materials can be recovered.

(d) High gas yields can be obtained per unit of fuel

gasified.

Important disadvantages of atmospheric pressure slagging ash gasi-

fiers, however, are increased oxygen consumption and the necessity

of compressing product gas from atmospheric to pipe-line pressure.

B. Fixed-Bed Concurrent, Down-Draft Gasification

The use of concurrent flow of blast gas in gasification

has found application primarily (1) to reduce carry-over of fines

at high rates of gasification and (2) to destroy tar and other vola-
tile materials resulting from gasification of low-grade fuels, such
as wood and peat, by passing the volatiles through the oxidation
zone of the fuel bed. With down-flow of blast gas, the fuel bed
acts like a filter, retaining small fuel particles and permitting
the use of gas rates higher than are possible with any other type of
fuel bed. Blast rates have been achieved that would have fluidized
an updraft fuel bed of small-sized fuel. Unfortunately, down-draft
systems are subject to limited rates of ignition; however, this diffi-
culty can be overcome by preignition of the gasification fuel. A
unique method for ignition is employed in the Flesh-DEMAG gasifier
in which the entire inventory of the generator is periodically fluid-
ized in order to distribute ignition nuclei throughout the fuel bed
and produce practically an unlimited ignition rate. A large variety
of fuels, including caking coals can be gasified in a down-draft
fixed bed if the bed is periodically renewed by up-draft fluidization
for declinkering and mixing in fresh feed.

The Flesh-DEMAG process is a continuous gasification process
employing two (or more) reactors which are interconnected at their
upper ends. Blast gas is admitted at the top of both shafts and
product gas is removed through the rotary grate which supports the
fuel bed. Periodically, the flow of gas in one reactor is reversed
and the reactor charge is fluidized using either blast gas or steam.
Clinker which has formed during gasification breaks up and falls
down to the rotary grate from which it is continuously removed.
During the fluidization, fresh feed is introduced and is thoroughly

mixed with the reactor inventory. The off-gas from the fluidization period flows through the connecting pipework between the two reactors and is passed in down-flow through the hot bed of the second reactor. When the fluidizing operation has been completed, the bed is allowed to settle, and introduction of the blast gas at the top of the reactor is resumed. The second shaft is then fluidized in a like manner. To date, the process has been demonstrated only on a semi-commercial scale in two 5-1/4 ft. I.D. reactors operated at Ludwigshafen, Germany, by DEMAG, which can gasify 100 tons of fuel per day at pressures up to 10 atmospheres.[7]

To summarize the advantages of down-draft gasification processes and, in particular, the Flesh-DEMAG process:

(a) Down-draft gasification processes can gasify with extremely high flow rates of oxygen and steam without appreciable carry-over of fine fuel particles.

(b) The Flesh-DEMAG process is able to handle a large variety of fuels which include caking coals.

(c) The Flesh-DEMAG process has the advantage over all other types of fixed-bed processes that the fuel bed is replenished and rebuilt before the beginning of each gasification cycle; i.e., about every 15 to 20 minutes.

C. Gasification in Suspension

Processes which gasify coal in suspension fall into two categories, those which use a fluidized bed of finely divided fuel, and those in which pulverized coal particles are entrained in the

moving blast gas stream. Both techniques can be carried out at
elevated pressures. Gasification in suspension has the advantage of
widely separating individual fuel particles which eliminates many of
the shortcomings of fixed fuel beds. Particles of fuel can swell,
soften and even slag without interfering with adjacent particles,
and without changing the characteristics of the fuel bed. Separation
of individual particles makes gasification in suspension much less
sensitive to the type of fuel used than is the case with fixed-bed
gasification processes. There is much research being devoted to
suspension gasification processes because of their great potential
as means for handling the many varieties of strongly caking American
coals.

1. Fluid-Bed Gasification

The success of fluid-bed processes for catalytic cracking
and reforming has led to the application of fluid techniques to
gasification of pulverized coal. Fluid-bed gasification processes
operate by passing blast gas upward through a bed of finely divided
fuel particles at velocities such that the solid particles are sus-
pended in the rising gas and are maintained in continual random
movement in a dense phase, wherein the solid fuel and blast gas react
to form a product gas comprised of CO, H_2, CO_2, CH_4, C_nH_{2n+2}, and H_2O.
A characteristic of fluid-bed operations in general is the absence
of an appreciable temperature gradient within the dense bed, since
the motion of the solid particles tends to equalize the temperature.
Gasification reactions in the fluid bed take place at lower maximum
particle surface temperatures than those observed in fluid-beds.

Chemical reactivity of the fuel tends to become important at lower surface temperatures. However, this effect can be minimized by operating fluid bed gasifiers at temperatures close to the softening point of the ash formed.

Large fluid-bed gasifiers are possible. Reactors are essentially empty vessels with auxiliary equipment for introducing pulverized fuel and blast gas. Sizes are limited primarily by the ability to maintain good fluidization. Uniform distribution of blast gas to the fuel bed is of the utmost importance since by-passage of oxygen through the bed in the form of bubbles can lead to the formation of explosive product gas mixtures.

A number of oil companies in the United States have conducted extensive research programs on fluid-bed gasification processes as sources of carbon monoxide-hydrogen mixtures for liquid fuels synthesis. Unfortunately, the results of these research programs, for the most part, have not been reported in the literature. This fact does not necessarily indicate that the fluid-bed gasification process lacks potential, but rather reflects a preoccupation on the part of oil companies in processes of more current interest and also a reluctance to release information which might be of interest to competitors. Actually, development of fluid-bed gasification processes has reached an advanced stage. Problems such as non-uniform blast gas distribution and stalactite formation of partially slagged ash particles at points in the reactor remain to be solved, but it is felt that with sufficient incentive a commercial process could be perfected.

2. Entrained Solids Gasification

A number of pilot plants have been built both in Europe and in the United States to investigate pulverized coal gasification processes.[8,9] The Bureau of Mines has conducted an extensive research program, and has demonstrated in pilot plant scale equipment that it is possible to gasify any type of American coal for short periods of time at pressures up to 300 psi with carbon conversions of 90 percent or higher.[8] However, the equipment used has not been satisfactory for long periods of operation.

Gasification of entrained solid fuel requires a high temperature level which can be provided by using either high oxygen concentrations or highly superheated steam in the blast gas. Temperatures as high as 1800°F are common. Ash removal in the form of a liquid slag is preferred. Elevated pressure operation is desirable in order to reduce the size of the reactor and auxiliary equipment as well as to reduce the amount of final product gas compression required. Small pilot plant units which have been used thus far suffer from high external heat losses and from erosion of reactor walls. Data obtained from these units are not easily extrapolated nor are they sufficient for the design of commercial size installations. Runs in larger pilot plants or in full-size experimental units are needed to fully demonstrate the gasification of American caking coals in entrained solids type equipment.

D. Summary and Conclusions

Three principle types of gasification processes, countercurrent, concurrent, and suspension gasification show promising

results. Extensive research programs both in the United States
and in Europe have led to the development of a number of processes
which are capable of producing synthesis gas from coal. Some of
these are well advanced, and the equipment has been tested and
perfected in many years of commercial operation. Still other
processes have not passed out of the pilot plant stage, and much
research will be required before successful commercial operation
can be realized. Those processes which have already reached com-
mercial status have used fuels that are not comparable to the types
of coal which must be used in this country, and while they provide
a "jumping-off point" for future research, they do not by any means
provide all the information needed to design a process for use with
American caking coals. Further research is needed to develop the
optimum gasification process, which not only will be able to handle
caking coals, but which will efficiently and economically produce
synthesis gas at pressures equal to or above pipeline pressures.
The three process which appear to offer the firmest foundation for
future efforts to develop better equipment and improved operating
procedures are:

1. The Lurgi countercurrent updraft fixed-bed gasifi-
    cation process.

2. Downdraft two-shaft gasification of the Flesh-DEMAG
    type at elevated pressure.

3. Suspension gasification either in a fluid-bed or as
    an entrained solid at elevated pressures.

The Lurgi gasifier, using a fixed fuel bed blown counter-
currently with oxygen and steam, appears to be one of the most
promising gasification processes. Modifications which would make
the process suitable for producing synthesis gas from American coals
for high BTU gas manufacture are:

1. The development of mechanical methods for breaking
   up caked ash to permit use of the process with
   caking coals.

2. Redesign of the equipment to operate at or above
   pipeline pressures.

3. Incorporation of slagging ash operation into the
   high pressure Lurgi design.

The Flesh-DEMAG process and suspension gasification processes offer
great promise, but need to be advanced from the pilot-plant stage
to semi-commercial or commercial size units to gain experience neces-
sary to improve designs. However, large size units are costly and
based on present-day economics for high BTU gas manufacture it is
doubtful that commercial size units can be justified for research
purposes.

To summarize the present status on gasification processes,
it can be said that while operable commercial processes do not now
exist, basic processes are available which can be adapted to produce
synthesis gas from American coals. Gasification and raw materials
comprise the major cost of producing high BTU gas from coal, and
any economies in gasification costs will do much to speed the day
when high BTU gas can economically be made from coal. In turn,

favorable economics for the integrated high BTU manufacturing process will offer great incentive to develop improved gasification processes. Factors other than technological improvements in gasification processes should not be overlooked. The cost of raw materials is an important part of the total gasification cost. Improvements in mining methods and in oxygen manufacture would lower raw material costs and result in more economical gasification. Research along these lines could be of benefit not only to gasification, but to a number of other non-related processes.

III. PURIFICATION OF SYNTHESIS GAS

When coal is gasified, much of the sulfur present is converted to gaseous sulfur compounds. Since all of the catalysts presently known to be active for methanation are susceptible to poisoning by sulfur, the purification of synthesis gas is an important step in the manufacture of high BTU gas. Sulfur is present in raw synthesis gas primarily in the form of hydrogen sulfide, carbonyl sulfide and carbon disulfide, and can range in concentration from about 200 to 500 grains per 100 SCF of synthesis gas. In order to obtain reasonable catalyst life with both nickel and iron methanation catalysts, it has been found necessary to reduce the sulfur content of synthesis gas to 0.1 grain of sulfur per 100 SCF or lower.

A large number of processes have been developed and used commercially for the removal of sulfur compounds from gaseous streams. A detailed bibliography of literature references is available.[10] Several of the sulfur removal processes commonly used in the refining and the manufactured gas industry will be briefly described.

A. Dry-Box Process

The dry-box process has long been used in the gas industry for removing relatively low concentrations of H_2S from industrial gases. Hydrated iron oxide is coated on wood shavings or other supporting material and spread in thin layers on trays in rectangular boxes. Raw gas to which sufficient air or oxygen has been added to provide an oxygen concentration of 0.6 to 1.0 volume % is passed over the iron oxide. Hydrogen sulfide present reacts to form iron

sulfide, which in turn is oxidized by oxygen added to the gas stream back to iron oxide and sulfur. After continued operation it becomes necessary to thoroughly revivify the iron oxide sponge, either by passing air or oxygen through the beds or by removing the iron oxide from the boxes and exposing it to the atmosphere for a prolonged period. The iron oxide sponge is finally discarded when the total sulfur content reaches 50 to 60%.

The dry box process has the disadvantage of not removing organic sulfur compounds. Consequently, for purifying synthesis gas a two-step process is required. The Germans employed such a combination process for the purification of the feed gas used in the synthesis of liquid fuels. Raw synthesis gas was passed over a mixture of hydrated iron oxide and sodium carbonate at 200 to 300°C. Organic sulfur components present were catalytically converted to hydrogen sulfide which was subsequently removed in dry-boxes.

Major advantages of the dry-box technique are the completeness of hydrogen sulfide removal and the simplicity of the process. However, the dry-box process does not appear practicable for purifying synthesis gas in sufficient quantity for economic high BTU gas manufacture because of the prohibitively large amount of iron oxide sponge required. For example, a high BTU gas plant producing 100 million SCF per day of 850 BTU gas would consume 364 million SCF per day of synthesis gas. Since about six cubic feet of iron oxide sponge are used to remove the hydrogen sulfide from 1000 SCF per day of gas, in excess of two million cubic feet of iron oxide sponge would be required to purify the synthesis gas for a 100 million SCF per day high BTU gas plant.

B. Girbotol Process

The Girbotol process, developed by the Girdler Company, has become the most widely used process for the removal of hydrogen sulfide from natural and refinery gases.[11,12] The process utilizes one of the ethanol amines (mono, di, or tri) to absorb hydrogen sulfide from gaseous streams in conventional bubble-tray towers. Diethanolamine is most commonly used in the treatment of refinery gases because of its inertness toward carbonyl sulfide. Diethanol-amine exhibits basic properties and absorbs acidic components (H_2S and CO_2) as shown by the following reactions:

$$2R_2NH + H_2S \rightleftharpoons (R_2NH)_2 \, H_2S \tag{6}$$

$$2R_2NH + H_2O + CO_2 \rightleftharpoons (R_2NH)_2 \, H_2CO_3 \tag{7}$$
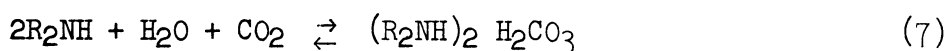
where

R represents a (CH_2CH_2OH +) group.

Regeneration of the absorbent is possible, since at the boiling point of the solution the amine becomes practically non-alkaline, releasing the H_2S and CO_2 from solution. The process is carried out in a two-column system as shown in Figure 1.

The relatively high cost of the ethanolamines necessitates special precautions to prevent excessive losses of the absorbent. Monoethanolamine, which has a high absorption capacity, reacts with carbonyl sulfide to form the relatively heat-stabel compound di-ethanolurea, $CO(NHCH_2CH_2OH)$, and thus, cannot be used economically with gas streams containing carbonyl sulfide, as is the case with raw synthesis gas produced from coal. In addition, impurities such as tars, cyanogen, and oxygen, which are often present in manufactured
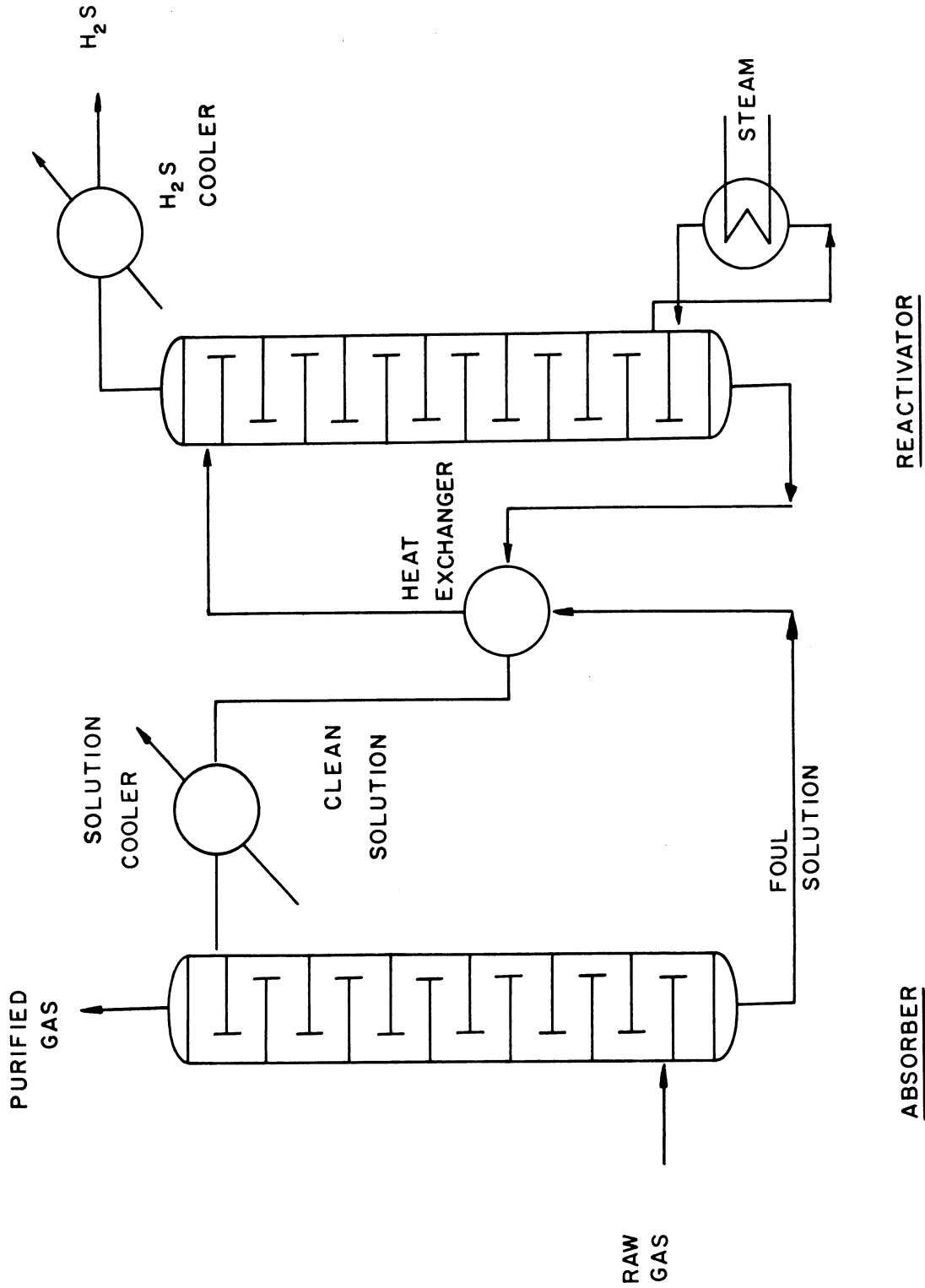
FIGURE I. FLOW DIAGRAM OF THE GIRBOTOL PROCESS

gases, react to form non-regeneratable compounds with the ethanolamines. Thus, while the Girbotol process would be satisfactory process-wise for the purification of synthesis gas, the presence of reactive impurities in the raw gas is likely to result in excessive absorbent losses.

C. Shell Phosphate Process

The Shell phosphate process[13] is essentially similar to the Girbotol process, but uses an aqueous solution of tripotassium phosphate as absorbent. The solution used normally contains from 40 to 45 wt. % tripotassium phosphate. Hydrogen sulfide is absorbed according to the reaction:

$$K_3PO_4 + H_2S \rightleftarrows K_2HPO_4 + KHS \tag{8}$$

Regeneration is accomplished by steam stripping. In general, the Shell phosphate process has higher operating costs than the Girbotol process.

D. Rectisol Process

Currently, the most promising process for the removal of sulfur from synthesis gas is the Rectisol process, developed cooperatively by Linde and Lurgi in Germany. The removal of moisture, carbon dioxide, all forms of sulfur, and gum-forming materials are combined into a single operation, thus, simplifying the purification step considerably and providing the Rectisol process with a distinct advantage over all other purification processes. The first Rectisol installation has recently been constructed as a part of the South African Fischer-Tropsch plant.

A simplified flow diagram for the Rectisol process is shown in Figure 2. Raw synthesis gas is contacted with methanol in an absorber which operates at -30°F and 500 psig. Purified synthesis gas leaves the top of the absorber, and after heat exchange with the raw gas is ready for the synthesis step. Methanol rich in sulfur compounds and carbon dioxide leaves the bottom of the absorber and is partially flashed. A portion of the methanol from the flash tank is pumped back to an intermediate plate of the absorber and the balance is sent to the stripper.

The flash gas, rich in gaseous sulfur compounds and carbon dioxide, is fed to the bottom of the reabsorber which operates at -30°F and atmospheric pressure. Sulfur is reabsorbed in methanol, and a carbon dioxide stream containing negligible quantities of sulfur compounds leaves the top of the reabsorber and is vented from the plant.

The methanol stream from the bottom of the reabsorber and methanol from the flash tank are combined and pumped to the top of the stripper. Gaseous sulfur compounds and the remaining carbon dioxide pass overhead from the stripper. Clean methanol leaving the bottom of the stripper is split into two streams and returned to the top of the absorber and the reabsorber towers. In addition to the absorption and stripping towers, refrigeration equipment and an extensive heat exchanger system is required.

E. Other Processes

The removal of hydrogen sulfide from gaseous streams can be accomplished by other processes than those discussed. Several
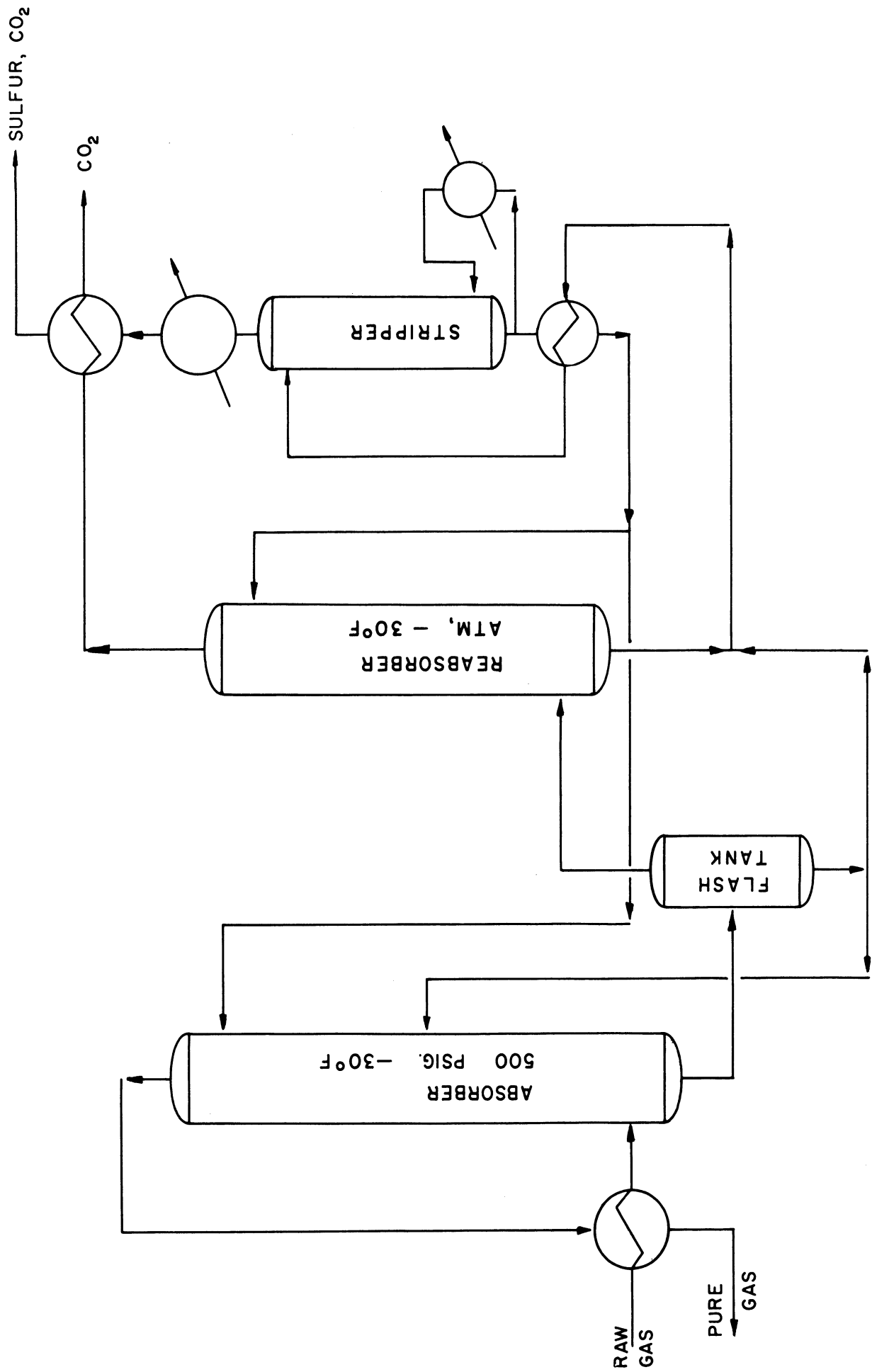
FIGURE 2. FLOW DIAGRAM OF THE RECTISOL PROCESS

additional processes are briefly described in Table IV. The chemical

reaction by which hydrogen sulfide is removed as well as the method

of regeneration of the absorbent are given. Most of the processes

listed are suitable only for removing hydrogen sulfide, though

several will also remove carbon dioxide. Purification of raw

synthesis gas produced from coal, which would contain hydrogen

sulfide and carbon dioxide as well as organic sulfur compounds

by any of the methods given in Table IV would necessitate a two-

step and in some cases a three-step process. Organic sulfur compounds

would first have to be catalytically converted to hydrogen sulfide.

The hydrogen sulfide formed could then be removed by any one of the

ten processes cited. However, if the hydrogen sulfide step does

not also remove carbon dioxide, an additional step is required for

this purpose. Carbon dioxide is commonly removed by water scrubbing.

F. Conclusions

High operating costs, expensive and large equipment in-

stallations, high absorbent losses, as well as the need for multiple

processes, all serve as serious disadvantages to the above-described

schemes for sulfur removal. The Rectisol process which can remove

moisture, carbon dioxide, all forms of sulfur and gum-forming materials

in a single operation, therefore, appears to be an outstanding process

for use in purifying synthesis gas for high BTU gas manufacture.

Reportedly, Rectisol gas purification cost has been cut to half

the cost of purification with conventional methods. A good deal more

information on the Rectisol process should be available when operations

of the South African Fischer-Tropsch plant are reported.

TABLE IV. CHEMICAL PROCESSES FOR HYDROGEN SULFATE REMOVAL

	Process	Reaction	Regeneration
1.	Caustic Soda	$2NaOH + H_2S \rightarrow Na_2S + 2H_2O$	None
2.	Lime	$Ca(OH)_2 + H_2S \rightarrow CaS + 2H_2O$	None
3.	Iron Oxide	Replacement of oxygen by sulfur	Oxidation with air to sulfur and iron oxide
4.	Seabord	$Na_2CO_3 + H_2S$ $NaHCO_3 + NaHS$	Release of H_2S by air blowing
5.	Vacuum Carbonate	$Na_2CO_3 + H_2S$ $NaHCO_3 + NaHS$	Release of H_2S by steam stripping
6.	Thylox	$Na_4As_2S_5O_2 + H_2S \rightarrow Na_4As_2S_6O + H_2O$	Oxidation with air to sulfur and $Na_4As_2S_5O_2$
7.	Girbotol	$2RNH_2 + H_2S$ $(RNH_3)_2 S$	Release of H_2S by steam stripping
8.	Phosphate	$K_3PO_4 + H_2S$ $KHS + K_2HPO_4$	Release of H_2S by steam stripping
9.	Alkazid	$RCHNH_2COONa + H_2S$ $RCHNH_2COOH + NaHS$	Release of H_2S by steam stripping

Even with the Rectisol process, gas purification costs represent 14 percent of the total cost of manufacturing high BTU gas from coal. In view of the large potential savings which might be made by improving existing processes or by developing new processes for purifying synthesis gas, further research in this area is clearly warranted.

IV. METHANE SYNTHESIS

Since the beginning of the century when Sabatier and
Senderens first produced methane by passing hydrogen and carbon
monoxide over reduced nickel and cobalt catalysts, there has been
a sizeable amount of research on the synthesis of methane, motivated
primarily by a need for suitable catalysts and processes to up-grade
the low heating values of gases manufactured from coal. Reports of
early investigations and processes can be found in the literature.[14-21]

Water-gas, comprised principally of carbon monoxide and
hydrogen in approximately equal proportions, is one of several gases
manufactured from coal. The heating value of water-gas is low,
ranging from about 280 to 330 BTU per cubic foot. European countries,
lacking natural gas, but with ample supplies of coal, have for years
manufactured large quantities of water-gas by the steam-carbon reaction.
The literature contains references to many early investigations on the
synthesis of methane from water-gas as a method of increasing its
heating value.[22-25] More recently, the British Gas Research Board
and the Fuel Research Board have conducted an extensive experimental
program on the synthesis of methane from water-gas and other in-
dustrial gases using nickel catalysts as a means of enriching town
gas.[26-31]

Kinetic studies of the synthesis of methane from both
carbon monoxide[32-35] and carbon dioxide-hydrogen[36,37] mixtures on
nickel catalysts have been made. The mechanism of the methanization
reaction has been considered.[38,39] There has been much research

on methanization catalysts,[40-43] particularly with regard to

supported nickel catalysts.[44-56] While most of the catalyst

development effort has been devoted to supported catalysts, some

work has been done on non-porous metal catalysts. A comparison

of a number of methanation catalysts will be presented later.

A. Chemistry and Thermodynamics

The predominant reaction in the synthesis of methane from

carbon monoxide and hydrogen is usually represented by the equation

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \tag{9}$$
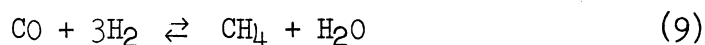
and is rapid in the presence of active catalysts at temperatures

above 250°C. Catalysts used for the synthesis also promote the

water-gas shift reaction.

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{10}$$
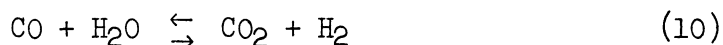
which produces carbon dioxide by interaction of water vapor, formed

according to equation (9), and unconverted carbon monoxide. Both

reactions are reversible, and from known equilibrium constants it

is possible to calculate the composition of the gas which would be

produced if various mixtures of carbon monoxide and hydrogen were

allowed to come to equilibrium at constant pressure and temperature.

The results of such calculations[30] are shown in Figure 3 to illustrate

the effect of temperature, pressure, and H_2/CO ratio of the feed gas

on the composition of the product which satisfies both the methane

and the water-gas equilibrium.

Figure 3 shows that the formation of methane from carbon

monoxide and hydrogen is favored by low temperatures and high pressures.

This would be expected in view of the decrease in volume and the

Top-left graph: H₂/CO ratio of feed gas = 3, Pressure: 1 atmosphere. VOLUME PERCENT OF PRODUCT vs TEMPERATURE, °C. Curves labeled H₂, CO, CH₄, H₂O, CO₂.

Top-right graph: H₂/CO ratio of feed gas = 3, Pressure: 25 atmospheres. VOLUME PERCENT OF PRODUCT vs TEMPERATURE, °C. Curves labeled H₂, CH₄, CO, H₂O, CO₂.

Bottom-left graph: H₂/CO ratio of feed gas = 1, Pressure: 1 atmosphere. VOLUME PERCENT OF PRODUCT vs TEMPERATURE, °C. Curves labeled CO, H₂, H₂O, CH₄, CO₂.

Bottom-right graph: H₂/CO ratio in feed gas = 1, Pressure: 25 atmospheres. VOLUME PERCENT OF PRODUCT vs TEMPERATURE, °C. Curves labeled CO, H₂, CH₄, CO₂, H₂O.

evolution of heat which occurs in the methane reaction. As the

H_2/CO ratio of the feed gas is reduced, much larger percentages of

carbon dioxide appear in the product gas, while the amount of unused

hydrogen is reduced.

During synthesis at high temperatures and low H_2/CO ratios,

free carbon can be deposited on the catalyst according to the equation

$$2CO \rightleftarrows CO_2 + C \tag{11}$$

[Other equations may be used to describe the appearance of carbon,

but all of them can be obtained by various combinations of equations

(9), (10) and (11).] For synthesis conditions at which carbon

deposition would be expected, it is possible to determine the theo-

retical product gas composition which simultaneously satisfies the

methane, the water-gas shift and the carbon equilibria[43] provided

equilibrium constants for equation (11) are known. Values for the

carbon equilibrium constants depend upon the nature of the carbon

formed, and it makes a considerable difference in the calculated

equilibrium product composition whether the equilibrium form of the

carbon is graphite, a more active metastable carbon, or perhaps a

metal carbide.

Equilibrium calculations predict only the composition of

the product gas which is theoretically possible from the standpoint

of thermodynamics. The composition of the product which actually

would be formed under a given set of reaction conditions is dependent

upon many factors: the rates of reaction on the catalyst surface, the

temperature distribution through the catalyst bed, the rate of mass

transfer to and from the catalyst surface; and must necessarily be

determined by experiment.

B. Catalysts and Processes

The objectives of research on methanation have been twofold: first, to develop processes which can be utilized in commercial size installations to upgrade product gases obtained from coal gasification to fuel gases with heating values of over 850 BTU/SCF; and secondly, to develop catalysts which not only are active for methanation, but which have process lives of such length that the cost of the catalyst is small compared to the total cost of the process.

A number of problems which have been encountered in developing methanation processes and catalysts are as follows:

1. The reactions associated with the production of methane are extremely exothermic and methods for removing heat must be incorporated into the methanation process equipment. The excessive temperature rise over the catalyst bed which would occur if the heat of reaction were not adequately removed, could result in catalyst deactivation, in less favorable equilibrium conditions for the synthesis of methane, in excessive carbon deposition, and in extreme situations in damage to process equipment.

2. When using synthesis gas with ratios of hydrogen to carbon monoxide lower than three to one, carbon deposition can, and often does, occur in regions of temperature and pressure where high yields of methane are obtained. The conversion of carbon monoxide to carbon and carbon dioxide rather than to methane results in a loss in potential heating value since carbon dioxide, not being combustible, would be scrubbed from the product gas before use as a fuel gas.

Excessive carbon deposition can result in blockage of fixed-bed reactors, in loss of fluidization in fluidized-bed reactors and, in the case of porous-type catalysts, in fragmentation of the catalyst particles.

3. Catalysts for the conversion of carbon monoxide and hydrogen to methane are susceptible to poisoning by sulfur compounds present in the feed gas. If synthesis gas is not purified of sulfur compounds by processes which have been described earlier, the active life of methanation catalysts is greatly reduced and catalyst costs may become excessive.

The development of processes and catalysts suitable for commercial methanation of carbon monoxide and hydrogen mixtures must necessarily deal successfully with these problems. In the following sections, developments in the field of methanation, catalysts and processes will be discussed to provide an indication as to the knowledge available on methanation and to the areas where further research would be profitable.

1. Catalysts

A number of metals have been found to be catalytic for the conversion of carbon monoxide and hydrogen to methane. These include ruthenium, iridium, rhodium, nickel, cobalt, osmium, platinum, iron, molybdenum, palladium, and silver.[41] Catalysts containing these active metals can be divided into two general classes: those which are porous in nature, and those which have non-porous structures.

Porous type catalysts are generally of the supported-metal type and are prepared by employing impregnation or precipitation

techniques on supports such as asbestos, alumina, kaolin, and
kieselguhr. A typical method for impregnating a catalyst support
with an active metal consists of adding the nitrate salt of the metal
plus any catalyst promoters used to a quantity of support to form
a slurry. The slurry is first dried and then heated to convert the
nitrate salts to oxides. Precipitated catalysts can typically be
prepared by treating the slurry of nitrate salts and support with a
carbonate solution. The mixture is boiled with constant stirring
and filtered. After washing with hot water, the filtered solid
material is dried. Dried residue obtained from either technique
is crushed, sized and reduced in hydrogen before use as a catalyst.

Iron filings, nickel pellets, and steel shot are examples
of non-porous catalysts. The catalytic area of such catalysts is
limited to the external surface of the particles, since these
materials lack the extensive internal pore structure characteristic
of highly active supported catalysts. By virtue of the absence of
pores, however, non-porous catalysts possess much higher mechanical
strength than do porous catalysts and are not susceptible to frag-
mentation by carbon deposition.

Extensive experimental programs to evaluate various porous
and non-porous methanation catalysts have been conducted and reported
by the United States Bureau of Mines, the British Gas Research Board,
the British Fuel Research Board, and the Michigan Gas Association
Laboratory at the University of Michigan. A number of nickel,
cobalt, and iron-base catalysts have been investigated both in
laboratory-scale fixed-bed and fluidized-bed reactors. The results of
experiments in fixed-bed reactors have been tabulated and are shown in
Table V.

TABLE V. EVALUATIONS OF FIXED-BED METHANATION CATALYSTS

CATALYST COMPOSITION AND PRETREATMENT	H_2/CO Ratio	Temp. Range °F	Pressure Range psig.	Space Vel. Range* V/V/hr.	Best Methanation Conditions				Investi- gator
					Temp. °F	Pressure psig.	CH_4 Yield Vol. % **	Htg.Val. BTU/SCF	
Iron-base Catalysts									
Cuban iron ore - reduced	1	484-610	0-300	100-300	610	300	37.5	834	43
Cuban iron ore - reduced	2	615-702	300	100-300	676	300	34.4	711	43
Fused Fe_3O_4, reduced and nitrided, N/Fe = 0.44	2	478-743	300	100-300	743	300	30.5	686	43
Fe_3O_4 (50%) and ball clay, reduced & nitrided, N/Fe = 0.48	2	475-594	0-300	100-300	594	300	27.5	643	43
Fe_2O_3, Al_2O_3 ppt. on kaolin - reduced	2.5	658-685	300	300	658	300	12.7	410	43
Fe-Ni-MgO-SiO_2 (58.8:12.4:21:0.2) reduced & nitrided, N/Fe 0.31	1	464-536	300	300	523	300	39.7	657	43
Steel Balls (S.A.E. C1013)	2.3	878-1202	441	5000	1080	441	40.5	630	58
Steel Balls (S.A.E. C1013)	1.5	816-1198	441	5000	1100	441	52.2	700	58
Steel Balls (S.A.E. C1013)		880-1227	441	3000	1120	441	59.3	745	58
Steel Balls (S.A.E. C1013)	0.8	1074-1210	441	3000	1140	441	56.2	736	58
Steel Balls (S.A.E. C1013)	2.4	852-1254	426	12000	1058	426	33.0	583	57
Steel Balls (S.A.E. C1013) - carburized	2.2-2.3	1050	426	12000	1050	426	35.4	602	57
Steel Balls (S.A.E. C1013) - nitrided 50 hrs.	2.2-2.3	905-1053	426	12000	1051	426	36.5	604	57
Nickel-base Catalysts									
Ni, ThO_2-Cr_2O_3 ppt. on kieselguhr (30.9:7.6:1.6:59.9) reduced	1	446-626	0-300	100-300	608	0	60.8	740	43
10% Ni impregnated on steam-treated cracking catalyst base-reduced	1	572+	300	300	----No appreciable activity----				43
5% Ni impregnated on cracking catalyst base - reduced	1,2	601-756	300	300	748	300	44.6	813	43
4.8% Ni on Al_2O_3 (Girdler catalyst) - reduced	1	608-745	0-100	100	720	100	24.9	428	43
10% Ni impregnated on cracking catalyst base - reduced	1	572+	300	300	----No appreciable activity----				43
5% Ni impregnated on cracking catalyst base plus K_2O - reduced	2.5	752	300	300	752	300	39.1	590	43
1% Ni impregnated on activated charcoal - reduced	1	604-763	300	100-300	----No appreciable activity----				43
Ni10-ThO_2-Cr_2O_3 ppt. on silica gel (6% Ni) - reduced	1	554-680	0-300	100-300	651	300	41.4	735	43
10% Ni ppt. on silica - reduced	1	608-716	300	100-300	671	300	48.3	670	43
Ni10-Al_2O_3 ppt. on kaolin (100:200:125) - reduced	2	572-588	300	300	572	300	98.9	>995	43
Ni10-Al_2O_3 ppt. on kaolin (100:200:125) - reduced	2.5	406-664	300	300	664	300	96.9	>980	43
Ni10-Al_2O_3 ppt. on kaolin (100:200:125) - reduced	1	415-770	300	300	572	300	97.5	>990	43
Ni10-MgO ppt. on kaolin (100:200:125) - reduced	2,2.5	410-644	300	300 300	507	300	97.3	>990	43
28% Ni, 5.5% Mn, 2.4% Al ppt. on kaolin - sintered and reduced	2.5	572+	300	300 300	----No appreciable activity----				43
32% Ni, 5.5% Mn, 2.4% Al ppt. on kaolin - reduced	2.5	525-554	300	300-400	525	300	94.4	965	43
NiO, MnO ppt. on Norton alumina pellets - reduced	2.5	752	300	300	752	300	30.3	520	43
NiO, MnO, Al_2O_3 ppt. on cracking catalyst - reduced	2.5	752-761	300	300	759	300	17.3	440	43
NiO-Al_2O_3 ppt. on Norton cylinders (6.2% Ni) - reduced	2.5	554-752	300	300-700	655	300	94.2	960	43
NiO-MnO_2, Al_2O_3 ppt. on zirconia cement - reduced	2.5	572-581	300	300-500	572	300	94.8	960	43
Nickel pellets steam-treated - reduced	2.5	752	300	100-300	----No appreciable activity----				43
Raney nickel (42% Ni, 58% Al), steam-treated - reduced	2.5	572+	300	300	----No appreciable activity----				43
Raney nickel (42% Ni, 58% Al), Al partly extracted with NaOH	2.5	536-576	300	300-1500	572	300	96.9	985	43
Cobalt-base Catalysts									
Co, ThO_2, K_2O (32.8:6.0:1.5) supported on kieselguhr - reduced	2.4	505-838	426	~5000	640	426	79.5	885	58
Raney cobalt (40% Co, 60% Al) steam-treated - reduced	2.5	572+	300	300	----No appreciable activity----				43
Raney cobalt (50% Co, 50% Al) Al partly extracted with NaOH	2.5	536-601	300	300-2800	547	300	92.1	980	43

* Volume of Synthesis Gas/Volume of Catalyst Bed/Hr.

** H_2O, CO_2 free basis

(a) Iron Catalysts

Table V shows that iron catalysts, in general, are less active for methane synthesis than nickel catalysts. In fact, with iron catalysts it is difficult to obtain product gases with heating values over 800 BTU/SCF. Most porous iron catalysts produce large quantities of C_3 + hydrocarbons in addition to methane and ethane over the range of temperatures where they are most active for converting carbon monoxide and hydrogen to products. Hydrocarbons containing more than three carbon atoms tend to condense in high-pressure pipe lines and for this reason do not constitute suitable components for inclusion in high BTU gas streams. Because of the conversion of synthesis gas to liquid products and the resulting reduction in the yield of gaseous products of high heating value, porous iron catalysts in general are not suitable for methane synthesis at temperatures below about 800°F. At temperatures above 800°F, thermodynamic equilibrium conditions become unfavorable for the formation of liquid hydrocarbons. Synthesis gas is converted primarily to methane and, to a much lesser extent, to ethane. While higher temperatures yield a more favorable distribution of hydrocarbon products for high BTU gas manufacture, two other factors combine to make porous iron catalysts generally unsatisfactory for methanation at these temperatures. Carbon formation becomes excessive, and its deposition in the pore structure of porous catalysts can eventually cause fragmentation of the catalyst pellets. In addition, supported type porous catalysts are often susceptible to sintering at temperatures above 800°F which can reduce catalyst surface area and decrease catalyst activity.

Non-porous iron catalysts are not subject to fragmentation by carbon deposition nor to loss of activity by sintering, and thus, would appear to be superior to porous iron catalysts for methanation. Smith[57] and Schatz[58] have rather thoroughly studied the hydrogenation of carbon monoxide on 1/8-inch diameter S.A.E. 1013 steel balls and have found that the catalyst exhibits a large increase in its ability to catalyze the reaction between carbon monoxide and hydrogen to form methane, water and carbon dioxide as the reaction temperature is raised from 900° to 1040°F. The catalyst shows a maximum activity at 1100°F to 1150°F, depending upon synthesis gas composition, and then declines with increase in temperature. The effect of temperature and synthesis gas composition on the gross heating value of the product gas is shown in Figure 4. This figure indicates that the optimum temperature and feed gas composition for the synthesis of a product of the highest heating value at 31 atmospheres pressure and a space velocity of 0.10 mols/hr/sq.ft. fall into the following ranges:

Temperature: 1090° - 1150°F

Percent CO in feed gas: 47% - 52%
(remainder H_2)

For these conditions, the heating value of the product gas, scrubbed free of carbon dioxide and water, ranges from 735 to 745 BTU/SCF.

Carbon deposition on the steel catalyst increases rapidly as the reaction temperature is raised from 900° to 1000°F, but decreases substantially at higher temperatures. This trend is clearly shown by Figure 5, in which the effect of temperature and synthesis gas composition on the amount of carbon deposited during synthesis is presented. Carbon deposition, though decreasing with
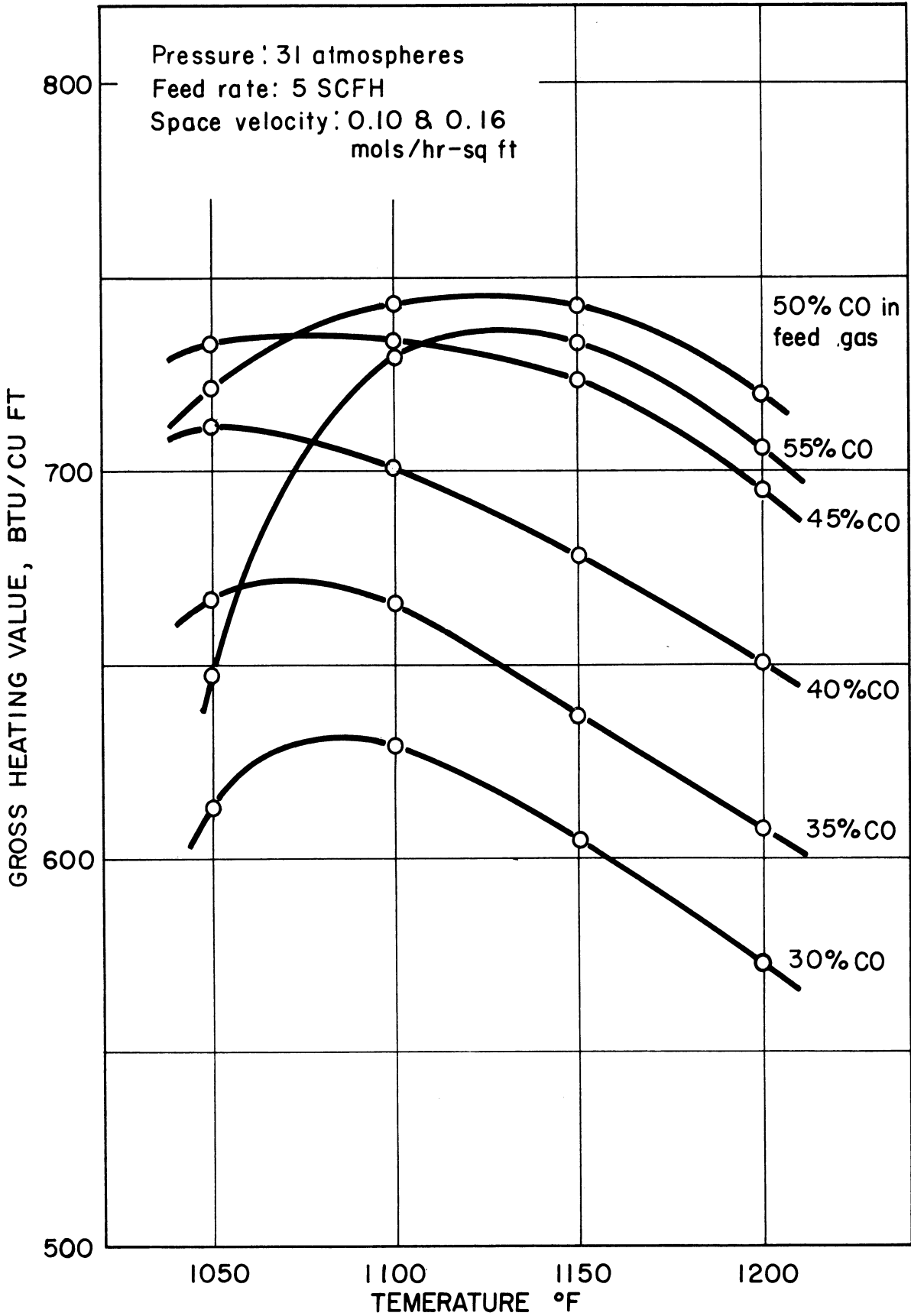
FIGURE 4. EFFECT OF TEMPERATURE AND FEED GAS COMPOSITION ON THE GROSS HEATING VALUE OF THE SCRUBBED PRODUCT GAS FROM METHANATION WITH A STEEL CATALYST
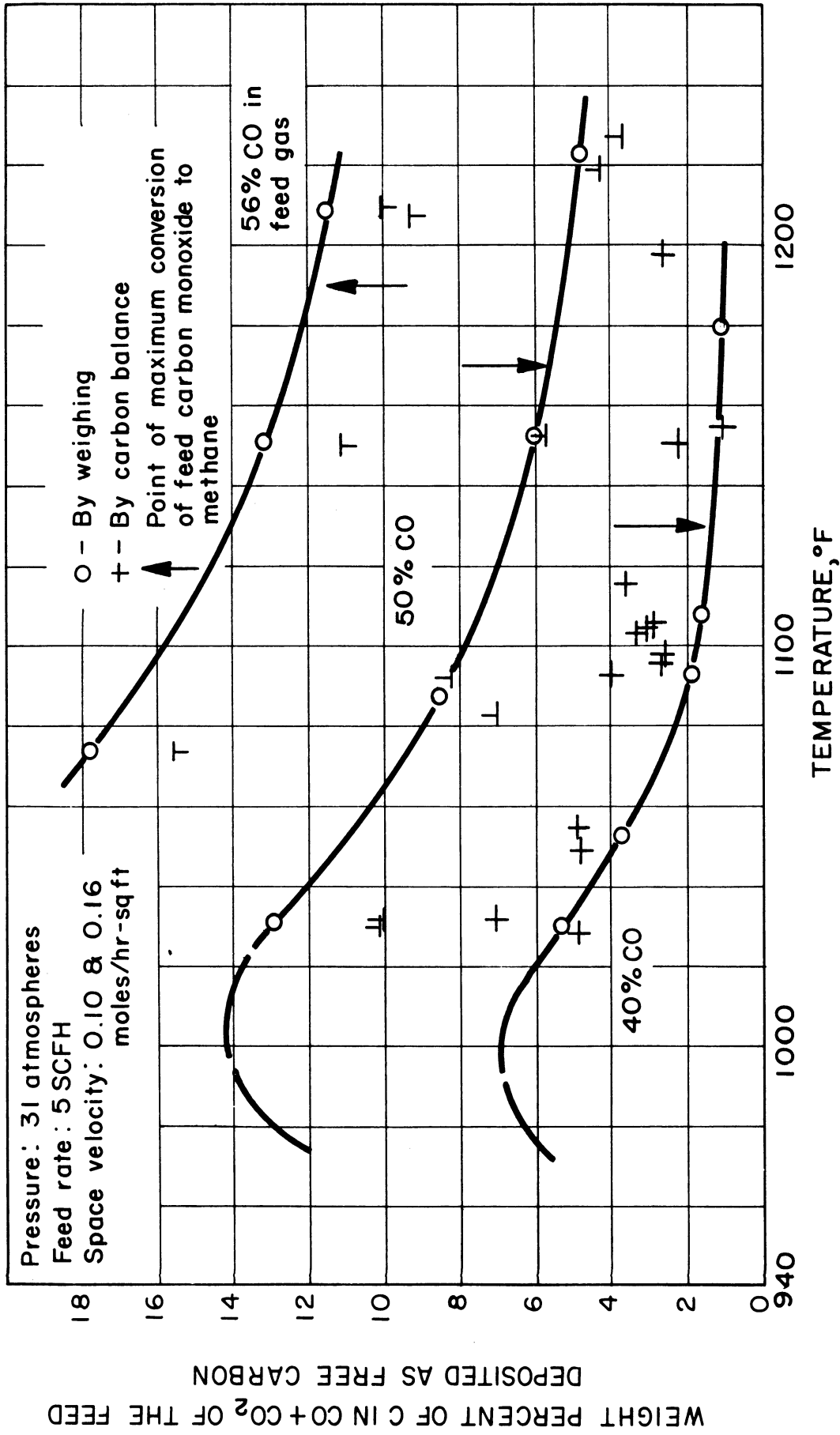
FIGURE 5. EFFECT OF TEMPERATURE AND FEED CARBON MONOXIDE CONCETRATION ON THE AMOUNT OF CARBON DEPOSITION WHICH OCCURS DURING SYNTHESIS USING A STEEL CATALYST

with increasing temperature, is appreciable at temperatures where maximum conversions of carbon monoxide to methane are obtained. However, carbon can be removed from the catalyst by air oxidation without deleterious effect on catalyst activity.

It is significant to note from Figure 4 that the heating value of the product gas reaches a maximum when the synthesis gas used contains approximately 50% carbon monoxide. At higher carbon monoxide concentrations in the synthesis gas, a decrease in product heating value results from a decreased conversion of carbon monoxide to methane and ethane and an increased conversion to carbon dioxide. It is apparent that with the non-porous steel catalyst studied, an upper limit on the heating value of the product exists which is below the 850 BTU/SCF value necessary for economical high BTU gas manufacture. On the basis of thermodynamic equilibrium considerations, it has been pointed out previously that low temperatures and high pressures are most favorable for the conversion of carbon monoxide and hydrogen to methane. Unfortunately, most non-porous steel catalysts are not active for methane synthesis at temperatures much below 1000°F. Thus, while steel possesses a number of attributes that make it an attractive methanation catalyst, it is necessary to use reaction temperatures that are not the most favorable for methane synthesis. As a result, it is not possible to approach complete conversion of synthesis gas to methane. Even at optimum reaction conditions for non-porous steel catalysts, appreciable quantities of carbon monoxide and hydrogen remain unreacted, thus, producing product gases with heating values lower than those necessary for

economic high BTU gas manufacture. Steel catalysts may be attractive in Europe, however, where the required heating values for commercial gases fall in the range of 500 to 600 BTU/SCF.

(b) Nickel and Cobalt Catalysts

Supported (porous) nickel and cobalt base catalysts, are active for methane synthesis at temperatures at which almost complete conversion of carbon monoxide and hydrogen to methane is thermo-dynamically possible. While such porous type catalysts are subject to sintering and to fragmentation by carbon deposition, making them less desirable from a structural standpoint, potentially they are capable of producing a product of higher heating value than is obtainable with either porous or non-porous iron catalysts.

Table V shows that nickel catalysts formed by precipitation techniques are more active than varieties of impregnated nickel catalysts. There is little difference in activity, however, between precipitated nickel catalyst and the extracted Raney nickel catalyst. Both are capable of producing product gases with heating values in excess of 900 BTU/SCF. Likewise, cobalt-thorium oxides supported on kieselguhr and also extracted Raney cobalt alloys are active methanation catalysts which can produce gases with heating values above 900 BTU/SCF.

The composition of the product gas which can be synthesized from a mixture of 29% CO and 71% H_2 using a cobalt-thoria catalyst, is shown in Figure 6 as a function of synthesis temperature. At temperatures ranging from 650° to 750°F carbon monoxide is almost completely converted to products. Some hydrogen remains unreacted, but a more judicious selection of synthesis gas composition could

Pressure: 30 atmospheres
Feed rate: 5 SCFH
Feed composition: 29% CO - 71% H_2
Catalyst: cobalt - thoria (200 pellets- $\frac{1}{8}$" dia. x $\frac{1}{8}$" long)
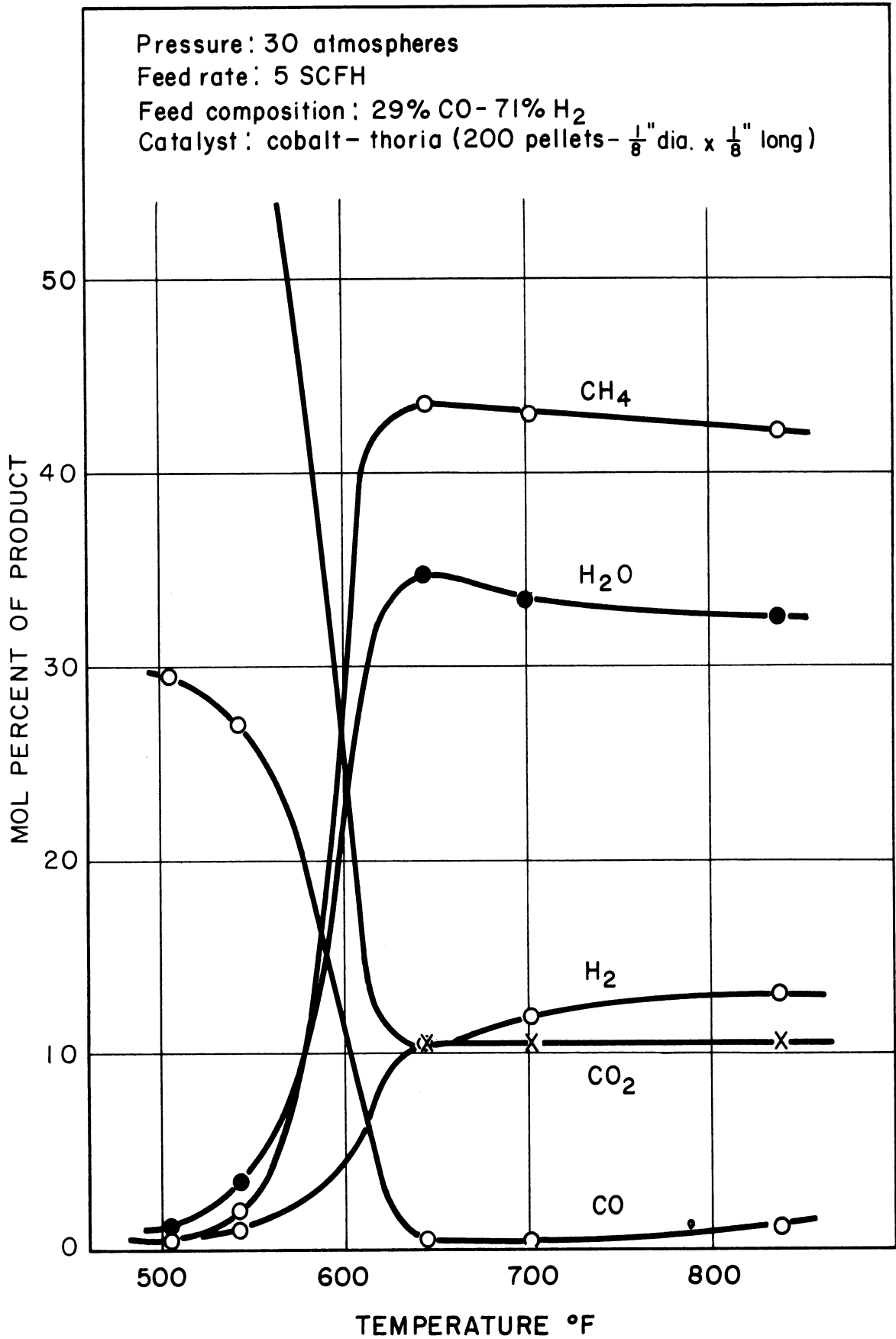
FIGURE 6. EFFECT OF TEMPERATURE ON THE PRODUCT GAS COMPOSITION USING A COBALT-THORIA CATALYST.

have resulted in virtually complete conversion to methane, water, and carbon dioxide. After removal of CO_2 and H_2O, the product stream would be close to 100% methane and have a heating value in excess of 1000 BTU/SCF.

(c) Carbon Deposition

Deposition of carbon during synthesis is generally considered to be detrimental to efficient methanation. Conversion of carbon monoxide to carbon constitutes a loss of potential heating value since yields of methane are reduced. Carbon deposition can fragment porous catalysts, plug fixed-bed reactors, or cause loss of fluidization in fluid-bed reactors. Nevertheless, because of the nature of the catalyst used or the composition of synthesis gas available, carbon deposition often must be tolerated even though it may be the most significant factor reducing catalyst life. Carbon deposition is encountered with all iron catalysts, and becomes excessive as the H_2 to CO ratio of the synthesis gas is reduced below three. In contrast, very little carbon is deposited on nickel catalysts when H_2 to CO ratios of 2.5 or higher are used. At lower H_2 to CO ratios, e.g., a ratio of 1.0, excessive carbon deposition is encountered with all of the active catalysts listed in Table V.

Carbon can be removed from some catalysts, notably non-porous iron catalysts, without deleterious effect on catalyst activity by passing air over the hot catalyst to convert the deposited carbon to CO and CO_2. With porous catalysts, this technique is not always successful for the high surface temperatures obtained during oxidation may cause sintering of the catalyst and subsequent reduction in catalytic activity.

(d) Fluid-Bed Catalysts

Catalysts which are found to be active for methanation of CO and H_2 in fixed-bed testing units are also active when used as fluidized catalysts. However, from a structural standpoint they do not always make satisfactory fluid catalysts. Catalysts must be physically stronger for service in fluid-bed reactors where maintenance of a constant particle size distribution is necessary for good fluidization. Data on a number of catalysts which have been tested in laboratory scale fluid-bed units are tabulated in Table VI. From an activity standpoint, fluid-bed catalysts are similar to fixed-bed catalysts. Iron catalysts are less active than nickel catalysts and are unable to produce high BTU fuel gas. High yields of C_3+ hydrocarbons are obtained at temperatures below 800°F. At higher temperatures, equilibrium conditions become less favorable for the formation of methane.

Carbon deposition, which can fragment porous catalysts and can ultimately result in plugging of fixed-bed reactors, is even a more serious problem in fluid catalyst operations. Changes in the size distribution of a charge of fluid catalyst because of particle fragmentation or carbon buildup can result in loss of fluidization at total carbon levels much lower than those which cause trouble in fixed-bed operations. Carbon deposition on the fluid iron catalysts described in Table VI is excessive even at synthesis gas CO to H_2 ratios as high as three over the range of temperatures covered. Thus, low catalytic activity, high yields

TABLE VI. EVALUATIONS OF FLUIDIZED-BED METHANATION CATALYSTS

	H₂/CO Ratio	Temp. °F	Space Vel. Range* V/V/hr.	Recycle Ratio R:FF	Pressure Range psig.	Process Catalyst Life lbs CH₄/lb Ni	Htg. Val. BTU/SCF	Investi-gator
Iron-base Catalysts								
Synthetic ammonia catalyst, Fe₃O₄:MgO + K₂O (10:1) reduced & nitrided	1	to 400	800-840	2:1	100	Excessive carbon		43
Scrap-steel shot fines, 69% Fe, 6.6% Si, 0.5% C, 0.2% S, reduced & nitrided	1	287-350	840	2:1	100	--	640	43
	3	340-350	1940-3100	1:1-3:1	230-275	--	706	
	2.5	320-350	3630-14500	0	300	--	530	
	2.5	340	1850-3700	1:1-3:1	300	--	585	
	2.5 + 2.6% steam							
Sintered magnetite and ball clay, 85% Fe₃O₄, 15% ball clay, reduced & nitrided	3	340	1800-4300	0-4:1	300	--	670	43
		300-400	880	2:1	100-200	--	715	
Nickel-base Catalysts								
NiO-Al₂O₃-kaolin (100:159:97) - reduced	2.5	300-312	5530-11000	0	300	--	960	43
NiO-Al₂O₃-MnO-kaolin (100:7.3:25.6:97) - reduced	2.5	350 avg.	7500	1:1	300	750	>900	43
NiO-Al₂O₃-MnO-kaolin (100:7.3:25.6:97) - reduced	3.0	345 avg	7500	1.5:1	300	1200	>900	43
NiO-Al₂O₃-MnO-Activated alumina (100:7.3:25.6:75) - reduced	2.5	360 avg	7500	1:1	300	900	>900	43
NiO-Al₂O₃-MnO-Filtrol S-185 (100:7.3:25.6:185) - reduced	3.0	350 avg.	7500	0.7:1	300	2500	>900	43
NiO-Al₂O₃-ThO₂-Activated alumina (100:7.3:11.0:240) - reduced	3.0	368 avg.	7000	1:1	300	6500	>900	43
NiO-ThO₂-Kieselguhr (100:13.6:78 4)	3.0	370 avg.	7000	1:1	300	4000	>900	43

* Volume of synthesis gas/vol. of catalyst bed/hr.

** Recycle to Fresh Feed

of C_3+ hydrocarbons, and excessive carbon deposition combine to make iron catalysts generally unsatisfactory for methanation of synthesis gas.

Nickel base fluid catalysts, on the other hand, are highly active for methanation. The nickel catalysts listed in Table VI produce methane yields high enough to give gases having heating values of over 900 BTU/SCF. Catalyst process lives as high as 6500 pounds of methane per pound of nickel have been obtained. A typical product gas composition is shown in Table VII.

TABLE VII.   ANALYSIS OF A TYPICAL PRODUCT GAS PRODUCED
BY METHANATION WITH A NICKEL CATALYST[43]

Catalyst Composition: $NiO-Al_2O_3$-Ka olin (100:   159:97)

Average reactor temperature	579°F
Reactor Pressure, psig	300
Fresh-feed space velocity, V/V/hr.	5530
Recycle ratio	1:1
H_2/CO feed ratio	2.5
Catalyst age, hrs.	65

Product Composition, volume %

CH_4	81.8
C_2+	0.0
CO_2	14.2
H_2	4.8
CO	1.2

Gross heating value, BTU/SCF   960

Carbon deposition has not proven to be a problem with nickel fluid catalyst as long as feed gas H_2/CO ratios are maintained above 2.5.

(e) Summary

The development of methanation catalysts has progressed
to the stage where active catalysts are now available for methanation
on a commercial scale in either fixed or fluidized bed processes. It
has generally been established that nickel is superior to iron as a
methanation catalyst for processes designed to produce only high
heating value fuel gas. However, it is conceivable that in a
combined operation to produce both gaseous and liquid products, iron
might prove to be a more suitable catalytic material. It is doubtless
that further research would result in improved methanation catalysts.
However, in view of the present advanced state of catalyst develop-
ment, and recognizing the need for intensive research effort in the
fields of solid fuels gasification and gas purification, further
research on methanation catalysts can best be deferred in favor of
work in fields of more immediate need.

2. Processes

The formation of methane from CO and H_2 is a highly exo-
thermic reaction, and the heat of reaction must be quickly and
effectively removed in order to prevent excessively high reaction
temperatures which could result in catalyst deactivation, unfavorable
equilibrium conditions, carbon deposition or in damage to process
equipment. Two primary means are available for temperature control:
1) Cooling by boiling a liquid (usually water) contained either in
tubes incorporated into the methanation reactor or in a jacket which
surrounds tubes containing catalyst. Equipment of this sort has been
used in the Fischer-Tropsch process for synthesis of liquid hydro-
carbons.[59]

2) Recycling a large quantity of cooled product gas. Since both methods are applicable to either fixed or fluidized-bed operation, four general types of methanation operations are possible. To summarize, these include:

(a) Use of fixed-beds of catalyst in which reaction heat is removed by boiling a liquid.

(b) Use of fixed-beds of catalyst in which reaction heat is removed by recycling cooled product gas.

(c) Use of fluid-beds of catalyst in which reaction heat is removed by a boiling liquid contained in tubes immersed in the catalyst bed.

(d) Use of fluid-beds of catalyst in which reaction heat is removed by recycling cooled product gas.

Control of reactor temperature by recycle of cooled product gas has the added advantage of reducing or preventing carbon deposition in the catalyst bed. The presence of carbon dioxide in the combined feed to a methanation catalyst serves to displace the equilibrium between carbon monoxide, carbon dioxide, and solid carbon, described by the equation

$$2CO \rightleftharpoons CO_2 + C \tag{11}$$

so that conversion of carbon monoxide to carbon is reduced. The heat of reaction of the methane synthesis is so great, however, that internal cooling of catalyst beds with boiling liquids may be required in addition to recycle of cooled product gas in order to maintain desired temperature levels.

Fixed-bed reactor systems have received the major attention

for use in methanation processes primarily because they have proven to be ideal units for both laboratory and pilot plant scale investigations. Fixed-bed reactors have the advantage over fluid-bed reactors that for a given diameter vessel, higher linear gas velocities are possible, allowing higher synthesis gas throughputs. On the other hand, fluid catalyst units have more uniform catalyst temperatures and improved heat transfer to cooling surfaces. Circulation of catalyst to a regenerative vessel in which carbon could be burned from the catalyst, is possible in a fluid catalyst system. Both fixed and fluidized-bed pilot plant units have been described in the literature.[43]

Operation of the methanation step at elevated pressure is desirable both from a thermodynamic and an engineering point of view. Pressure operation allows higher flow rates and reduces the size of equipment. Elevated pressures favor the formation of methane as shown earlier in Figure 3. Furthermore, methanation at high pressure reduces the amount of work required to compress the final high BTU gas to pipe line pressures. Operation of the gasification, methanation, and purification steps above pipe line pressures (800 to 1200 psig), would eliminate the need for a final compression step, and is one goal toward which research in these fields should be directed.

C. Conclusions

Research on both methanation processes and catalysts has reached an advanced stage. Methanation has been demonstrated on a pilot plant scale, and no particular problems are expected in building

and operating commercial size units as long as the synthesis gas is

purified of sulfur compounds and adequate means of removing reaction

heat are incorporated into methanation reactors. To be sure, further

research will be helpful in arriving at the optimum reactor design

and the most effective methanation catalyst. However, this research

is not urgent, and can best be postponed until the economics for

high BTU gas manufacture become favorable. Until that time, research

effort is more urgently needed in the field of gasification and gas

purification, where the economic incentives for developing improved

processes are greater.

V. ECONOMICS OF HIGH BTU GAS MANUFACTURE FROM COAL

Previous sections of this report have dealt with the process

steps required to manufacture high BTU gas from coal. Specific

processes have been cited which have been developed, some only on

the pilot plant scale, to accomplish the various steps which con-

stitute the integrated process of making high BTU gas. These are

of obvious importance, for a workable process is a fundamental

requisite. Nevertheless, the ability to produce high BTU gas is not

the ultimate story. Unless the price of the product, delivered to

the consumer, can compete with the price of natural gas and of other

forms of energy, coal will not be used as a raw material for high

BTU gas production. It is the purpose of this section to present

economics for the overall process of making high BTU gas from coal

in the light of present day costs.

A. Basis for Economics

In 1951, Blaw-Knox Construction Company prepared an economic

study of the production of methane from coal[60] and this work has

served as the basis for the economics presented herein. Investment

and production costs have been escalated from 1951 to January 1957

levels. A simplified flow plan for a typical plant to produce

100 million SCF/day of high BTU gas is shown in Figure 7.

Non-caking coal is reacted with oxygen and superheated

steam in Lurgi pressure gasifiers. The gas produced is completely

purified of sulfur compounds in an initial purification step employ-

ing the Rectisol process. Simultaneously, the CO_2 content of the

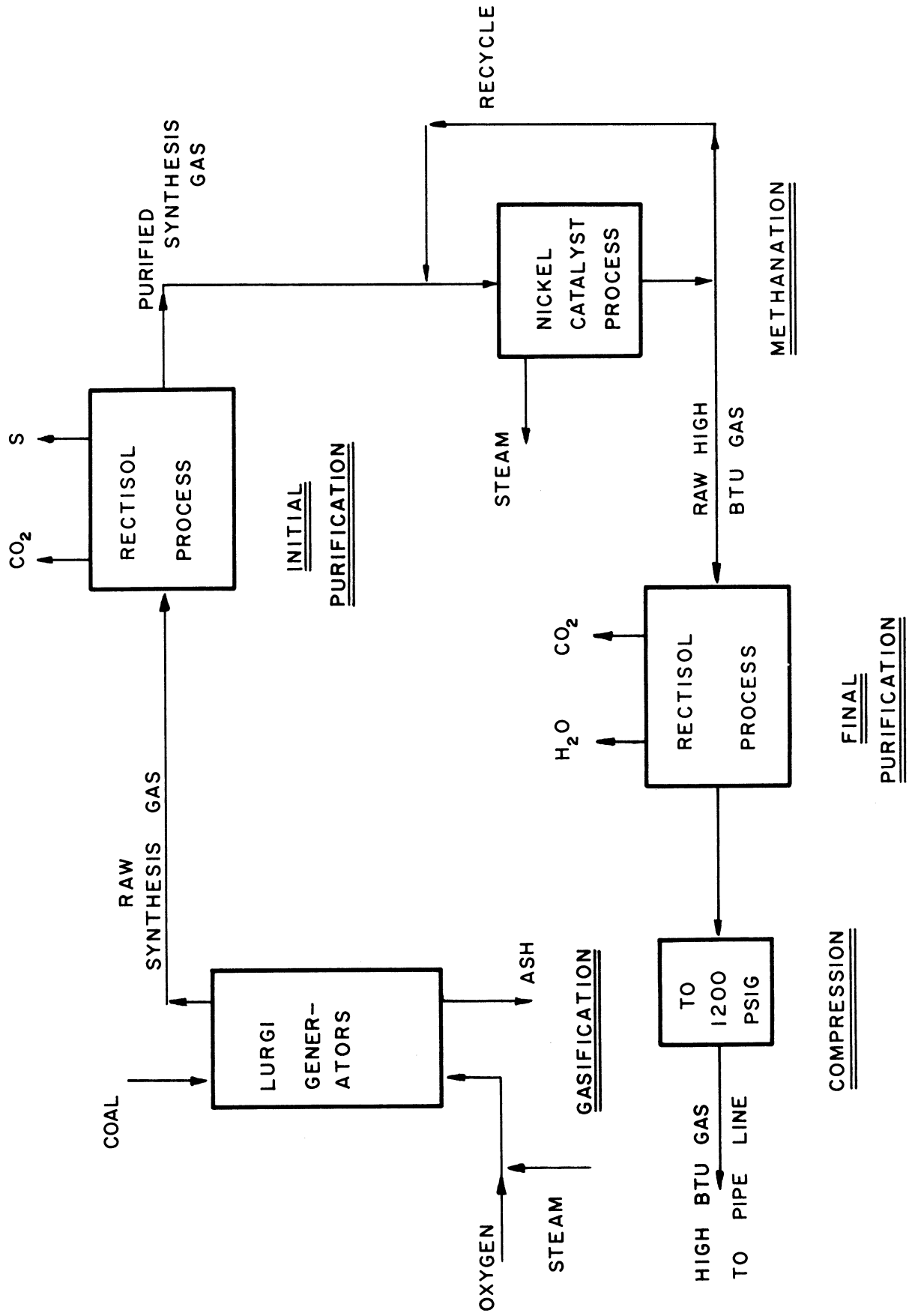gas is reduced. Following purification, the gas is passed over a

FIGURE 7. SCHEMATIC DIAGRAM OF A HIGH BTU GAS SYNTHESIS PLANT

supported nickel methanation catalyst which converts the synthesis gas to CH_4, CO_2 and H_2O. A final purification of the methanation product with the Rectisol process removes CO_2 and H_2O. The resulting gas stream has a heating value in excess of 900 BTU/SCF, and is ready for compression to transmission pipe line pressure.

In the Blaw-Knox study, fuel consumption is based upon a hypothetical non-caking coal having a heating value of 13,000 BTU/lb. which would not produce tars or oils in the gasifiers. To produce 100 million SCF/day of high BTU gas, daily consumption of fuel would amount to 4,500 tons. Oxygen requirements would be 2,070 tons of 95% oxygen supplied at 375 psig. In addition, 13,380 tons/day of 375 psig, 850°F steam would be consumed. Representative compositions of the gas stream at various points in the overall process to convert coal to high BTU gas as outlined by the flow diagram in Figure 7, are shown in Table VIII.

B. Investment Costs

The investment costs for the process units and the utilities involved in the production of high BTU gas are presented in Table IX. Investments have been escalated from the 1951 level to January 1957, using a 1.39 escalation factor. These costs include the design and procurement of equipment, and also the labor and overhead charges incurred during construction. The designation "auxiliaries" include site preparation, grading, storage tanks, loading facilities, roads, rail sidings, administration buildings, warehouses, shops, etc. Interest charged on the capital required during the construction period has been added to these costs. Working capital has also been

TABLE VIII. GAS COMPOSITIONS AT VARIOUS POINTS
IN A HIGH BTU GAS PLANT

	Raw Lurgi Gas	Gas Leaving Initial Purification	Gas Leaving Methanization	High BTU Gas
H_2	40	54.8	)	)
			) 8.6	) 10.9
CO	20	27.4	)	)
CO_2	30	4.1	22.1	1.0
CH_4	8	10.9	63.6	80.9
C_2H_6 & ill.	1	1.4	2.85	3.5
N_2	1	1.4	2.85	3.7
	100	100.0	100.0	100.0
Volumes	100	73	35.0	27.5
Heating Value (BTU/SCF)	293	401	721	915

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TABLE IX. INVESTMENT COST SUMMARY

Process Units	Labor, Material & Overhead
Gasification	$ 8,150,000
Initial Purification	5,160,000
Methanation	3,560,000
Final Purification	1,510,000
Final Gas Compression	1,070,000
Auxiliaries	9,150,000

Utilities	
High Pressure Steam	10,520,000
Low Pressure Steam	1,320,000
Electric Power	2,700,000
Cooling Water	4,070,000
Boiler Feed Water	3,280,000
Oxygen Production	14,380,000
Oxygen Compression	1,270,000
Total Construction Cost	$66,140,000
Interest on Capital During Construction (assumed)	3,480,000
Working Capital (assumed)	3,320,000
TOTAL INVESTMENT	$72,940,000

provided. Investment costs total $73,000,000 and have increased

about $20,000,000 since 1950.

C. Production Costs

A summary of costs involved in producing 100 million SCF/day

of high BTU gas is presented in Table X. The costs shown are based

upon coal at $4.00 per ton. The sale of 100 million SCF/day of high

BTU gas involves a public utility which would be limited by law to

a maximum return on capital investment of 6%. Depreciation costs

average about 6% on capital investment. An additional 2.5% on in-

vested capital has been included in the cost of producing high BTU

gas to cover items such as real estate and personal property taxes,

annuities, insurance, etc.

Maintenance and repair costs have been assessed on the

basis of a fixed percentage of the capital investment. Two percent

has been used for electric power generation, cooling water supply,

oxygen production and compression, and final gas compression. For

all other units, maintenance and repair costs have been assumed to

be 4%. Direct operating labor costs have been escalated to account

for current average wage levels. Overhead and administrative expenses

have been taken as 60% of the direct labor costs.

The total cost of producing high BTU gas as shown in

Table X amounts to 61.5 cents/MSCF, based on coal at $4.00 per ton.

Inspection of Table X indicates that gasification represents 70% of

the total cost of producing high BTU gas. The cost of initial puri-

fication is 11.5% of the total, methanation is 4%, final purification

is 2.5%, final gas compression to 1200 psig is 2%, and auxiliaries

TABLE X. PRODUCTION COST SUMMARY, CENTS/MSCF*

	Gasification	Initial Purification	Methanization	Final Purification	Final Compression	Auxiliaries	Total Process Units
Capital Costs							
Return on Investment	1.49	0.93	0.65	0.28	0.20	1.65	5.20
Depreciation	1.35	1.28	1.00	0.35	0.33	1.59	5.90
Real Estate & Personal Property Taxes, Insurance, Etc.	0.61	0.39	0.26	0.11	0.08	0.69	2.14
Total Capital Costs	3.45	2.60	1.91	0.74	0.61	3.93	13.24
Process Raw Materials							
Fuel for Gasification**	18.02	--	--	--	--	--	18.02
Process Steam	10.68	--	--	--	--	--	10.68
Oxygen	8.51	--	--	--	--	--	8.51
Catalyst	--	--	2.66	--	--	--	2.66
Solvent	--	0.24	--	0.09	--	--	0.33
Total Process Raw Materials	37.21	0.24	2.66	0.09	--	--	40.20
Utilities							
Steam	0.14	2.83	(3.87)	0.22	0.54	0.06	0.06
Electricity	0.03	0.04	0.02	0.04	--	1.03	1.03
Cooling Water	0.06	0.47	0.04	0.05	0.06	--	0.68
Boiler Feed Water	0.02	--	0.99	--	--	--	1.01
Waste Heat	(0.44)	--	--	--	--	--	(0.44)
Total Utilities	(0.19)	3.34	(2.82)	0.31	0.60	1.10	2.34
Labor & Overhead							
Direct Operating Labor	0.99	0.14	0.21	0.10	0.03	--	1.47
Overhead & Administrative	0.60	0.08	0.14	0.06	0.02	--	0.90
Total Labor and Overhead	1.59	0.22	0.35	0.16	0.05	--	2.37
Maintenance & Repair	0.99	0.62	0.43	0.18	0.07	1.10	3.39
TOTAL COSTS	43.05	7.02	2.53	1.48	1.33	6.13	61.54

* Cents per thousand standard cubic feet

** Coal at $4.00 per ton

amount to 10%. Production of the purified synthesis gas accounts for fully 84% of the total cost of producing high BTU gas (when coal is charged at $4.00 per ton) which clearly points out the areas where the greatest economies can be made, namely, in the processes of mining coal (lower fuel costs), gasification of coal, and purification of synthesis gas.

D. Effect of Fuel Cost

The effect of variation in fuel cost on the production cost of high BTU gas is shown in Figure 8. This figure indicates that the cost of high BTU gas increases linearly with the cost of coal. The 1951 Blaw-Knox study was based on coal priced at $4.00 per ton, and showed that high BTU gas could be produced for 55.4 cents/MSCF. The corresponding figure for January 1957 production costs is 61.5 cents/MSCF, an increase of 6.1 cents/MSCF over 1951 costs. This increase is the result of much higher investment costs, slightly higher catalyst cost, and increased wage rates.

Since 1951, the wholesale price of bituminous coal has increased only very slightly. It is reasonable to assume that coal which cost $4.00 per ton in 1950, is available for approximately the same price today. Thus, comparison of the revised production costs for high BTU gas shown in Table IX with the 1951 Blaw-Knox study is a valid comparison, which shows that with coal at $4.00 per ton the true increase in the cost of high BTU gas over 1951 costs amounts to about 6.1 cents/MSCF.

E. Comparitive Cost of Natural Gas and High BTU Gas

In the interval 1951 to 1957, the average wholesale price of natural gas increased by 13%.[61] During this same interval, the
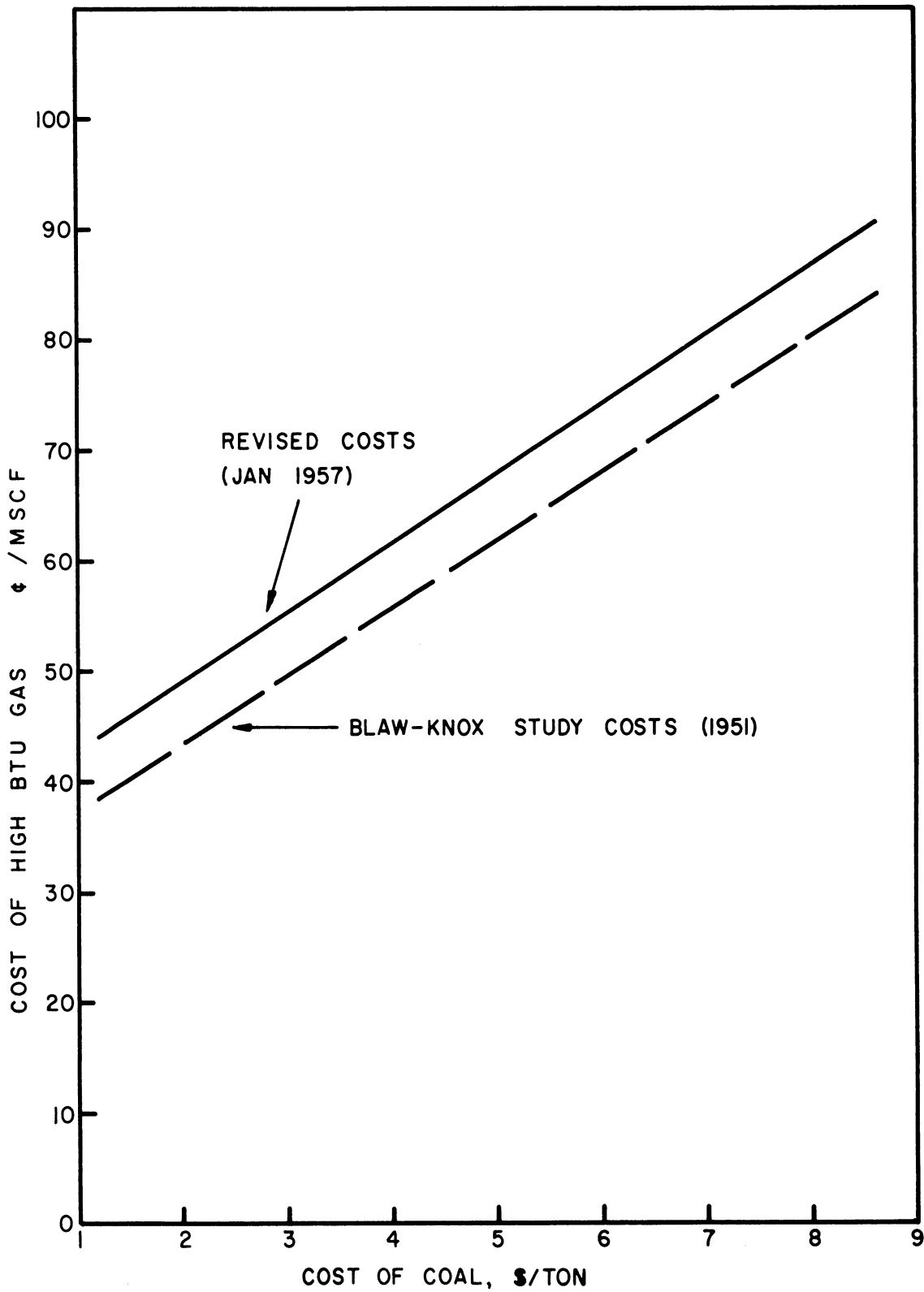
FIGURE 8. EFFECT OF FUEL COST ON THE COST
OF PRODUCING HIGH BTU GAS.

cost of producing high BTU gas has risen about 11% from 55.4 to

61.5 cents/MSCF. These statistics point out that while the price of

natural gas has risen considerably over the last six years, the cost

of producing high BTU gas has increased at a nearly comparable rate.

The sizeable gap between the price of natural gas and that of high

BTU gas produced from coal has not been narrowed an appreciable

extent during this period.

F. Summary

It has been estimated, that the investment for a plant

designed to produce 100 million SCF/day of high BTU gas would be

approximately $73,000,000. The cost of gas production has been esti-

mated to be 61.5 cents/MSCF when charging coal at $4.00 per ton. The

cost of producing high BTU gas is closely related to the cost of coal.

For example, with coal costing $4.00 per ton, fuel represents about

40% of the cost of high BTU gas, while at $8.00 per ton, fuel is

roughly 55% of the gas cost. By far the greater portion of the total

cost of producing high BTU gas lies in the production of the purified

synthesis gas. Therefore, efforts to reduce costs should be directed

toward reducing the cost of the synthesis gas. The escalation of the

1951 Blaw-Knox economics to present cost levels, shows that production

costs of high BTU gas are rising at a rate which is nearly equal to

the rate of increase of natural gas prices. This fact raises a very

valid question as to whether high BTU gas manufactured from coal will

become competitive with natural gas before the day when large supplies

of inexpensive nuclear energy are available for general commercial

and household use.

The economics presented in this section are based on an overall process as outlined in Figure 7. Selection of other sub-processes for gasification methanation purification, etc., than those used in this study could change these economics to some extent. However, the numbers presented herein are believed to be typical of the cost of producing high BTU gas using the most advanced of the commercially proven processes available.

VI. CONCLUSIONS

Before the day when natural gas reserves near depletion, a replacement must be ready. High BTU gas manufactured from coal can serve as that replacement, and much research has been devoted to developing an efficient and economical process. Coal is a logical choice as the basic raw material from which to manufacture high BTU gas because of the ample reserves of coal which lie within easy reach of the highly industrialized and densely populated areas of the United States now supplied with natural gas.

Present engineering know-how is adequate to design a workable plant to produce high BTU gas from non-caking coal. Such a plant would be comprised of five sections wherein 1) coal is gasified with steam and oxygen to produce a mixture of carbon monoxide, hydrogen, and carbon dioxide; 2) the raw synthesis gas is purified of carbon dioxide plus sulfur compounds which poison methanation catalysts; 3) the mixture of carbon monoxide and hydrogen is catalytically converted to methane, water and carbon dioxide using a supported nickel catalyst; 4) carbon dioxide and water are removed from the gas produced; and 5) the product high BTU gas is compressed to pipe line pressure. Possible alternative subprocesses for accomplishing these operations have been discussed in previous sections of the report. Research devoted to the development of processes to gasify American caking coals has been noted. Areas where additional research may lead to improved processing and to large economies in the production of high BTU gas, have been pointed out. In general, these lie in the manufacture of the purified synthesis gas.

The development of methanation catalysts and processes has reached an advanced state. Further research on methanation can best be deferred in favor of work on gasification and purification processes, where a greater return on research effort can be realized.

Estimated economics for the production of high BTU gas from noncaking coal have been presented and indicate that with coal priced at $4.00 per ton, production costs would amount to 61.5 cents/MSCF of gas. Production costs have increased by 11% since 1951. Moreover, the total capital investment required to build a high BTU gas plant has risen by roughly $20,000,000. During the period 1951 to 1957, the average wholesale price of natural gas increased by 13%. This rate of increase has been only slightly more rapid than the increase in the estimated production cost of high BTU gas. This fact clearly points out that the gap between the cost of natural gas and high BTU gas manufactured from coal, has not been closing at a very rapid rate. The day when manufactured high BTU gas will be competitive with natural gas appears to be still quite far in the future.

The potential of obtaining tremendous quantities of inexpensive useful atomic energy from fission or fusion cannot be overlooked. The advent of atomic power complicates the problem of predicting not only the future of high BTU gas from coal, but of all our present supplies of energy as well. However, no matter how uncertain the future may be, the possibility of utilizing gasification and methanation to produce and upgrade low BTU gas cannot be discounted.

While at present, the construction and operation of a large plant to produce high BTU gas from coal would be prohibitively expensive, plans for the future should be made. There is a need for

much pilot plant scale work to improve and reduce the cost of presently
proposed processes , and further, to answer many questions concerning
the optimum design of a commercial size plant. When a shortage of
natural gas becomes imminent and a replacement is needed, the design
of a plant to manufacture high BTU gas from coal should be ready.