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# GASIFIER STUDY FOR MOBIL COAL TO GASOLINE PROCESSES. FINAL REPORT

MOBIL RESEARCH AND DEVELOPMENT CORP. PAULSBORO, NJ

OCT 1978



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## GASIFIER STUDY FOR MOBIL COAL TO GASOLINE PROCESSES

## FINAL REPORT

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#### I. Executive Summary and Introduction

Our extensive coal reserve will be needed in the future to prepare high quality transportation fuels (for example, gasoline, diesel fuel and methanol). In order to insure that our limited technical, financial and construction resources are used to the best advantage, the most cost effective and thermally most efficient processes must be identified and used. There are two principle routes for converting coal to high quality transportation fuels. One method is to gasify the coal to obtain synthesis gas, which is a mixture of H<sub>2</sub> and CO. This synthesis gas can then be converted to high quality liquid fuels by a number of conversion processes. The other is to preserve the molecular structure of the coal as much as possible while hydrogenating the coal and reducing the molecular weight of the coal components.

In a previous paper (Reference 1), it was shown that the indirect route via gasification and synthesis provides a very promising route for high grade fuels, both for the near range and for the long range. The gasifiers and the associated offsites that produce the synthesis gas are a large part of the cost of a complex to produce high quality transportation fuels. The thermal efficiency of this gasification step is also a large contribution to the overall thermal efficiency of the complex. To fully utilize the advantages of this route, it is important to develop better gasifiers and to match the synthesis processes such that they take full advantage of such a gasifier. The objective of this study was to evaluate which of the gasifiers presently under development could meet this goal. This objective is to be accomplished by the use of open literature data on gasifiers and by a study of data from pilot plants currently in development stage.

This study shows that synthesis gas at the lower ratios of H<sub>2</sub> to CO and steam to cxygen has inherent thermal efficiency advantages which arise from basic scientific and engineering principles. Gasifiers that can be made to operate consistent with these principles have a substantial cost advantage. The cost advantages are demonstrated in this study by a differential economic analysis that is essentially independent of the absolute values of the cost basis.

The British Gas Corporation-Lurgi slagging gasifier, which is presently close to commercialization, conforms closely to the basic requirement and potentially could produce syngas at a low production cost relative to other gasifiers such as the dry ash Lurgi gasifier. The H<sub>2</sub> to CO and steam to oxygen ratios of this gasifier are about 0.5 and 1.3, respectively. These values are very close to the best theoretical values of 0.45 and 1.6, respectively.

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There is considerable evidence from the data obtained from fluid bed gasifier pilot plants that a multi-staged fluid bed gasifier could be developed which operates at low  $H_2$  to CO and steam to oxygen ratios required by the basic concepts. However, a better conceptual design and considerably further developing is required before the multi-staged fluid bed gasifier is ready for large-scale pilot plant tests and commercialization. Potentially such a gasifier could operate on coals not well suited for the BGC-Lurgi slagging gasifier.

For a gasifier to attain the full cost advantage of the concepts outlined in this report, maximum recovery of the volatile matters contained in the coal is needed. The amount of oxygen used to combust the coal in order to heat all the reactants to the gasification temperature must also be minimized. This requires a low gasifier exit temperature, and therefore, a counter-current flow scheme in which the feed coal exchanges heat with the hot product gas. This scheme will lead to a co-production of methane obtained from coal devolatilization.

If a syngas containing no methane is required, the Texaco gasifier is the best choice at the present. It closely approaches the basic requirement but has a high oxygen demand and high exit temperature that lead to a reduced thermal efficiency and an increased cost over gasifiers such as the BGC-Lurgi slagger. The water content in the coal slurry feed of a Texaco gasifier, however, greatly affects the thermal efficiency. For For coals that can be slurried with low amounts of water it achieves a thermal efficiency close to that of a dry ash Lurgi gasifier with Western coal. The investment cost of the Texaco gasifier with such a coal is higher than that of a BGC-Lurgi slagger and approximately the same as that of a dry ash Lurgi gasifier with western coal. The thermal efficiency of the Texaco gasifier is higher and its investment cost is lower when compared to the dry ash Lurgi gasifier using eastern coals. This is because the dry ash Lurgi qasifier has large cost and thermal efficiency penalties when operating with these less reactive coals as compared to with western coals. On the other hand, the BGC-Lurgi slagger can convert some eastern coals without these penalties and therefore still has a significant advantage over the Texaco gasifier for such coals.

The low  $H_2$  to CO ratio gasifiers have to be matched with syngas conversion processes that use such low ratios. If the syngas conversion process cannot use low  $H_2$  to CO ratio gases, the gas has to undergo further reaction of the CO with steam (water-gas shift reaction) in an external reactor to produce additional  $H_2$ . For example, conversion of syngas to methanol requires a  $H_2$  to CO ratio of at least 2. In many cases external shift of low  $H_2$  to CO ratio syngas is more cost effective than producing high  $H_2$  to CO ratios in a single gasifier vessel because the conditions can be chosen for the external shift to be more efficient and cost effective. On the other hand, a number of syngas conversion processes produce high quality fuels from low  $H_2$  to CO ratio syngases requiring little or no additonal shift from the 0.5  $H_2/CO$  ratio obtained from the high efficiency gasifiers. The slurry Fischer-Tropsch syngas conversion process operates with a  $H_2$  to CO ratio of 0.6. A ratio of unity can be used to produce dimethylether which can be converted to high octane gasoline by a Mobil process.

" The gasifiers that conform to the basic requirements developed in this study also provide the thermally most efficient and lowest cost route to the production of clean industrial fuel gas (medium BTU gas). One might envision a central gasification plant for supplying both medium BTU fuel gas for industrial use and syngas to a concentration of petrochemical complexes for preparation of transportation fuels all within a radius of 20 miles of each other. Such medium BTU fuel gas can be substituted by many industries for natural gas or oil with only minimum modification of the boiler or furnace. It is clean burning and provides an attractive route to substitute coal for oil and gas in many industrial applications where local concentration of industries justifies a central generation plant. The BGC-Lurgi slagger as well as a properly developed fluid bed gasifier discussed in the report could reduce the cost of fuel gas by about 30% over presently available commercial gasifiers. They could also reduce the cost of high grade synthetic liquid fuels by 20-30%. Reference 1 indicated that the co-production of SNG and liquid fuels using an advanced indirect liquefaction process under development by Mobil could co-produce SNG and gasoline cheaper and thermally more efficient than existing SNG processes. The results of this study confirm that the estimates given there for the gasifier are realizable.

These two promising potential applications, cheap clean industrial fuel on the one side and a thermally efficient and cheap indirect liquefaction process on the other, are strong incentives for accressive development and commercialization of such gasifiers. The BGC-Lurgi slagger must be shown to be scalable to commercial size and to be operable for long periods of time. The range of coal for which it can be used needs to be established. The development of other gasifiers such as multi-staged fluid bed gasifiers that operate in the high thermal efficiency region should be very actively pursued. Such gasifiers would not only be the thermally most efficient but would also provide the most cost effective route to the production of high quality clean transportation fuels as well as clean industrial fuel gas.

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#### II. Technical Overview

Two kinds of considerations are involved in the design and operation of gasifiers. One is the basic scientific and process engineering principles that underlie the gasification process and the other is the mechanical aspects that determine whether a practical device can be constructed to implement these principles. The device must be scalable to a sufficiently large size to be practical and must operate reliably with an acceptable stream factor. Much of this study is concerned with the guidance that can be obtained from scientific and process engineering principles as to what kind of gasifier will be most thermally efficient if an appropriate mechanical embodiment can be developed. For gasifiers constructed according to sound and reasonable engineering principles, there is a close correlation between thermal efficiency and costs — the more efficient is the gasification process, the less the cost. Thus, a search for the most efficient gasifier should result in also determining the one that has the potential of producing gas at the lowest cost.

The major sources of decreased thermal efficiency in gasifiers are energy losses caused by:

- 1. high steam demand and excess steam in product gas,
- 2. heating and cooling of process streams,
- 3. gas compression,
- 4. high oxygen demand in high temperature operations, and
- 5. production of tars and other undesirable products:

The steam requirement is often a dominant factor in determining the thermal efficiency of a gasifier. This is illustrated in Figure 1, which shows that the amount of excess steam in the product gas correlates with the efficiencies of actual gasifiers producing syngas at 400 psia. When the H2/CO ratios of the gasifiers in Figure 1 are examined, it is found that low H2/CO ratios occur in the gasifiers at the left-hand and high thermal efficiency end of the correlation line in Figure 1. There are basic stoichiometric and thermodynamic reasons why this correlation exists.

This can be seen by examining the reactions of carbon with steam and oxygen to produce CO, CO<sub>2</sub> and  $H_2$ . It is sufficient to consider only the four reactions,

 $C \div \frac{1}{2} O_2 \longrightarrow CO$   $\Delta H = -26.36$  (1)

 $C + O_2 \longrightarrow CO_2$   $\Delta H = -94.14$  (2)

- $C + H_2O \longrightarrow CO + H_2$   $\Delta H = 32.23$  (3)
- $C + 2H_2O \longrightarrow CO_2 + 2H_2 \qquad \Delta H = 23.04$  (4)

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Figure 1

GASIFIER NET THERMAL EFFICIENCY



Nei Thermal Efficiency (% LHV of Coal)

Other reactions of interest, such as CO<sub>2</sub> + C --->2CO and  $CO + H_2O \longrightarrow CO_2 + H_2$ , can be derived from these four reactions. In fact, each of the above four reactions can be derived from the other three. The heats of reaction ( AH kcal/mole at 700°F) are given to the right of the stoichiometric equations. Depending upon the particular combination of these four reactions that are taking place under a given condition, the amount of carbon, .... oxygen and steam that react together will vary and the product gas produced will also vary in composition. The amount of variation in the relative proportional of the reactant carbon, oxygen and steam is limited as shown in the triangular diagram of Figure 2. This diagram shows all possible fractional compositions of a mixture of carbon, oxygen and steam. The allowable combination given by the set of reactions (1) to (4) is confined to the outlined area of Figure 2. For example, point X tells us that 50 molecules of carbon, 20 molecules of oxygen and 30 molecules of steam could completely react away (no equilibrium constraints) to CO, CO<sub>2</sub> and  $H_2$  while point Y which reacts 67 molecules of carbon, with 20 molecules of oxygen and 13 molecules of steam cannot all react away to CO,  $CO_2$  and  $H_2$  (too much carbon to satisfy any combination of the reactions of (1) to (4)).

In adiabatic gasifiers, the exothermic reactions of carbon with oxygen (reactions (1) and (2))are used to supply heat to the endothermic reactions of carbon with steam (reactions (3) and (4)). The exact balancing between the heat released by reactions (1) and (2) and the heat absorbed by reactions (3) and (4) required for adiabatic operation further constrains the possible combination of carbon, oxygen, and steam to lie on the line AB of Figure 2. To the left of the line AB too much heat is generated and to the right too little. Since the product gas of a real gasifier is usually hotter than its feeds, its point usually lies to the left of the line AB.

How the number of moles of steam and oxygen needed to convert one mole of carbon changes as we move along the line AB is shown in Figure 3. The amount of oxygen required decreases somewhat on going from A to B, but the amount of steam required increases sharrly. The ratio of steam to oxygen is a convenient variable in discussing gasifiers. The variation of this ratio along AB is shown in Figure 4. The composition of the product gas also varies as we move along AB. The H<sub>2</sub>/CO ratio varies from 0.45 at point A to  $\infty$  (no CO) at point B as shown in Figure 5.

There is energy consumed in the practical production of the oxygen and steam needed in the carbon conversion process defined by line AB. The loss in thermal efficiency resulting from these energy requirements is shown in Figure 6 as a function of steam to oxygen ratio. In Figure 6, the thermal efficiency loss has been decomposed into the two major parts — one due to the production of oxygen at 400 psia and 700°F and the other due to the production of steam at 400 psia and 700°F. The conclusion is clear — the variation in thermal efficiency in carbon conversion is dominated by the steam requirement with low







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steam to oxygen and low  $H_2/CO$  ratios giving higher thermal efficiencies. This is true in spite of the fact that it takes approximately four times as much energy to produce one mole of oxygen as to produce one mole of steam.

In the above treatment of the stoichiometry of the gasification of carbon, all the reactants are converted to gaseous products. In actual fact, chemical equilibrium does not allow complete conversion of the water in reactions (3) and (4). Excess. steam is required to be present. On the other hand, the heat producing oxidation reactions (1) and (2) allow essentially complete conversion of oxygen; i.e., these reactions can be considered to be irreversible for practical purposes. The amount of excess steam required when equilibrium constraints are introduced into reactions (3) and (4) is given in Figure 7 as a function of the steam to oxygen ratio. The excess steam rises sharply as the steam to oxygen ratio increases. As the steam to oxygen ratio increases, the H2/CO ratio also increases as comparison of Figures 4 and 5 shows. This excess steam has to be generated, passed through the gasifier and as much of its energy recovered from the product stream as possible. The effect of this excess steam on the thermal efficiency is given in Figure 8 where the stoichiometric thermal efficiency curve of Figure 6 is repeated. The introduction of the constraint of chemical equilibrium increases the losses in thermal efficiency at higher steam to oxygen and  $H_2/CO$  ratios and reinforces the conclusion from the stoichiometric consideration that steam requirement is one of the dominant factors in determining gasifier thermal efficiency.

All of the above discussion concerns the gasification of carbon. Coal is much more than carbon and the difference between coal and carbon influences both the basic design principles and the mechanical implementation. The volatiles in the coal can have a strong influence on the thermal efficiency of gasifiers. These volatiles are obtained when coal is subjected to heat in the absence of oxygen. Many gasifiers such as the dry ash Lurgi and the BGC-Lurgi slagger have devolatilization zones while others such as the Texaco entrained bed do not. Little energy is required for devolatilization so that any useful products formed, such as methane, contribute to increasing the thermal efficiency of coal gasifiers. On the other hand, such products as tars can decrease the thermal efficiency by impeding efficient heat recovery.

The thermal efficiencies similar to those of Figure 8 but with the improved thermal efficiency obtained by including the devolatilization of an approximate eastern coal are shown as a function of excess steam in Figure 9. This is the same kind of graph used in Figure 1 for the real gasifiers. The gasifier data of Figure 1 have been repeated in Figure 9. The trend of the real gasifiers to lower efficiencies at higher amounts of excess steam clearly agrees with the trend expected from stoichiometry, heat, and equilibrium considerations for the gasification of carbon.







Excess Steam in Product Gas (Lb/MSCF Syn Gas)



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The direct formation of methane from carbon by the reactions

С	+	$\frac{2}{3}$ H <sub>2</sub> O>	$\frac{1}{3}$ CH <sub>4</sub>	$+\frac{2}{3}$	со	ΔH	H	14.78	kcal/ mole	(5)
С	÷	$H_2O \longrightarrow \frac{1}{2}$	CH4 +	co <sub>2</sub>		ΔH	=	1.46	kcal/ mole	(6)

has been neglected in the above discussion but is discussed in the detailed report. Since less heat is required with methane formation, the efficiencies should be improved because of reduced oxygen requirements. Figure 10 shows that the thermal efficiency is much improved for high steam to oxygen ratios when direct methane formation occurs. On the other hand, the low steam to oxygen and low H2/CO ratio gasifiers are more thermally efficient than the high steam to oxygen ratio gasifiers even with direct methane formation. The direct formation of methane from carbon is favored by low temperature, high pressure operation and does not play a dominant role in operation of most gasifiers.

Many variables other than steam utilization enter into the determination of gasifier thermal efficiency. These are responsible for the departure of the observed points from the theoretical line of Figure 9. The effects of some of these variables can be large. If the gasification process is carried out near atmospheric pressure and 400 psia product gas is needed, the energy loss in compressing the gas to 400 psia is substantial. In Figure 11 data are added to Figure 9 for the low pressure (near atmospheric) Winkler and Koppers-Totzek gasifiers with compression to give 400 psia product gas. A large portion of the thermal efficiency loss for these gasifiers over the gasifiers of Figure 9 is in the compression to 400 psia. Clearly, a gasifier should not be operated at a much lower pressure than the pressure at which the gas is expected to be used.

The operating conditions in many gasifiers are such that the rate of reaction is too slow for chemical equilibrium to be reached in the time that the gases spend in the reaction zone of the gasifier. Such gasifiers are kinetic rather than equilibrium constrained. The amount of steam in the product gas of a kinetic constrained gasifier is greater than that of equilibrium constrained gasifiers and its thermal efficiency will be correspondingly lower. The H<sub>2</sub>/CO ratio will be lower than expected from the steam to oxygen ratio. This effect is illustrated in Figure 12. In this figure, the H<sub>2</sub>/CO ratio as a function of steam to oxygen ratio is plotted for an equilibrium adiabatic gasifier similar to a dry ash Lurgi gasifier. Two points based on design data for dry ash Lurgi gasifiers are shown. The large departure of the observed H<sub>2</sub>/CO ratios for the Lurgi gasifiers from that expected from equilibrium constraints is caused for the most part by the actual gasifier being kinetically constrained.

The relative direction of flow of steam, oxygen and coal in the gasifiers can have substantial impact on the thermal efficiency by influencing both the heat recovery and the devolatilization process. Countercurrent flow of steam and oxygen relative to the flow of coal aids both processes. Countercurrent flows can improve the efficiency substantially. There is, however, a Figure 10



# NET THERMAL EFFICIENCY (ADIABATIC CHAR GASIFIER WITH EQUILIBRIUM CONSTRAINT)

(%) Vet Thermal Efficiency (%)

60

Steam / Oxygen (Molar) 4 2

0

50

00

Figure 11



Steam in Product Gas (Lb/MSCF Syn Gas)

Net Thermal Efficiency (% LHV of Coal)

- 14 -

Figure 12



- 15 -

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penalty for this higher thermal efficiency due to the formation of tar and methane formed by devolatilization of coal. The tar requires separation and recycling. The methane formed increases the thermal efficiency and is a penalty only if we want methane free syngas. For fuel gas the fact that methane formed by devolatilization requires only a small energy input is an important benefit. Syngas processes which can tolerate the presence of metham and co-produce fuel gas or SNG have therefore an important advantage which results from the properties of such gasifiers.

The sources of the losses of thermal efficiency for various gasifiers are shown by the bar graph in Figure 13. Four gasifiers were chosen from those used in preparation of Figure 11. One gasifier, the dry ash Lurgi, has a large amount of excess steam and the other three have low amounts of excess steam. One of the low excess steam gasifiers, the Winkler, is a low pressure gasifier that requires compression work to compress the product gas to 400 psia. The first set of bars of Figure 13 gives the LHV of the products and is positive. The second set gives the useful heat recovery and is positive. The next three are negative and give three sources of loss, steam generation, air separation and compression work. The last set is the net thermal efficiency and is the algebraic sum of the first five sets.

The BGC-Lurgi slagger loses thermal efficiency primarily by having poor heat recovery (second set). This is caused by the presence of tar in the product stream interfering with the heat exchange process. For the dry ash Lurgi gasifier the primary loss is in steam as anticipated by the high excess steam of this gasifier. The Texaco losses thermal efficiency by a high oxygen demand. The Winkler gasifier loses by both a high oxygen demand and compression requirements.

The dominant role of steam in determining the thermal efficiency difference between the BGC-Lurgi slagger and the dry ash Lurgi gasifier is also reflected in determining the investment differential in the two gasifiers. Table 1A gives the breakdown on a relative basis as percentage of the investment of a BGC-Lurgi slagger. The dry ash Lurgi gasifier (western coal) requires 42% more investment than that of a BGC-Lurgi slagger (Frances coal). The sources of investment differences associated with the steam requirements are indicated by asterisk. These total 28% and contribute more than half of the investment differences between the two gasifiers.

The bar graph in Figure 13 shows that the high oxygen demand is the largest contribution to the thermal efficiency loss in a Texaco gasifier. This high oxygen demand, however, also means a very hot gasifier effluent gas from thich a substantial fraction of the sensible heat can be recovered as shown in the second set of bars in Figure 13. The waste heat boilers required to recover this heat are expensive as shown in Table 1B. In the Texaco gasifier, this sensible heat can supply most of the energy requirement for air separation, whereas in a BGC-Lurgi figure 13

NET THERMAL EFFICIENCY BREAKDOWN BASED ON NET COAL LHV



% LHV of Coal

- 17 -

#### TABLE 1A

Source of Investment Differential of Dry Ash Lurgi Gasifier (Western Coal) Over BGC-Lurgi Slagger (Frances Coal) as Percentage of Investment of Slagger

+ Increase Over Slagger Investment

Decrease From Slagger Investment

	Investment Differential (% Slagger's Investment)
Gasifier, including Coal Feed and Ash Removal	+13
Gas Cocling and Waste Heat Boiler	+ 7*
Gas Liquor Treatment	+ 6*
Oxygen Plant	- 4
Steam Boiler + Superheater (including BFW Preparation)	+15*
Others	+ 5
Total Investment	+42

#### TABLE 1B

Source of Investment Differential of Dry Ash Lurgi Gasifier (Eastern Coal) and Texaco Gasifier (Eastern Coal) Over BGC-Lurgi Slagger (Frances Coal) as Percentage of Investment of Slagger

> + Increase Over Slagger Investment - Decrease From Slagger Investment

	Dry Ash Lurgi Eastern Coal	Texaco .5 Water/Dry Coal Eastern Coal
Gasifier, including Coal		· _
Feed and Ash Removal	+ 16	- 6
Gas Cooling and Waste Heat Boiler	+ 12	+ 28
Gas Liquor Treatment	+ 10	~ 4
Oxygen Plant	÷ 4	+ 23
Steam Boiler +		
Superheater (including BFW Preparation;	+ 27	- 13
Others	+ 10	÷_ <u>6</u>
Total Investment	+ 79	+ 34
	- 18 -	

slagger this energy has to be supplied by either burning part of the product gas or coal. In a syngas process a significant part of this energy can be supplied by the steam produced in the syngas conversion process itself making the BGC-Lurgi slagger a particular efficient gasifier to be used in combination with such a conversion process.

Table 1B shows that the sources of the thermal efficiency losses for the Texaco gasifier relative to the BGC-Lurgi slagger is reflected themselves on the sources of investment differentials. The high oxygen demand is reflected in the high oxygen plant relative investment cost and the need to recover heat from the hot gasifier effluent gas is reflected in the large relative investment cost for the waste heat boilers. On the other hand, since no steam boiler is required a relative investment credit is given. Also included in Table 1B is the relative investment differential for a dry ash Lurgi gasifier with an eastern coal which shows the large impact of the high steam requirement to the gasifier caused by the low reactivity of the eastern coals.

In the following report the above conclusions are derived in detail. The report is divided into two main parts. In the first part (Section III-XIII, pages 20-101), the design criteria for gasifiers are examined by first introducing the stoichiometric constraints (Section III to V), then the equilibrium and kinetic constraints (Section VI) and finally by quantifying the design variables on the performance of the gasifiers (Section VII to XIII). In the second part (Section XIV, pages 102-139), the performances of the real gasifiers are compared to the predictions obtained in the first part. The impact of this comparison on the investment requirement is developed on a differential basis. Although the last part is based on the first part, the technical overview should provide sufficient background for those readers who wish to proceed directly to the consideration of the real gasifiers which begins on page 102.

#### III. Stoichiometric and Thermodynamic Constraints

Since the cost of coal conversion is strongly related to the overall thermal efficiency of the process used (see Reference 1), it is essential to understand how various constraints affect the thermal efficiency. The first constraints to be discussed are those arising from the stoichiometry of the coal gasification reactions, from the heat requirements of the reactions, and from the energy requirements to prepare the oxygen and steam used in the stoichiometric reactions. It is useful to divide the coal conversion reactions into two classes: devolatilization and gasification. These two kinds of reactions usually occur in different parts of a gasifier and can be treated separately for many kinds of gasifiers and for many purposes.

A. Devolatilization

#### Coal -> Char + Volatiles (7)

Volatiles include methane, tars, phenols, oils, naphtha, hydrogen sulfide, and ammonia as well as some CO and H<sub>2</sub>. Not enough is known about how the composition of the devolatilized product depends on reaction conditions (2,3). This is a desirable area or further studies. About 30-40% (wt) of the coal is volatile and the proper use of this fraction is very important in obtaining high thermal efficiencies in gasifiers. Devolatilization itself requires little heat other than that required to raise the coal to devolatilization temperatures. Under conditions of tar formation, approximately 10% of the heat content of the coal is in the tar and naphtha fraction and about 20-30% is in the methane, H<sub>2</sub>, and CO fraction.

The handling of the tars can be troublesome but there are conditions under which they are not formed. It has been shown that if coal is introduced rapidly into a hot fluid bed (1400°F) no tar is produced during devolatilization (4,5). In a high temperature gasifier (~2000°F) only  $H_2$  and CO are formed. These shifts in products have important effects on the thermal efficiency of the process.

#### B. Gasification Reactions

The char formed in the devolatilization process contains ash, sulfur, oxygen, and a small amount of hydrogen. These will be neglected in this section and the char formed from the devolatilization process will be considered to be pure carbon. There are many ways to write the various reactions that occur in gasification, but because of the constraints imposed by the conservation of mass, there will be only four independent reactions when the products are CO,  $H_2$ , CO<sub>2</sub> and methane and only three when no methane is produced directly from the char. A useful set of gasification reactions for the char is given by (Ref. 2):

- 20 -

Combustion

 $C + \frac{1}{2} O_2 \longrightarrow CO$  -26.36 (1)

$$c + o_2 \longrightarrow co_2 -94.14$$
 (2)

Gasification

 $C + H_2 O \longrightarrow CO + H_2$  32.23 (3)

$$C \div 2H_2O \longrightarrow CO_2 \div 2H_2$$
 23.04 (4)

$$C + CO_2 \longrightarrow 2CO$$
 41.42 (8)

Shift

 $CO + H_{2}O \longrightarrow CO_{2} + H_{2} -9.19$  (9)

Methanation

$$C + \frac{2}{3} H_2 O \longrightarrow \frac{1}{3} C H_4 + \frac{2}{3} C O \qquad 14.78 \qquad (5)$$

$$C + H_2 Q \longrightarrow \frac{1}{2} CH_4 + \frac{1}{2} CO_2 \qquad 1.46 \qquad (6)$$

where the value following each reaction is the value of the heat of reaction (  $\Delta H$  kcal/mole at 700°F).

Consider a gasifier for char in which the inlet and outlet streams are at the same temperature — 700°F will be used in the discussion in this section. If the gasifier is operated such that the reactions taking place satisfy the condition  $\Sigma X_i \ \Delta E_i = 0$ , the thermal efficiency will be 100% based on lower heating value at 700°F. To satisfy this condition, the combustion reactions (1) and (2) are coupled to the gasification, shift and methanation reactions to supply heat to these reactions. In the equation  $\Sigma X_i \ \Delta H_i = 0$ ,  $X_i$  is the fractional amount of carbon converted to products by the ith reaction and  $\Delta H_i$  is the heat of the reactions for the ith reaction. The condition  $\Sigma X_i = 1$  is satisfied by the  $X_i$ 's. There are an infinite number of combinations of the reactions that satisfy  $\Sigma X_i \ \Delta H_i = 0$ . In discussing these combinations, the reactions will be separated at first into two classes; one that considers combinations that produce only CO, CO<sub>2</sub> and H<sub>2</sub> with no methane and the other that produce only CO, CO<sub>2</sub> and methane with no H<sub>2</sub>. The results obtained from the discussion of the two classes of reactions will then be combined to obtain an overall picture of the effects of stoichiometric and  $\Sigma X_i \ \Delta H_i = 0$  constraints on the entire set of reactions.

Figure 14 is a triangular stoichiometric diagram of the three reactants, carbon, water and oxygen. On this diagram, a trapezium area has been defined which gives the possible stoichiometric fractional amounts of carbon, oxygen and water converted to CO, CO<sub>2</sub> and H<sub>2</sub>. Chemical equilibrium is not considered here. Reactions (1). (2). and (3) have been chosen as the three independent reactions with (4), which is a linear combination of (1), (2), and (3) [(2) + 2(3) - 2 (1)]. defining the lower

- 21 -


righthand corner of the trapezium. The two areas labeled excess carbon and excess steam and oxygen are not accessible due to the stoichiometric constraint.

When the constraint  $\Sigma X_i \Delta H_i = 0$  is added, the possible stoichiometrics will lie along the line connecting pointsA and B of Figure 14. To the left of this line too much heat is produced to satisfy the required  $\Sigma X_i \Delta H_i = 0$  and to the right too little. (In actual practice the outlet stream is usually hotter than the inlet and the operation will be to the left of line AB.) The heat constraint reduces the number of independent reactions to two. The overall reactions defined by points A and B will be chosen to be these two reactions. All the stoichiometric along the line AB will be linear combinations of the two reactions subject to the condition  $\Sigma X_i = 1$ . The two reactions defining points A and B are:

 $C + 0.275 O_2 + 0.45 H_2 O \longrightarrow CO + 0.45 H_2$ 

 $C + 0.195 O_2 + 1.61 H_2O \longrightarrow CO_2 + 1.61 H_2,$ 

respectively. The first equation is obtained from combining reactions (1) and (3) in the proportions,

 $C + \frac{1}{2} O_2 \longrightarrow CO$ 

 $0.82 \text{ C} + 0.82 \text{ H}_{20} \longrightarrow 0.82 \text{ CO} + 0.82 \text{ H}_{2}$ 

and the second is obtained from combining reactions (2) and (4) in the proportions,

 $C + O_2 \longrightarrow CO_2$ 4.09 C + 8.17 H<sub>2</sub>O  $\longrightarrow$  4.09 CO<sub>2</sub> + 8.17 H<sub>2</sub>

All of the stoichiometric lying along the line connecting points A and B have a thermal efficiency of 100% based on lower heating value at 700°F with respect to the reactions, but the energy needed to prepare and heat the steam and oxygen has been neglected. This will be taken into account now. Let the pressure be 400 psia and the inlet (and outlet) temperature be 700°F. Point A requires 0.28 moles of oxygen and 0.45 moles of steam to give a steam-to-oxygen ratio of 1.6. On the other hand, point B requires 0.2 moles of oxygen and 1.61 moles of steam to give a steam-to-oxygen ratio of 8. One mole of oxygen at 400 psia and 700°F requires the same amount of energy to produce as 4.1 moles of steam (Appendix A). Thus, the saving of 0.08 moles of oxygen for point B compared to point A is equal to 0.33 moles of steam so that, to balance, 0.78 moles of steam could have been used at point B. However, 1.61 moles of steam was required for point B which represents a net energy loss of 0.83 moles of steam. This represents a 9% loss in thermal efficiency compared to point A. The energy needed to prepare the oxygen and steam in these two cases drops the thermal efficiency from 100% to 81% for point A and 72% for point B.

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The composition of the product varies greatly along the line AB of Figure 14. The composition triangular diagram for the product is shown in Figure 15. The product changes from all CO and H<sub>2</sub> with a ratio of H<sub>2</sub>/CO of 0.45 at point E to a product that is all CO<sub>2</sub> and H<sub>2</sub> with a H<sub>2</sub>/CO ratio of infinity at point F. The equation for this product variation along the line EF is given by  $H_2/CO = 0.45 + 1.61 CO_2/CO$ . These compositional variations enter strongly in influencing the choice of process to be used.

It was shown in Reference 1 that, if the product of a liquid fuel plant has a carbon-hydrogen ratio characteristic of CH<sub>2</sub>, a syngas process that makes use of internal shift reaction could use a feed with a  $H_2/CO$  ratio as low as 0.5. This is close to point A, which has a ratio of 0.45. If a higher ratio is desired, a gasifier that combines point A and point B (as most gasifiers do) is needed or else external shift can be relied upon.

One advantage of point A is that the gas is free of CO<sub>2</sub> (or in reality with little  $CO_2$ ). This absence of CO<sub>2</sub> (or very low CO<sub>2</sub> content) makes it cheaper and easier to remove H<sub>2</sub>S since the Claus process can be used instead of the Stretford process. This advantage holds for both fuel gas and syngas production.

Point A also gives a smaller investment. The investment savings for the smaller oxygen plant for point B is more than offset by the investment required for the larger steam plant. The total investment required per mole of oxygen is about equal to that required to produce five to six moles of steam (see Table 2). The present cost ratio of oxygen and steam is approximately 5. At \$25 a ton for oxygen, 1000 scf costs\$1.05 while at \$8.50 a ton for steam, 1000 scf costs20 cents. The ratio of additional moles of steam required to moles of oxygen saved for point B over point A is 16.5. In this report, the basis is Gulf Coast cost (1977) which fits the DOE Guidelines(8).

Let us now turn to the case that produces only methane, CO and CO<sub>2</sub>. The cases that produce only CO, CO<sub>2</sub> and H<sub>2</sub> are approximately realizable in practice whereas the cases that produce no H<sub>2</sub> are limiting cases since a substantial production of H<sub>2</sub> always occurs. The triangular diagram of Figure 16 shows the stoichiometric's accessible area for this set of reactions. The reactions at the four corners of the trapezium are given by reactions (1), (2), (5), and (6). Again only three of these reactions are independent. The heat balance condition  $\Sigma X_1 \ AH_1 = 0$  reduces these to two independent reactions and all stoichiometrics will lie on a line with ends defined by points c and D. The reactions defining these two points are:

<u>Point C</u> a)  $C + O_2 \longrightarrow CO_2$ 

b) 64.53 C + 64.53 H<sub>2</sub>O ---> 32.26 CH<sub>4</sub> + 32.26 CO<sub>2</sub> which combine to give,

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### TABLE 2

Investment Requirements - Oxygen Versus Steam

Basis: Dollars per mscfd oxygen or steam at 400 psia and 700°F

Boiler <sup>(a)</sup> Oxygen Plant	<u>Oxygen</u> 300 1360 700 1500	<u>Steam</u> 140 [170]
Total (no contingency or interest during construction) Investment Ratio (Oxygen to Steam)	1000 860} 6.25 {5.4}	140 {170}

The numbers without parentheses are taken from ref.(6) whereas the numbers in { } are from ref. (7).

a) Boiler is assumed to be standard tar boiler equipped with scrubber. In case fuel gas is used the investment is reduced by a factor of four which is compensated for by the incremental investment for fuel gas.



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 $C + .015 O_2 + .985 H_2O \longrightarrow .4925 CH_4 + 0.5075 CO_2$ <u>Point D</u> a}  $C + 0.5 O_2 \longrightarrow CO$ 

b) 1.78 C + 1.19 H<sub>2</sub>O  $\longrightarrow$  1.19 CO + 0.59 CH<sub>4</sub> which combine to give,

 $C + .180 O_2 + .428 H_2O \longrightarrow .213 CH_4 + .788 CO$ 

The compositional diagram for the products is given in Figure 17. The product compositions are given by the equation  $CH_4 = 0.272 CO + 0.970 CO_2$ . The thermal efficiencies when steam and oxygen preparation is taken into account are 87% for point C and 86% for point D. Both points C and D give a substantial higher thermal efficiency value than those of points A and B. However, there are severe equilibrium and kinetic constraints on points C and D.

The results of Figures 14 and 16 are combined into the triangular diagram shown in Figure 18. When all four products are possible, the permissible reactions consistent with the constraint  $\Sigma X_i \Delta H_i = 0$  will lie within the trapezium ABCD. The product composition corresponding to the reactant region ABCD is shown on the tetrahedral diagram of Figure 19. A tetrahedron is needed since there are four products. The possible heat balancedproduct compositions are confined to the trapezium EFHG of Figure 19. The results for the four corner points are summarized in Table 3.

The idealized stoichiometric char gasifier that has been discussed provides important background information that can be used to help understand real gasifiers. The oxygen and steam that <u>disappear to convert coal</u> to products must satisfy the stoichiometric constraints to lie within the appropriate regions of Figures 14, 16 and 18. This is true regardless of equilibrium and kinetic constraints that will be discussed later. These equilibrium and kinetic constraints tell us how much excess steam is needed to drive the reaction and have an important bearing on the thermal efficiency. Usually oxygen is essentially completely consumed since reactions (1) and (2) are for all practical purposes irreversible and proceed at a more rapid rate than the other reactions.

Because of the differences in the energy requirements in preparing steam and oxygen, the relative amount of these reactants required has an important bearing on the thermal efficiency of the processes as shown earlier in this section. Figure 20a shows the thermal efficiency as a function of the steam-to-oxygen ratio for the idealized stoichiometric char gasifier with no methane formation. Note that the highest thermal efficiency occurs at the lowest steam-to-oxygen ratio that satisfies the stoichiometric and  $\Sigma X_i \land H_i = 0$  constraints--namely at point A. This is also the point with the lowest H2/CO ratio --- namely 0.45. The dashed curve in Figure 20a





- 30 -

## Figure 19

# PRODUCT STOICHIOMETRIC AND ENERGY CONSTRAINTS ON GASIFICATION REACTIONS



Table 3 .

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		Point A	Point B	Point C	Point D
	Overall Reaction	$C + 0.275 0_2 + 0.45 H_2^{0} + C^{0} + 0.45 H_2^{0}$	C + 0.195 0 <sub>2</sub> + 1.61 H <sub>2</sub> 0 + CO <sub>2</sub> + 1.61 H <sub>2</sub>	$C + 0.015 O_2 + 0.985 H_2O + 0.4925CH_4 + 0.5075 CO_2$	C + 0.18 0 <sub>2</sub> + 0.428H <sub>2</sub> O+ 0.21 <sup>3</sup> CH <sub>4</sub> + 0.788CO
	Bteam to Oxygen Ratio	1.6	8.2	64.5	2.4
	Steam Regulrements, lbs per HMBTV (LHV) Gas	47.8	170.9	104.7	45.4
- 32	Şteam - MBTU per 1b mole of Carbon	9.2	32.7	20.0	6.7
-	Okygen Requirements, acf per MHBTU Gae (sof/mscf)	(190)	411 (124)	35 (10)	405 (126)
-	Oxygen, HBTU/1b mole of Carbon	23.0	14.9	1.3	15.0
-	Thermal Effloiency, .	10	72	87	B6

Couditions: Feed and outlet temperature, 700°F. No heat recovery from products below 700°F. BIV requiremente of feeds; 220 BTV/scf oxygen 1130, BTV/1b steam; both at 700°F and 400 peia.

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divides the region of loss in thermal efficiency into two areas representing the loss due to steam preparations and the loss due to oxygen preparations. Figure 20b shows that the thermal efficiencies used here differ only negligibly from the net thermal efficiency defined in Appendix A.

Let us compare the differences of this idealized stoichiometric char gasifier with no methane formation with a real gasifier where methane comes for the most part from devolatilization. This comparison is made in Table 4; the second column gives the actual performance of a BGC-Lurgi slagging gasifier demonstration plant. Problems arise in comparing the results from real gasifiers with the idealized char gasifiers of Table 3 because the feed to the idealized char gasifier is char while coal is fed to the real gasifier. The volatiles in the coal improve the thermal efficiency of a real gasifier over what it would be if char were used. The last column gives the computed performance of the gasifier when the effect of the volatiles is removed so as to simulate a char BGC-Lurgi slagger. The char BGC-Lurgi slagger has a thermal efficiency of 78% compared to 81% for point A. The char slagger is very close in product composition to point A. Its  $H_2/CO$  ratio is about 0.5 as compared to 0.45 for point A. Note that the char slagger makes good use of its steam but requires more oxygen than point A.

Let us look at some of the causes for this kind of additional loss in thermal efficiency in gasifiers. Two of the major causes are the incomplete conversion of steam due to equilibrium and kinetic constraints and the loss of heat in the outlet stream caused by the outlet temperature being higher than the average inlet temperature especially since coal is fed cold. The extra heat for this difference in temperature is supplied by combustion of additional coal inside the gasifier. This shifts the stoichiometric to the left of the line AB and CD of Figure 14 and 16, respectively. It is true that part of this heat can be recovered and used to generate steam but this process is less efficient than the generation of steam in a separate high efficiency boiler. The generation of steam in a gasifier is equivalent to using oxygen instead of air to combust coal and is more expensive and less thermally efficient.

The role of equilibrium and kinetic constraints in decreasing the thermal efficiency will be examined further after a discussion of the possible role of indirect heating of the gasifier, and a discussion of some problems in computing the thermal efficiencies of real gasifiers.



Figure 20a

Thermal Efficiency (%)

- 34 -





- 35 --

### Table 4

# Comparison of Point A with Data from a BGC-Lurgi Slagger <sup>(9)</sup>

	Point A (Char)	BGC-Lurgi Slagger (Coal)	Char Gasification in BGC-Lurgi Slagger (Corrected for Volatiles <sup>a</sup> )
Steam/Oxygen	1.6	I.33	1.33
<b>scf Oxy</b> gen/MMBTU Gas (LHV)	119	555	768
lb Steam/MMBTU Gas (LHV)	47.8	35.0	48.4
Thermal Efficiency, % (same conditions as Table 3)	18	84	78

The difference between the BGC-Lurgi slaqger thermal efficiency and this column is due to the volatiles which are assumed to be volatilized with no consumption of steam and oxygen. a)

### IV. Indirect Heating of the Gasifiers

If heat can be supplied to a gasifier from some indirect source, then the reactions need not satisfy  $\Sigma X_i \Delta H_i = 0$  and the process can rely entirely on the reactions such as the gasification reaction (3). If indirect heating could be used with reaction (3), the lower heating value at 700°F of the product would rise 34% above that of the coal used.

Electrical heating has been proposed for such a process. At the present price of electricity, direct electric heating is not viable. At present, the cost of 1 million Btu of electricity is about \$9.00. If coal is burned for heat, with oxygen internally, the cost of the heat is calculated as follows: 1 million Btu of coal costs \$1.00 and the oxygen that is needed to combust the coal is \$2.40 (\$25 a ton) to give \$3.40 per million Btu of heat. Of course, when heating electrically, the product would contain less CO<sub>2</sub> but this gives a saving of only 5 to 6 cents per million Btu (utility financing) for syngas and for fuel gas even less. There is one use of electricity that may be competitive today for a fuel gas plant. If the plant is not energy selfsufficient in power generation by process heat and a power plant or boiler is needed for the oxygen plant and for compression of gases, then electricity from a nuclear reactor may be competitive for these purposes.

Indirect heating by heat from a nuclear reactor has also been proposed. There is no reliable process information for this application, and it is a more complex question than originally thought. A secondary heat exchanger cycle would probably be needed between the primary exchange loop inside the reactor and the gasifier to minimize the escape of tritium. Optimistically, the cost of heat from a <u>high temperature</u> nuclear reactor would be about \$4.00 per million Btu and the equipment would be complex, which does not make it attractive at the present time.

### V. Computation of Thermal Efficiency

There are two kinds of thermal efficiencies that will be used: cold gas efficiency and net efficiency. The cold gas thermal efficiency is defined as the ratio of the low heating value of clean fuel gas produced to the low heating value of the net coal or char fed to the gasifier, where net coal LHV  $\equiv$  LHV coal - LHV (char + tar + phenol). The net thermal efficiency is obtained by making an energy balance around the entire gasification plant and is aimed to reflect the net energy recovered by including the energy used in the oxygen and steam preparation and other important energy consumptions and recoveries. The definition of a net thermal efficiency is, of course, by no means unique. The one that reflects a very realistic way and that will be used in this study is defined in Appendix A in which guidelines are given for computation. In order to avoid the construction of a complete flow diagram for each process, this net thermal efficiency is computed in a simplified way that is explained in Appendix A.

In computing net thermal efficiencies, the definition of "usable" products has to be decided and a decision has to be made as to the method to be used to account for the energy content of those products that do not fall into the "usable" category.

The fines and chars produced by some gasifiers can fall into this latter category. It is not clear whether these fines and chars can be sold or shipped but if a gasifier is in a region where electricity is needed, they will probably be burned in a power plant. They are, therefore, at best, not different from coal and cannot be counted as products. In some studies these fines and chars are counted as "usable" products which give an artificially high thermal efficiency to the gasification plant. On the other hand, not counting them gives an artificially low value to the thermal efficiency. The best procedure, and the one used in this study, is to subtract their heating value from the heating value of the input coal.

Another similar problem is how to account for the energy content of the tars. The light oils and other light hydrocarbons will be classified as "usable" clean fuel. There is doubt as to whether tar should be counted as a "usable" clean fuel. In a very large plant, upgrading of this tar to "usable" clean fuel might be justified. The proper handling of this tar is a problem that merits serious attention and research. In this study tar will not be considered as a usable clean fuel and its heating value will be subtracted from the input.

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### VI. Effect of Equilibrium and Kinetic Constraints on Steam Requirements of Gasifiers

As pointed out in the discussions of the idealized stoichiometric char gasifier, an actual gasifier requires an excess of steam over the stoichiometric amount that is converted to products to drive the reaction to equilibrium or to increase the rate of reaction. This excess steam exits from the outlet of the gasifier. Although energy can be recovered from this exit steam, there is a substantial energy degradation. A simplified gasifier will be used to show the magnitude of the amount of excess steam required. This simplification will also be used in the next section to show how equilibrium and kinetic constraints affect various other variables. Such a simplification illustrates many of the main features of all real non-catalytic gasifiers.

Consider a gasifier in which part of the coal (approximately 25% by LHV) is devolatilized on entering the gasifier and leaves the gasifier at outlet conditions. The coal will contain 10% ash and enter the gasifier at ambient temperature. Its oxygen content will be neglected in calculation but will be discussed as a perturbation. Two different moisture contents will be used: 10% and 30%. 10% moisture is more characteristic of eastern and 30% of western coals. The methane formed during devolatilization is not considered to be present in the char gasification zone. The steam and oxygen enter the gasifier at 700°F and the reactor pressure is 400 psia.

The char formed in the devolatilization zone is reacted with steam and oxygen in a gasification reaction zone. The combustion reaction goes to completion. Two general cases will be considered for the carbon-steam reaction (3). In Case X, this reaction will go to equilibrium and in Case Y it will be limited by kinetic constraints. To get the effect of incomplete carbonsteam reaction, the reaction is assumed to reach a steady state given by pseudo-equilibrium conditions in which the pseudoequilibrium constant is a fraction of the actual equilibrium constant. This fraction will be 0.1 for Case Y.

No exit steam existed in the outlet stream of the idealized stoichiometric char gasifier described previously. Equilibrium and kinetic constraints cause a considerable amount of steam to appear in the exit stream as shown in Figure 21. This figure gives the ratio of exit steam to steam converted to products as a function of steam-to-oxygen ratio. Those of the approximate eastern coal are given by the heavy solid and dashed lines and those of the approximate western coal by light solid and dashed lines. The equilibrium constrained cases are given by the solid lines and the kinetic constrained cases for the steam-carbon reaction by the dashed lines. Clearly a considerable amount of excess steam is required and this amount increases greatly as the steam-to-oxygen ratio rises. This means that the energy losses by excess steam increase as the steam-to-oxygen ratio rises and the thermal efficiencies are decreased. Figure 22 shows the ratio of exit steam to

Figure 21





Steam / Oxygen (Molar)

- 40 -

Figure 22





converted steam as a function of  $H_2/CO$  ratio. The introduction of equilibrium and kinetic constraints has not altered the conclusion obtained from the idealized stoichiometric char gasifier that the most thermally efficient operation is at low steam-to-oxygen and  $H_2/CO$  ratios. In fact, the introduction of these constraints increases the differences in thermal efficiency seen frompoint A to point B.

### VII. Effect of Steam-to-Oxygen Ratio on the Performance of the Simplified Gasifier

The simplified gasifier with the equilibrium and kinetic constraints as in the preceding section will be used now to explore the effect of steam-to-oxygen ratio on the following variables:

- a) Gasifier temperature
- b) Cold gas thermal efficiency
- c) Net thermal efficiency
- d) lb steam/mscf syngas
  (l scf methane counted as 3.scf syngas)
- e; scf cxygen/mscf syngas
- f) scf syngas per 1b of dry ash-free coal
- g) H<sub>2</sub>/CO ratio
- h) CO2 concentration

Figures 23a-h provide graphs of the values of these variables as a function of steam-to-oxygen ratio.

The adiabatic temperature of the reaction zone is a monotonously decreasing function of the steam-to-oxygen ratio (Figure 23a). The best cold gas and net thermal efficiencies occur at low steam to oxygen ratios as Figures 23b and 23c show. The results presented in these figures clearly illustrate the advantage in thermal efficiency that can be achieved by operating at low steam to oxygen ratio. It will be shown later that including methanation in the reaction scheme will not alter the basic form of Figures 23b and 23c and will not alter this conclusion. Gasifier design and coal properties can change these thermal efficiencies but they will always have their best values in the region of low steam to oxygen ratios.

Steam consumption increases monotonically as steam to oxygen ratio increases; on the other hand, oxygen consumption has an almost flat curve. The least value of the oxygen required is larger than the value for point B, Table 3, and is at a lower ratio of steam to oxygen. Thus, operating close to point B increases the steam requirements without savings in oxygen consumption.

The amount of gas produced per 1b of dry ash-free coal is shown in Figure 23f. For the equilibrium case, the amount of gas produced increases with steam-to-oxygen ratio. Furthermore, above a ratio of 1, the increase is very small (less than 2%). On the other hand, for the kinetic constrained case a maximum is obtained at a ratio in the range 2 to 3. Thus, the increase in gas production will not be significant enough to offset the net Figure 23a





(3°) enuterequer reilized

- 44 -

Figure 23b

COLD GAS THERMAL EFFICIENCY (SIMPLIFIED GASIFIER)



Figure 23c





Steam / Oxygen (Molar)

(%) Vet Thermal Efficiency (%)

- 46 -

Figure 23d

# STEAM FEED (SIMPLIFIED GASIFIER)









Figure 23f





SCF Syn Gas/Lb DAF Coal

Figure 23g

H<sub>2</sub>/CO RATIO (SIMPLIFIED GASIFIER)



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CARBON DIOXIDE YIELD (SIMPLIFIED GASIFIER)

Flgure 23h

thermal efficiency loss to justify higher steam-to-oxygen ratios.

The H<sub>2</sub>/CO ratio increases monotonically with steam to oxygen ratio (Figure 23g). If a low steam to oxygen ratio is used to obtain higher thermal efficiencies, then the H<sub>2</sub>/CO ratio must be low. This does not make much difference for fuel gas but does require a syngas conversion process for making liquid fuel to be able to utilize this gas directly in order to benefit from the higher thermal efficiency of the gasifier(1). Low H<sub>2</sub>/CO ratio syngas conversion processes were discussed in Reference 1 and will be discussed again later in this study.

The production of  $CO_2$  is given in Figure 23h. Low  $CO_2$  production occurs at low steam-to-oxygen ratios. As pointed out earlier, low  $CO_2$  content in the gas has an advantage since, for low  $CO_2$  contents, cheaper H<sub>2</sub>S removal processes can be used. More complete data on this example can be found in Appendix B.

The curves for both 10% and 30% moisture content coals have been given. The additional moisture in the 30% moisture content characteristic of western coals has a penalty in that it increases oxygen consumption and reduces both the cold gas and net thermal efficiencies. This extra moisture is equivalent to adding cold water instead of steam to the gasifier.

For gasifiers that are coupled to syngas conversion processes, there is an advantage to raising cold gas thermal efficiency relative to net thermal efficiency. Syngas conversion processes generate steam that can be used to satisfy the steam requirements of the gasifier and to prepare the oxygen; thereby, obtaining a gain in overall thermal efficiency. For fuel gas production this effect is less useful in that it only shifts heat production from an oxygen combustion process to an air combustion process in an external boiler.

To summarize, high steam-to-oxygen ratios give decreased net thermal efficiencies without compensation in cold gas thermal efficiency, increased gas production or reduced oxygen consumption. The CO<sub>2</sub> production is also high. The only positive benefit shown in this example is the increased  $H_2/CO$ ratio required for some syngas conversion processes. These results again point to gasifiers with low steam-to-oxygen ratios as the direction to look for cheaper second generation gasifiers for fuel gas and syngas production.

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### VIII. Methane Formation

The data in Figures 16, 17, 18, and 19 were used to show ways in which the stoichiometry of the gasification reactions, and the heat requirements for the reactions influenced the thermal efficiencies of and the products produced from the methane forming reactions. Let us now consider how the equilibrium constraints influence the thermal efficiencies and other properties of the gasifier with methane formation.

It is instructive to examine equilibrium constraints using an idealized char gasifier in which the heat is supplied indirectly so that only steam and char are fed to the reactor. This eliminates the oxygen feed required for adiabatic operation and by excluding the combustion reactions (1) and (2), only three independent reactions need be considered. Figure 24a gives the ratio of exit steam to converted steam as a function of temperature for three different pressures (100, 400 and 1000 psia) when the methane formation (reactions (5) and (6)) is present (Case Z). The corresponding data at 400 psia when no methane formation occurs (Case X) is given for comparison. The ratio of the total steam required to the carbon converted and the ratio of the amount of methane formed to carbon converted are given in Figures 24b and c respectively. A comparison of the data in these figures shows that:

- a) the presence of the methane formation reactions decreases both the excess steam and total steam required at a given temperature over that required when the methane formation reactions are absent.
- b) increasing pressure increases the steam required for Case Z.
- c) methane formation is favored at low temperatures and high pressures.

A catalyst is required to obtain substantial methane formation since low temperatures are required. At these low temperatures, the rates of the reaction are too low to be practical otherwise. When no catalyst is present and higher temperatures (for example 1800°F) are needed, the difference in steam requirements between Case X and Case Z is small, however, little methane is formed unless the pressure is high. This increased pressure is expensive.

The results in Figures 24b and c show that if the operation is in the region of good methane formation, say at 1400°F and 1000 psia (methane to carbon conversion ratio ~0.35) the steam requirement is considerably greater than that for an operation at 400 psia and 1800°F with no methane formation. Thus, unless there are good reasons such as improved thermal efficiencies and reduced costs, there is no driving force to go to the catalytic, low-temperature, high-pressure operation to produce methane for fuel gas production. Figure 24a





Equilibrium Temperature (°F)

H20 in Product Gas/H20 Converted

- 54 -







Equilibrium Temperature (°F)

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Methane Yield (Lb-Mole/Lb-Mole C Gasified)

Equilibrium Temperature (°F)

A simplified (perfectly mixed, adiabatic) gasifier with oxygen present will be used to examine the thermal efficiencies and other properties of the gasifier with methane formation. All gasification reactions are at equilibrium and the inlet streams are introduced at 700°F and 400 psia except the char which is at ambient temperature. Figure 25a shows that, when the combustion reactions are included and the heat balance constraint is introduced, the presence of the methane formation reactions still decreases the excess steam requirements at any particular temperature over that required when no methane formation occurs. Figure 25b gives the reactor temperature as a function of the steam to oxygen ratio and Figures 25c and d give the cold gas and net thermal efficiencies, respectively. These figures give results at 400 and 1000 psia pressures and show that the presence of the methane formation reactions increases both thermal efficiencies over those obtained when methane formation is absent. Figure 25e gives the methane formation as a function of steam to oxygen ratio. At a steam to oxygen ratio of 8 the reactor temperature is ~1400°F for 1000 psia operation with methane. The net and cold gas thermal efficiencies are 75% and 91% respectively. On the otherhand, for operation at a steam to oxygen ratio of 1.2, a temperature of 1800°F and a pressure of 400 psia with no methane, the net and cold gas thermal efficiencies are 78 and 91%, respectively. With methane formation under these same conditions, the net and cold gas thermal efficiencies are approximately the same since very little methane is formed. Therefore, the conclusion is that there is no advantage in fuel and syngas production to go to the low temperature, high pressure conditions that favor methane formation. Conditions that favor methane formation limit steam conversion and increase excess steam requirements. Any methane that is formed is neither detrimental nor beneficial for fuel gas, but it is not desirable for syngas. While methanation itself always leads to a better thermal efficiency because of reduced oxygen requirement this effect is negligible in the operating region which is desirable for high thermal efficiency fuel gas production. Reforming of the methane in syngas production leads to decreased chermal efficiency as will be shown later. Operation at low steam to oxygen ratio is again indicated, accepting whatever methane that is formed under these conditions. It is the methane produced by devolatilization that is most beneficial since it is produced with little or no thermal penalty.

The lack of a strong incentive to use a catalytic gasifier is limited to fuel gas and syngas production. This study does not include substitute matural gas (SNG) production. For SNG production, whether the methane formation has an advantage requires a detailed evaluation of such gasifiers and is outside the scope of this study.

Exactly how much of the methane observed in a real gasifier is due to direct methane formation is not known for certain. The picture is complicated by the fact that the devolatilized products themselves depend upon process conditions and gas composition in many unknown ways.




Gaslfier Temperature (°F)

Figure 25b



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## Figure 25d





(%) yonsiditi lemnant fu

Figure 25e



Steam / Oxygen (Molar)

Table 5 gives the methane production of various gasifiers arranged in order of steam to oxygen ratio. The gasifier pressure is also given. The methane production varies less than what might be expected from the wide range of steam to oxygen ratios and pressures of these gasifiers. The IGT-Hygas pilot plant, which operates at 1000 psia, does not give a much higher methane production than the Lurgi dry ash gasifier, which operates at 400 psia. This is particularly true if the use of the toluene slurry is taken into account. If part of toluene enters the gasification zone, it will be cracked to produce extra methane. Computer estimates for Hygas and Synthane gasifiers predict higher values for methane production but this has not been demonstrated in the pilot plants to date.

A comparison of the dry ash Lurgi gasifier and the BGC-Lurgi slagger shows an increased methane production for the dry ash Lurgi. How much of this is due to direct methane formation and how much is caused by differences in the devolatilization conditions and the volatile content of the coalare not known. Table 6 gives the computed equilibrium methane formation in the gasification zone of a simulated dry ash Lurgi gasifier for combustion zone temperaturesof 1600, 1800, and 2000°F. More complete data on this case are given in Appendix B. At the higher temperatures at which the rate of direct methane formation is expected to be appreciable, the equilibrium amount formed is small.

In the literature there has been considerable disclosure that some gasifiers show a larger amount of methane at the outlet than the equilibrium amounts given in Figures 24c and 25e. This is mainly due to the fact that devolatilization in these cases occurs at the top of the bed above the reaction zone and at temperatures where methane decomposition and reforming are slow. Our computation refers to the reaction zone below and there the equilibrium constraints on methane hold. The relative rate of reactions(5) and (6) versus reactions (3), (4), and (8) strongly depends on the properties of the char. Reference 3 gives sources that claim the methanation rate at medium pressures compares with that of reactions (3), (4), and (8). Large scale pilot plant data do not seem to support this as Table 5 shows.

Equilibrium concentrations of methane only show a part of the picture. In the absence of a catalyst, methane formation is strongly limited by the kinetics of the system itself, since all reactions are very slow at the low temperatures that favor methane formation. Kinetically, the reaction rates strongly depend on the coal and also on the composition of the ash as some ash constituents have catalytic activity. In the absence of an effective catalyst, however, a reasonably high temperature (>1600°F) will be required in the gasification section; otherwise, low steam and coal conversion will result.

There is not enough known to draw any firm conclusions with regard to the actual amount of methane that is directly formed in non-catalytic gasifiers. For the purpose of this study, all methane will be considered to be produced by devolatilization

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# Methane Production of Various Gasifiers

Gasifier	Соа		Ref.	Steam/Oxygen Ratio	Pressure, psia	scf Methane <sup>(a)</sup> per 1b Coal DAF
Grand Forks Slagger	Lignite		10	1.0	400	2.1
BGC-Lurgi Slagger	Scottish-	Frances	5	1.3	450	2.65
Synthane PDU	Rosebud ()	Western)	Ś	5,5	300	2.86 <sup>(c)</sup>
Synthane PDU	Rosebud (I	Western)	Ŋ	6.8	600	3,44 <sup>(c)</sup>
Dry Ash Lurgi	Wyoming (I	Western)	Ŷ	7.5	400	4.2
Synthane Pilot Plant	Rosebud (I	Vestern)	4	8.0	600	3.57
Dry Ash Lurgi	Illinois	#6 (East)	11,12		450	3.85
IGT-Hygas Pilot Plant	<sup>6)</sup> Lignite		13,14	10.3	1000	3.2 (b) (c)
IGT-Hygas Pilot Plant	o) Rosebud (f	Vestern)	13,14	, 12.8	1000	4,39 (b) (c)
IGT-Hygas Pilot Plan <sup>(k</sup>	o) Peabody (F	Sastern)	13,14	14.4	1000	4.65 (b) (c)

(a) I scf  $C_{2}H_{6}$  counted as 1.7 scf  $CH_{4}$ .

- In the IGT reactor, the coal is fed in a toluene slurry. The toluene may enter the gasification zone and crack to produce methane. Thus, the methane yields from the coal are difficult to estimate from these data. (q)
- (c) The material balances are poor.

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### Table 6

Equilibrium Methane Formation intheGasification Zone of a Simulated Dry Ash Lurgi Gasifier (Approximate Eastern Coal) at 400 psia and 8.0 Steam to Oxygen Ratio

Temperature •F	Equilibrium Methane Formation <sup>a)</sup> (scf per 1b DAF Coal)
1600	2.35
1800	1.01
2000	0.37

a) Equilibrium methane formed above that made by devolatilization.

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for the higher temperature, non-catalytic gasifiers of interest to us.

The only cases where large amounts of methane have been reported are in catalytic gasifiers (3) although few data are available. If the catalyst is cheap or easily recoverable, methane formation has the advantage of allowing high coal conversion at lower temperatures. This improves the thermal efficiency slightly since less heat is generated. Some catalyst also cracks tars and phenols, offering a significant advantage. The only catalysts presently known that are cheap are natural constituents of the ash, but they are not very active. Large amount of catalyst is usually required and catalyst make-up can be expensive. For syngas and fuel gas production, a catalyst which promotes reactions (3), (4) and (8) without promoting reactions (5) and (6) would be preferred. Even then its value is limited since a reasonably high temperature is always needed for proper steam conversion because of equilibrium considerations. However, the lower temperature requirement would help avoid ash and coal agglomeration.

Stoichiometric, thermal, equilibrium, and kinetic constraints, such as those given above, only provide guidelines since to devise an operable gasifier is the prime consideration. For example, the BGC-Lurgi slagger approaches the operation of point A and as will be shown later, this point may be approached by the multi-stage fluid bed gasifier. However, the BGC-Lurgi slagger at present only operates with a limited number of coals. Thus, other gasifier conditions even though less optimum, have to be considered if they lead to an operable gasifier.

### IX. Countercurrent Feed of Coal

The cold gas thermal efficiency of a gasifier is improved by feeding coal countercurrently to the steam and oxygen as will be discussed here. Two simplified countercurrent schemes are given in Figure 26. The scheme labeled model 2 has a devolatilization zone in which the coal flows in countercurrent to the hot gases coming from a well-mixed gasification zone. The other scheme labeled model 3 has the countercurrent devolatilization zone of model 2 replaced by a well-mixed devolatilization zone. In the devolatilization zones of these countercurrent gasifiers the coal is dried, devolatilized and heated by the hot gases coming from the gasification. The char produced flows into the gasification zone and the devolatilization product and moisture along with the gaseous products from the gasification zone exit the gasifier.

These gasifier models are combined with the simplified gasifier used to prepare the data in Figures 23a-h to determine the effects of countercurrent flow. The scheme used in Figures 23a-h will be called model 1. The data from Figures 23a-h are repeated for comparison with the results obtained with models 2 and 3 in Figures 27a-g. Figures 27a-d show that both the net and cold gas thermal efficiencies are improved. There is a maximum near the low steam to oxygen ratio characterized by point Figures 27e-f show that the oxygen required decreases. Figures Α. 27g-h show that the temperature in the reaction zone is higher for models 2 and 3 which results in better conversion. This effect is especially apparent in the case of high moisture content coals. Figures 27i-j show that a considerably lower exit gas temperature is achieved in the countercurrent cases. As pointed out earlier, this is especially desirable in case of syngas production.

SCHEMATIC REPRESENTATION OF COUNTERCURRENT GASIFIERS



Figure 26

COLP GAS THERMAL EFFICIENCY (APPROXIMATE EASTERN COAL) Figure 27a



(%) Yonsicificiency (%)

- 69 -





Cold Gas Thermal Efficiency (%)

- 70 -

NET THERMAL EFFICIENCY (APPROXIMATE EASTERN COAL) Figure 27c



- 71 -

NET THERMAL EFFICIENCY (APPROXIMATE WESTERN COAL) Figure 27d



(%) Yonsioiii Efficiency (%)

72 -

Steam / Oxygen (Molar)





- 73 -



GASIFIER TEMPERATURE (APPROXIMATE EASTERN COAL) Figure 27g











76

Steam / Oxygen (Molar)

Figure 27i









Steam / Oxygen (Molar)

- 78 -

### X. Methane Reforming and Direct Injection of Coal into a High Temperature Reaction Zone

If the coal is introduced into the high temperature reaction zone itself, methane from the devolatilization will be reformed and methane formation by direct hydrogenation will be suppressed. Furthermore, tar and phenol formation is eliminated. Reforming methane will reduce the net thermal efficiency. The most serious problem is the thermal efficiency loss due to the oxygen and steam requirements of the reforming reaction:

 $CH_4 + H_2O + CO + 3H_2$   $\Delta H = 52.35$  kcal/ mole (10)

To balance it with reaction (1) (combustion of char to CO), 1 mole of oxygen and 2 moles of carbon are needed. To gasify these same two moles of carbon would have required 0.55 moles of oxygen by the set of reactions of point A. Hence, an additional 0.45 moles of oxygen per mole of methane reformed is required. No additional steam is required since the steam used for reforming is approximately equal to the steam saved in gasification. If the methane in the gas from the BGC-Lurgi slagger in Table 4 were reformed, it would require an additional 35 scf of oxygen per 1000 scf syngas or an increase of 20% in oxygen consumption. This is, however, less than what would be required if the methane is reformed in a separate step. For fuel gas, reforming is detrimental; for syngas it is beneficial.

Figures 28a-f give a comparison of model 1 with methane reforming at steam to oxygen ratio of 0.63 with the countercurrent model 2. Figures 28a and b show that the penalty on net and cold gas thermal efficiencies is substantial. The methane in the outlet gas drops dramatically as shown in Figure 28c. The oxygen required rises (Figure 28d) and the gasifier temperature drops (Figure 28e). In spite of this loss in thermal efficiency, the methane reforming in the gasifier can be quite attractive for both hydrogen and certain syngas production cases as will be discussed later.

A major themal penalty of introducing the coal into a high temperature zone to achieve methane reforming is that the outlet temperature of the product gases is much higher than otherwise since these product gases do not exchange heat with the incoming coal (Figure 28f). The coal must be dry to avoid further increasing the oxygen consumption. The increase in oxygen consumption decreases the cold gas thermal efficiency. Part of this loss can be recovered by using the heat of the product gases to generate steam for the feed.

On the other hand, a low exit temperature is desired to minimize the amount of heat that has to be supplied to the gasifier by combustion. The BGC-Lurgi slagger achieves this by using the heat of the product gases to heat the coal feed and devolatilize it. In a gasifier for fuel gas production, the conditions of low exit temperature can be relaxed. The sensible heat of the exit gases can be used to generate steam used by the

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Cold Gas Thermal Efficiency (%)

80



- 81 -

Steam / Oxygen (Molar)



Figure 28b





Steam / Oxygen (Molar)

Figure 28d OXYGEN FEED (APPROXIMATE WESTERN COAL)









Steam / Oxygen (Molar)

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84 -





- 85 -

process (such as for oxygen production), but not more than required since exporting power or steam in a coupled mode has severe economic penalties. If the exit gas is at low temperature, the steam used by the process has to be supplied by the combustion of fuel gas or from other sources. To supply this heat one can use fuel gas with air, whereas all the heat in a gasifier with high exit temperature comes from combustion with pure oxygen which itself requires energy to generate. The difference in these two cases is, however, small.

For the syngas processes, a low exit temperature is desirable as syngas conversion processes generate both excess steam and low guality heat from off gases that can be used for power generation. This is one important difference between the production of fuel gas and syngas.

## XI. The Effects of Coal Properties on Gasifier Design

The term coal is applied to substances with a very wide range of physical properties. It is, therefore, hard to expect that one gasifier will be optimal for all coals. Even if a gasifier proves the best for one coal, it might require considerable modification for other types of coal. The main properties of coal that affect gasification are:

- 1) Coal reactivity.
- 2) Tendency to cake and agglomerate when heated.
- 3) Ash content and its properties.
- 4) Heating value per unit weight and also per unit volume.
- 5) Amount and nature of volatile materials.
- 6) Sulfur content.

For our discussion, two broad main classes will be considered:

- a) Subbituminous coals and lignites (western coals).
- b) Bituminous coals (eastern coals).

The first are more reactive, have higher oxygen content, lower sulfur content, lower heating value and a higher fraction of the heating value in volatile components. They are non-caking and, at present, cheaper at the mine mouth.

Bituminous coals have, in most cases, a higher heating value and lower oxygen content and are less reactive with a tendency to cake and agglomerate. One can reduce that tendency by pretreatment, which is expensive. Dealing with this problem is an important criterion for development of gasifiers for such coals. Most of the eastern coals have a higher sulfur content. There are exceptions to all these statements, but the classification is sufficient for an adequate discussion of the limitations of each gasifier.

For syngas conversion processes, western coal has the advantage of being cheaper. As a large fraction of coal is going to be used directly in power plants, it is important that synthetic fuels should be made from coals which are less suited for power plants. These are coals that have either a low heating value or are far from the user and are, therefore, expensive to transport. A more detailed study of the cost and availability of different coals and the way they affect gasifier design is desirable but outside the scope of this study. Western coals have a property that makes them attractive for gasification. They have a high volatile content and a high oxygen content. If coal contains more volatiles, the net and cold gas thermal efficiencies increase whereas steam and oxygen consumption decrease. The oxygen in the coal is partially converted to CO, which is desirable as the only energy needed to produce it is that needed to heat the feed. This situation is in contrast to coal liquefaction processes where the oxygen in the coal is highly detrimental as it consumes valuable hydrogen. This effect is illustrated in Figures 29a-d, in which 15% of the coal is volatilized as CO corresponding to the oxygen content of the coal  $\binom{2^{j}}{2^{j}}$  upon devolatilization for model 1, and "igures 30a-d for model 2. Figure 29a





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