## INFORMATION TO USERS

This reproduction was made from a copy of a document sent to us for microfilming. While the most advanced technology has been used to photograph and reproduce this document, the quality of the reproduction is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help clarify markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure complete continuity.
2. When an image on the film is obliterated with a round black mark, it is an indication of either blurred copy because of movement during exposure, duplicate copy, or copyrighted materials that should not have been filmed. For blurred pages, a good image of the page can be found in the adjacent frame. If copyrighted materials were deleted, a target note will appear listing the pages in the adjacent frame.
3. When a map, drawing or chart, etc., is part of the material being photographed, a definite method of "sectioning" the material has been followed. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.
4. For illustrations that cannot be satisfactorily reproduced by xerographic means, photographic prints can be purchased at additional cost and inserted into your xerographic copy. These prints are available upon request from the Dissertations Customer Services Department.
5. Some pages in any document may have indistinct print. In all cases the best available copy has been filmed.

University
Microfilms
International

300 N. Zeeb Road
Ann Arbor, MI 48106

8312373

**Shapira, Dan**

# SNG FROM COAL: THERMODYNAMIC AND KINETIC CONSTRAINTS; USE OF NUCLEAR ENERGY

*City University of New York* PH.D. 1983

University
Microfilms
International 300 N. Zeeb Road, Ann Arbor, MI 48106

# SNG FROM COAL
# THERMODYNAMIC AND KINETIC CONSTRAINTS
# USE OF NUCLEAR ENERGY

by

DAN SHAPIRA

A thesis
presented to City University of New York
in partial fulfillment of the
requirements for the degree of
DOCTOR OF PHILOSOPHY
in
THE GRADUATE SCHOOL, THE CITY UNIVERSITY OF NEW YORK

New York, New York, 1982

This manuscript has been read and accepted for the Graduate Faculty in Engineering in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

12/9 82 Reuel Shinnar
date Chairman of Examining Committee

12/9/82 Paul R Karmel
date Executive Officer

Prof. H. Weinstein Weinstein
Prof. A. LaCava Alberto LaCava
Prof. R. Pfeffer
Supervisory Committee

The City University of New York

# ABSTRACT

## SNG FROM COAL
## THERMODYNAMIC AND KINETIC CONSTRAINTS
## USE OF NUCLEAR ENERGY

by

Dan Shapira

Adviser: Professor Reuel Shinnar

Part I contains an analysis of the thermodynamic constraints of converting coal to SNG. It is shown that the thermodynamic constraints that limit the thermal efficiency are not inherent, but are the result of design decisions, based on available technology, as well as on the kinetic properties of available catalysts. The latter, limits the yield of methane to that obtainable at global equilibrium over carbon in the presence of CO, $H_2$, $CO_2$ and $H_2O$. The equilibrium composition is shown to be independent of the thermodynamic properties of the char or coal fed. These limitations give the nonisothermal two-stage processes significant thermodynamic advantages. The analysis in part I results in suggesting directions for modifying present processes in order to obtain higher thermal efficiencies. It

also presents two-stage process schemes which may have significant advantages over present technology. As the methodology used for the thermodynamic analysis contains some novel elements, it should be of interest to the reaction engineer in general, and should be applicable to a wide range of catalytic and noncatalytic processes.

Part II focuses on the use of nuclear energy in the production of synthetic fuel. Two processes for the production of hydrogen (which is used in coal-to-SNG processes) are analyzed and compared. The two processes are:

1. Hydrogen from electrolysis of water using nuclear heat.
2. Hydrogen from steam reforming of methane using nuclear heat.

The method used is differential economic analysis which focuses on evaluating the inherent advantages and disadvantages of the proposed technologies. The method tries to quantify directly any potential advantage over existing technology. The method is especially suitable for evaluating new technologies at a stage where much of the detailed process information is still missing.

Part II shows that the use of high temperature heat in production of hydrogen from coal is less attractive than the use of the same heat to generate electricity and split water into $H_2$ and $O_2$. It is under the most optimistic assumptions, slightly more expensive per unit of coal saved, and has less potential for saving coal.

# ACKNOWLEDGEMENTS

The author expresses his gratitude for the generous help, advice, and guidance given by Professor Reuel Shinnar, throught the entire period of this study and the preparation of this manuscript.

The author is also thankful to his wife, Daniella, for her constant help, encouragement and assistance during the preparation of this manuscript.

Finally, the financial help recieved from the Department of Energy, Washington, D.C., under contract DE AC01-79 ET14811, and the Department of Chemical Engineering at C.C.N.Y is gratefully acknowledged.

# CONTENTS

## PART I -- Thermodynamic and Kinetic Constraints of Catalytic SNG Processes

Chapter

page

PART II -- Use of Nuclear Energy in Production of SNG and Hydrogen from Coal

Chapter

page

Appendix

## LIST OF TABLES

Table

# LIST OF FIGURES

# PART I

# THERMODYNAMIC AND KINETIC CONSTRAINTS OF CATALYTIC SNG PROCESSES

# Chapter 1

# INTRODUCTION (PART I)

There has been considerable attention in recent years to second law or to availability analysis of coal gasification processes as a tool to avaluate their thermal efficiency [IGT 1978-1979, Gaggioli and Petit 1976, Johnson 1980]. Thermal efficiency is a very important consideration in conversion of coal to either SNG, fuel gas or syngas. The importance of thermal efficiency is far more than utilization of coal, or for determining the amount of $CO_2$ released to the atmosphere. The required capital investment for a process is strongly correlated to thermal efficiency [Shinnar and Kuo 1978, Stone and Webster 1977, Gaensslen 1978]. Therefore, any clues for improvement in a given thermal efficiency are valuable. However, the constraints that limit thermal efficiency are not really thermodynamic but mainly kinetic, process and material constraints, which interact in a complex way. If the temperature of a process is limited due to material constraints, then this may have thermodynamic implications which limit the thermal efficiency. Kinetic properties of catalysts also have thermodynamic implications. In order to draw important inferences for improved process schemes and reactor design in SNG processes, it will be shown that it is sufficient to know that some reactions are faster than others. Thermodynamics is a powerful tool for utilizing such knowledge. The methods presented here should be of general interest to those engaged in either reactor or process design. In the following (part I), a complete analysis of the factors which determine the thermal efficiency of SNG processes will be presented. It will also be shown how present processes are compared with one another and how they can be improved.

# Chapter 2

# DEFINITION OF THERMAL EFFICIENCY

## 2.1 POWER PLANTS

There are several ways in which thermal efficiency for a synthetic fuel plant can be defined. A power plant which operates with combustible fuel will be examined first. The definition can be based on the higher heating value of the fuel $Q_H$,

$$\eta_H = \frac{W}{Q_H} \tag{1}$$

or the lower heating value $Q_L$,

$$\eta_L = \frac{W}{Q_L} \tag{2}$$

where W is the output power of the power plant. A more consistent definition to be used is

$$\eta_A = \frac{W}{A} \leqslant 1 \tag{3}$$

where A is the standard available energy of the fuel defined with respect to the ambient surroundings [Keenan 1932] (see Table 1). The only strict thermodynamic constraint is that $\eta_A < 1$. Equation (3) gives an important constraint on $\eta_L$;

## TABLE 1

### Availability standards

**Datum Level:** $T_o = 298^oK$ $P_o = 1$ atm.

**Stable Reference:** Air: 0.21 $O_2$
0.79 $N_2$

$H_2O$: liquid

**Availability of Gas Mixture:**

$$A_{mix}(T,P) = \int_{T_o}^{T} \sum X_j [C_{pj} - \frac{T_o}{T} C_{pj}] dT + RT_o \ln \frac{P}{P_o}$$
$$+ \sum X_j [h_j(T_o) - T_o s_j(T_o, X_j P_o) - \mu_{jo}]$$

$\mu_{jo}$ - chemical potential of species j in the reference environment

$h_j, s_j$ - partial molar enthalpy and entropy of species j.

$$\eta_L \leqslant \frac{A}{Q_L} \tag{4}$$

While $\eta_A$ is always less than unity, it is not necessarily true for $\eta_L$. However, for most fuels the ratio $A/Q_L$ is close to unity (see Table 2).

A power plant does not directly utilize the chemical energy of the fuel but only its heat. Therefore, the Carnot principle

$$\eta_L < 1 - \frac{T_a}{T_p} \tag{5}$$

is a more severe constraint on $\eta_L$. ($T_a$ is the ambient temperature and $T_p$ is the maximum temperature in the power plant). The last constraint is not an inherent thermodynamic constraint but rather a thermodynamic consequence of a design decision. $T_p$ is not limited by conversion but by material constraints.

In the analysis of steam power plants or combined cycle power plants, cycle efficiency $\eta$(cycle) is usually used ($\eta$(cycle)<$\eta$(Carnot)). This efficiency is obtained by computing the efficiency of a process equivalent to that used in the real plant, with the assumption that all process stages are carried out reversibly. To estimate real efficiencies of power plants $\eta$(cycle) has to be multiplied by an experience factor $\varepsilon$

## TABLE 2

Heat of combustion and available energy for hydrocarbons

| | | Standard Chemical Availability [Kcal/gr-mole] | Heat of Combustion (LHV) [Kcal/gr-mole] |
|---|---|---|---|
| Methane | $CH_4$ | 195.5 | 191.76 |
| Ethane | $C_2H_6$ | 350.73 | 341.26 |
| Propane | $C_3H_8$ | 503.93 | 488.53 |
| n-Hexane | $C_6H_{14}$ | 962.44 | 928.93 |
| Ethylene | $C_2H_4$ | 318.18 | 316.19 |
| Propylene | $C_3H_6$ | 467.81 | 460.43 |
| Benzene | $C_6H_6$ | 766.62 | 757.52 |
| Toluene | $C_6H_8$ | 915.81 | 901.5 |
| Cyclopentane | $C_5H_{10}$ | 763.98 | 740.79 |

$$\eta_L = \eta_L(\text{cycle}) \times \varepsilon \qquad (6)$$

which takes into consideration losses due to finite rates and driving forces.

## 2.2 CHEMICAL PROCESSES

The analogue of a power cycle in a chemical process is an idealized flow sheet in which heat transfer and separation processes are carried out reversibly, and in which driving forces are neglected. In that case the definition for the efficiencies must be modified in the following matter;

$$\eta_A = \frac{A(\text{useful product})}{A(\text{total plant input})} \qquad (7)$$

and

$$\eta_L = \frac{Q_L(\text{useful product})}{Q_L(\text{total coal input to plant})} \qquad (8)$$

Such analysis is useful as long as the efficiency of the real process is close to that of the ideal one, which applies in many cases. Exceptions are separation processes for which real efficiencies are often very low (<15%).

Thermodynamic Second Law analysis (availability analysis) is frequently being suggested in the literature as a tool for the evaluation of preformance for chemical processes [Gaggioli and Petit 1976, Lin 1977, Riekert 1974]. Such analysis indicates the places in the process at which the main losses in availability occur, and where improvements will have a maximum effect. Theoretically, $\eta_A=1$ can be achieved as long as fictitious technology without irreversibilities is used. This is not very useful information for design. Availability analysis can only be attractive when process constraints are incorporated in the analysis [Flower and Linnhoff 1979]. Availability analysis is useful in finding weak points in a specific design. The cycle approach or the idealized flowsheet, are sometimes more useful for evaluating the thermodynamic implications of design decisions or process constraints.

## Chapter 3

## CATALYTIC GASIFICATION OF CHAR

### 3.1 OVERALL REACTIONS OF SNG FORMATION

Understanding char gasification is important since in almost all current processes the coal devolatilizes first to char and the char is then gasified. The analysis will concentrate first on the reaction of carbon (graphite) which is more simple than the char itself but has similar properties. It will be shown later that the results are also valid for gasification of char and coal.

The overall reaction of methane formation from carbon and water is reaction I in Table 3

$$2C + 2H_2O_{(1)} \dashrightarrow CH_4 + CO_2 \qquad (9)$$

$$\Delta G^o_{298} = 7.0 \quad \text{Kcal/gr-mole}$$

$$\Delta H^o_{298} = 24.65 \quad \text{Kcal/gr-mole}$$

The heat of reaction is supplied by combusting carbon with oxygen or air and can be described by reaction II

$$C + O_2 \dashrightarrow CO_2 \qquad (10)$$

$$\Delta G^o_{298} = -94.26 \quad \text{Kcal/gr-mole}$$

$$\Delta H^o_{298} = -94.05 \quad \text{Kcal/gr-mole}$$

## TABLE 3

## Thermodynamic Constants for Reactions Used

| | | $\Delta G^{o}_{298}$ (Kcal) | $\Delta H^{o}_{298}$ (Kcal) | $\Delta S^{o}_{298}$ (cal/°K) |
|---|---|---|---|---|
| **A.** | **Graphite** | | | |
| | gas-solid reactions | | | |
| I) | $2C + 2H_2O_{(l)} \longrightarrow CH_4 + CO_2$ | 6.99 | 24.65 | 59.27 |
| II) | $C + O_2 \longrightarrow CO_2$ | -94.26 | -94.05 | 0.7 |
| III) | $C + H_2O_{(l)} \longrightarrow CO + H_2$ | 23.9 | 41.88 | 60.3 |
| IV) | $0.5C + H_2O_{(l)} \longrightarrow 0.5CO_2 + H_2$ | 9.56 | 21.29 | 39.36 |
| V) | $1.5C + H_2O_{(l)} \longrightarrow 0.5CH_4 + CO$ | 17.83 | 32.95 | 50.76 |
| VI) | $C + 2H_2 \longrightarrow CH_4$ | -12.14 | -17.89 | -19.3 |
| VII) | $C + CO_2 \longrightarrow 2CO$ | 28.64 | 41.22 | 42.21 |
| | gas-gas reactions | | | |
| VIII) | $CO + H_2O \longrightarrow CO_2 + H_2$ | -6.81 | -9.84 | -10.16 |
| IX) | $CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$ | -27.15 | -39.41 | -41.16 |
| X) | $CO + 3H_2 \longrightarrow CH_4 + H_2O$ | -33.96 | -49.26 | -51.32 |
| XI) | $2CO + 2H_2 \longrightarrow CH_4 + CO_2$ | -40.78 | -59.1 | -61.49 |
| **B.** | **Coal** | | | |
| XII) | $1.74CH_{0.8}O_{0.1} + 1.3H_2O_{(l)} \longrightarrow CH_4 + 0.74CO_2$ | -8.42 | 7.4 | 53.08 |
| XIII) | $CH_{0.8}O_{0.1} + 0.9H_2O_{(l)} \longrightarrow CO + 1.3H_2$ | 17.54 | 38.07 | 68.89 |
| XIV) | $CH_{0.8}O_{0.1} + 1.9H_2O_{(l)} \longrightarrow CO_2 + 2.3H_2$ | 12.78 | 38.75 | 87.1 |
| XV) | $2.3CH_{0.8}O_{0.1} + 1.07H_2O_{(l)} \longrightarrow CH_4 + 1.3CO$ | 4.43 | 28.03 | 79.19 |

The overall reaction of the process can be written as:

$$(2+\alpha)C + 2H_2O_{(1)} + O_2 \longrightarrow CH_4 + (1+\alpha)CO_2 \qquad (11)$$

$$\Delta G^o_{298} = 7.0 - 94.26\alpha \quad \text{Kcal/gr-mole}$$

$$\Delta H^o_{298} = 24.65 - 94.05\alpha \quad \text{Kcal/gr-mole}$$

It is noted that for $\alpha=0.074$, $\Delta G^o_{298}=0$ for the overall reaction. The overall process can be realized as long as $\alpha>0.074$, since this meets the only strict constraint of $\eta_A<1$.

Reaction (11) is written for standard conditions. In practice, the methane produced is required at higher pressures. Since at least part of the pressure is achieved in the reactor itself it can be incorporated in the analysis. For methane at a pressure of 1000 psia or 68 atm., $\Delta G^o_{298}$ of reaction I increases to 9.5 Kcal/gr-mole $CH_4$, whereas $\Delta H^o_{298}$ remains unchanged and the corresponding $\alpha$ increases to 0.1.

## 3.2 INHERENT THERMODYNAMIC CONSTRAINTS

It is important to realize that there are no inherent thermodynamic constraints for the direct conversion of coal to SNG. The normally called thermodynamic constraints are really thermodynamic consequences of process constraints. There is no thermodynamic reason why reaction I cannot be run under reversible conditions where $\eta_A=1$, like in the hypothetical process given in Figure 1, or in an electrolytic cell. In Figure 1, water is reacted with carbon at ambient conditions, the $CH_4$ and $CO_2$ formed are separated through a membrane, the $CO_2$ is compressed to atmospheric pressure and the $CH_4$ to 68 atm. The work required is generated in a reversible process from either the methane or the char, and the heat required is absorbed from the surroundings. Since the heat supplied to the process has zero availability, the free energy of the product is generated by compression. If the process is carried out reversibly at higher temperatures, the heat of reaction has to be supplied by a heat pump. The theoretical compression requirements will decrease exactly by the amount of power required by the heat pump.

Theoretically, $\eta_A=1$ can be achieved at any temperature, as long as ideal semipermeable membranes are used to separate the products, and heat pumps are used to transfer heat from the surrounding to the process. Since chemical plants are not usually designed in this manner, real design decisions have to be incorporated in the analysis.

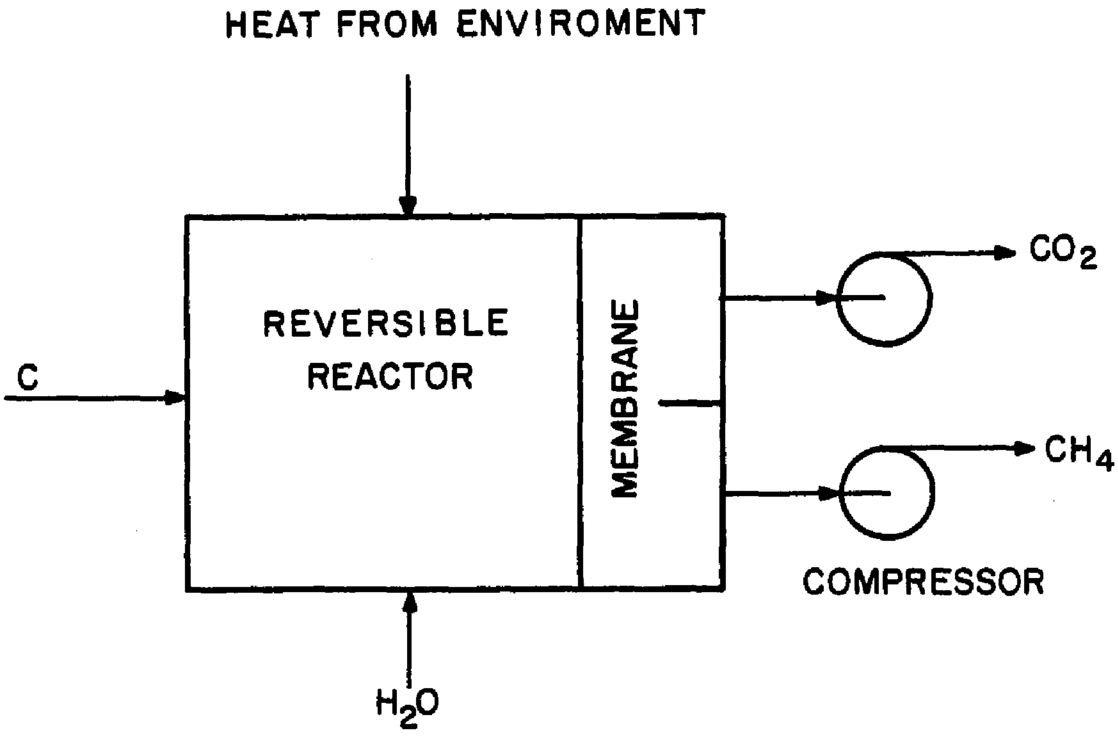


Figure 1: Hypothetical reversible SNG process.

## 3.3 THERMODYNAMIC IMPLICATIONS OF DESIGN DECISIONS

The standard constraints used in plant design for SNG plants (and for most chemical plants) are:

1. The plant must be heat balanced.
2. No heat pumps are allowed for high temperature streams.
3. No high temperature topping cycles can be used.
4. No semipermeable ideal membranes are allowed. Separation processes in one phase have very low real efficiencies and should be minimized.
5. Steam recompression at high temperatures and at high pressures is too costly and has to be avoided.

Large SNG plants often have another constraint. The total plant should be energy balanced and it cannot import large amounts of electricity. Present SNG plants have thermal efficiencies less than 70%. It will be useful to know what fraction of this loss is due to rate constraints, and what fraction is due to the thermodynamic constraints imposed by the design limitations.

The limitation that the reaction is heat balanced, requires in equation (11) that $\alpha > 0.26$. In that case

$$\eta_A < \frac{196.1}{2.26 \times 93.33} = 93\% \qquad (12)$$

where the availability of 1 mole methane is 196.1 Kcal/gr-mole and the availability of carbon is 93.33 Kcal/gr-mole.

Design considerations further reduce this limit. In chemical plants there are basically two ways, used in conjuction, to generate $\Delta G$ under the constraints listed. One is to run the process at a high temperature, utilizing the fact that the entropy change of the reaction is positive. The other is to run the process at high pressure, gaining free energy by compression of the feed. Both are utilized in SNG production. The steam conversion as a function of temperature is shown in Figure 2. It is noted that temperatures above 1200K are required for high steam conversion.

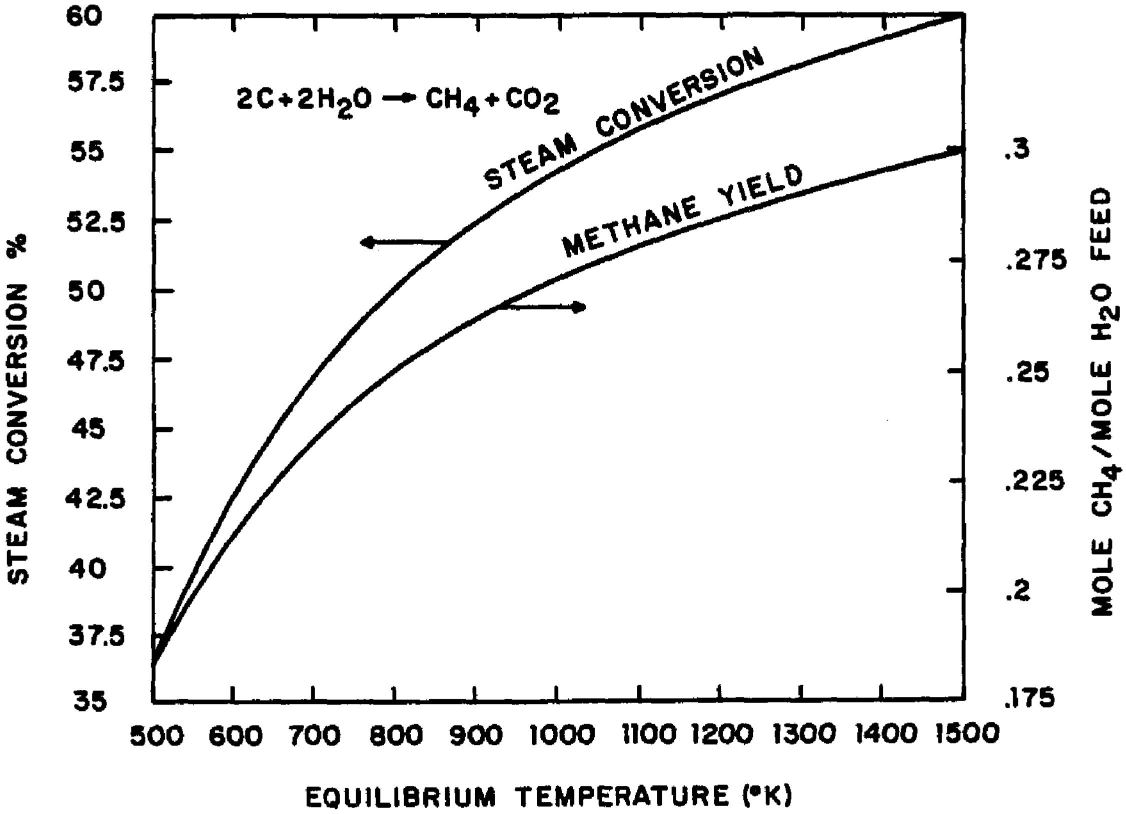
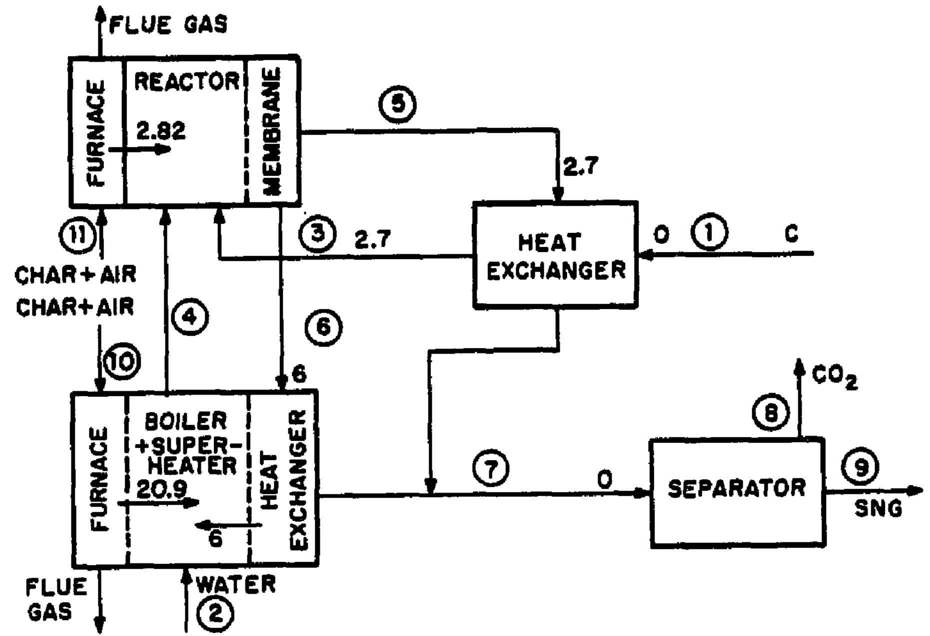


Figure 2: Steam conversion and methane yield for the overall reaction at equilibrium.

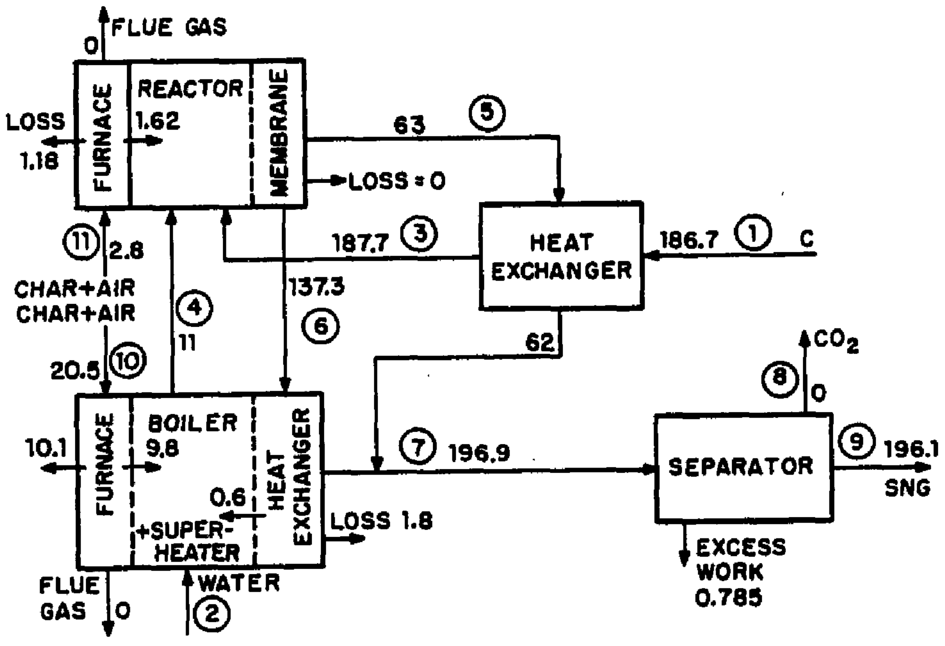
## 3.4 THE CONCEPT OF SEMIPERMEABLE MEMBRANES

In order to understand the effect of design constraints, some of them, which were mentioned before, are removed. The products $CO_2$ and $CH_4$ in the process shown in Figure 3, are separated by a semipermeable membrane. The heat requirements are theoretical, assuming no driving forces are needed. The flowsheet in Figure 3 comprises the following steps:

1. Water is heated to 558K at 68 atm. (1000 psia), evaporated and then heated to 700K. The heat is supplied partially by heat exchange with the products, and partially by combusting carbon in a furnace with air.
2. Carbon is heated to 700K by heat exchange with the product gas, and fed directly to the reactor which is at 700K and 68 atm.
3. $CO_2$ and $CH_4$ are removed from the reactor through a semipermeable membrane and cooled by heat exchange with the feed.
4. In the separator, the $CO_2$ is expanded through a turbine to the atmosphere and the work recovered is used to compress the methane from 16 to 68 atm. (Theoretically, this leaves a slight excess (0.8 Kcal) of usable work).



ENTHALPY [KCAL]



AVAILABILITY [KCAL]

Figure 3: Hypothetical gasifier (reaction I only) using semipermeable mambrane to separate $CH_4$ and $CO_2$ from the reactor (see enclosed table for details).

Figure 3 Cont.

| Stream No. | Pressure [atm.] | Temperature [$^{o}K$] | Availability [Kcal] | Component [Mole] | | | |
|---|---|---|---|---|---|---|---|
| | | | | C | $CO_2$ | $CH_4$ | $H_2O$ |
| 1. Process char | 1 | 298 | 186.7 | 2 | | | |
| 2. Water | 1 | 298 | 0 | | | | 2 |
| 3. Process char | 1 | 700 | 187.7 | 2 | | | |
| 4. Steam | 68 | 700 | 11 | | | | 2 |
| 5. Product gas | 32 | 700 | 63 | | 0.32 | 0.32 | |
| 6. Product gas | 32 | 700 | 137.3 | | 0.68 | 0.68 | |
| 7. Product gas | 32 | 298 | 196.9 | | 1 | 1 | |
| 8. $CO_2$ vent | 1 | 298 | 0 | | 1 | | |
| 9. SNG product | 68 | 298 | 196.1 | | | 1 | |
| 10. Char to boiler | 1 | 298 | 20.5 | | 0.22 | | |
| 11. Char for heat of reaction | 1 | 298 | 2.8 | | 0.03 | | |

This is a totally hypothetical process which illustrates an ideal limit. The main idealization here are the semipermeable membranes. The overall efficiencies in Figure 3 are:

$$\eta_A = 93\% \qquad \eta_L = 90.2\% \tag{13}$$

Figure 3a shows the heat flows, and Figure 3b the availability of all the streams. Out of the total increase in availability of 9.5 Kcal/gr-mole $CH_4$, only 1.6 Kcal/gr-mole are generated in the reactor, and the rest comes from the heat supplied in generating the steam prior to the reactor. The generation of availability in the steam boiler is described graphically in Figure 4. The overall efficiency in generating the availability of the steam is $\eta_A$=48%. The availability loss in the boiler is 11.1 Kcal. Another 1.2 Kcal of availability are lost in supplying the heat of reaction to the reactor by combustion of char at 700K. The main irreversibility in this idealized case is in the boiler, which uses carbon with high availability to generate steam at a significant availability loss, dictated by the Carnot principle.

The efficiency of this hypothetical process is equal to that of equation (13). The same efficiency would have been obtained if the conversion in the reactor was increased by

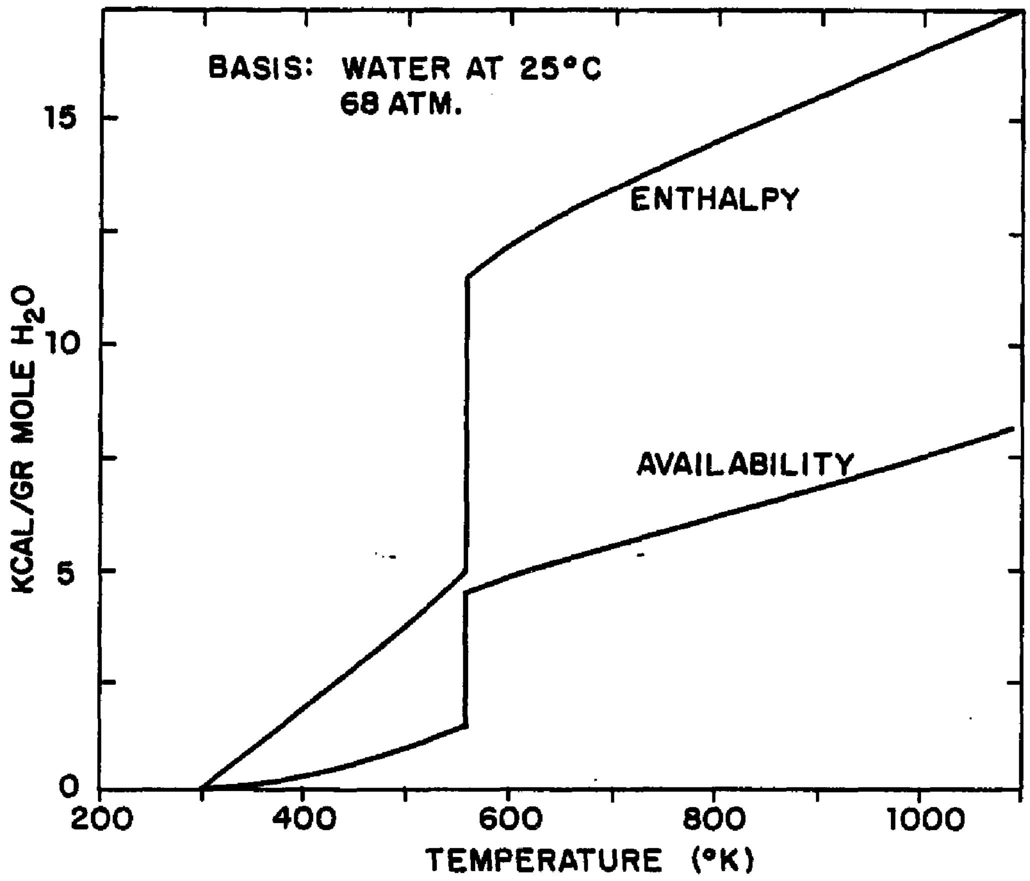
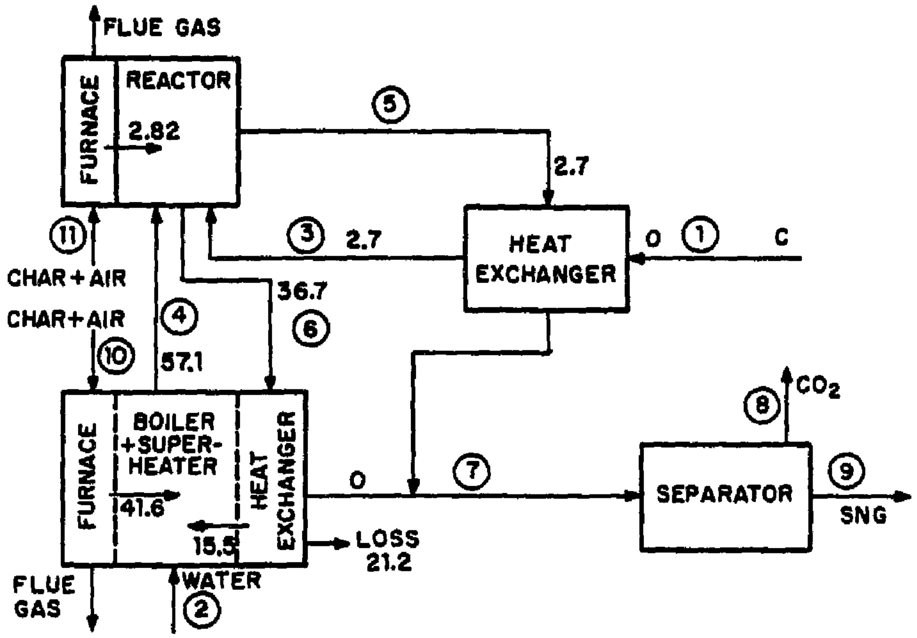


Figure 4: Availability generation in steam boiler.

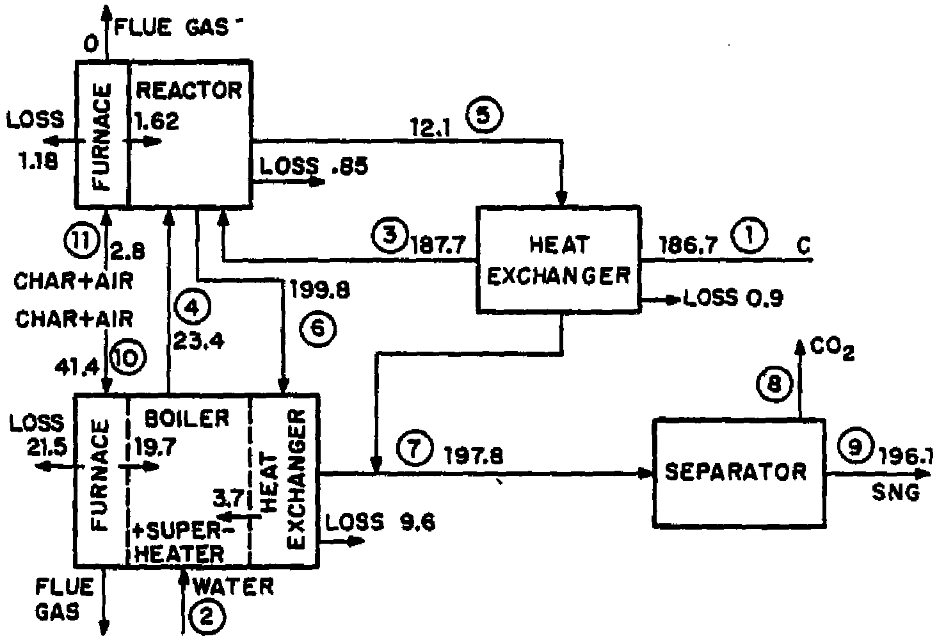
increasing temperature, though in that case, work from expanding the $CO_2$, would have been produced.

Figure 5 shows an availability analysis of a case where the mambrane is removed. The unconverted steam is separated from the product gas by condensation. Since there is a pinch in the heat balance, the unconverted steam's heat of condensation cannot be completely used to generate the steam feed, even under the assumption that no driving forces for heat transfer are required. The incremental minimum net loss due to excess steam is about 7.8 Kcal. Some of this heat can be used for other process requirements which are not considered in this idealized process scheme.

Excess steam, which has to be condensed from gas streams, is one of the main sources of inefficiency in most synthetic fuel processes [Shinnar 1978]. However, an availability analysis around the reactor will not indicate it [Lin 1977; IGT 1978]. Straightforward thermodynamic analysis states that steam should be separated by a semipermeable membrane and compressed back to 68 atm. The work required is 0.85 Kcal which is the availability loss from the reactor in Figure 5. This loss is due to the irreversible expansion of the excess steam into the reactor.



ENTHALPY [KCAL]



AVAILABILITY [KCAL]

Figure 5: Hypothetical gasifier (reaction I only) with no semipermeable membrane (see enclosed table for details).

Figure 5 Cont.

| Stream No. | Pressure [atm.] | Temperature [$^{o}K$] | Availability [Kcal] | Component [Mole] | | | |
|---|---|---|---|---|---|---|---|
| | | | | C | $CO_2$ | $CH_4$ | $H_2O$ |
| 1. Process char | 1 | 298 | 186.7 | 2 | | | |
| 2. Water | 1 | 298 | 0 | | | | 4.25 |
| 3. Process char | 1 | 700 | 187.7 | 2 | | | |
| 4. Steam | 68 | 700 | 23.4 | | | | 4.25 |
| 5. Product gas | 68 | 700 | 12.1 | | 0.06 | 0.06 | 0.13 |
| 6. Product gas | 68 | 700 | 199.8 | | 0.94 | 0.94 | 2.12 |
| 7. Product gas | 68 | 298 | 197.8 | | 1 | 1 | |
| 8. $CO_2$ vent | 1 | 298 | 0 | | 1 | | |
| 9. SNG product | 68 | 298 | 196.1 | | | 1 | |
| 10. Char to boiler | 1 | 298 | 41.2 | | 0.44 | | |
| 11. Char for heat of reaction | 1 | 298 | 2.8 | | 0.03 | | |

## 3.5 PROCESS CONSTRAINTS AND SECOND LAW OF THERMODYNAMICS

As noticed in the previous section, the main limitation on thermal efficiency, for the process in Figure 5, was the excess steam due to incomplete conversion. At a given temperature this conversion is limited by the second law of thermodynamics. Higher temperatures give higher conversions (see Figure 2). The temperature of the reaction is chosen considering kinetic (avoidance of side reactions, available catalysts) or material limitations. Thermodynamics enables to evaluate the impact of these constraints on thermal efficiency. This is done by analyzing an idealized flowsheet which incorporates the first law in the heat balance, and the second law in the conversion obtained in the reactor.

By closely examining the heat balances of a large number of detailed flowsheets for SNG processes, as well as other synthetic fuel processes from coal, one fact becomes clearly apparent: since the plant has a large steam boiler, recovery of any heat above 650K can be integrated into steam production at the same value as coal itself. This holds as long as a substantial fraction of coal is used for steam generation. Coal can always be switched to generate heat above 650K and the heat recovered can be used to generate steam. Heat below 650K has to be more carefully evaluated, as the driving force becomes important, and heat recovered below the boiling temperature of the water feed, in the main power plant, has a reduced value. Simplified experience values can be used to evaluate the value of this heat [Shinnar and Kuo 1978].

In this case, availability analysis can also be helpful. But one has to remember that the value of heat in a refinery or synthetic fuel plant is not continuously increasing with temperature as availability analysis indicates, but rather has discontinuities and maximum values which depend on the specific plant design.

As mentioned before, the approach in this work is to analyze thermodynamic implications of design decisions. Improvments in gasification technology will be suggested in the framework of accepted and available technology, for all elements outside the gasifier. Therefore, straightforward availability analysis can present some pitfalls which become obvious in Figure 5, and appear repeatedly in the literature. The only interesting way in which the flowsheet in Figure 5 can be improved is by changing reactor conditions such that steam conversion improves. Straightforward availability analysis does not indicate that. Even if conversion would have been incomplete and excess steam triple the required, the availability loss in the reactor would be small. On the other hand the availability losses in the boiler would have increased. The above information is not interesting if present technology for steam boilers is accepted.

Therefore, in the following, present technology for boilers, power plants, separation processes, etc., will be accepted, and the analysis will be focused on the flowsheet of the gasifier itself. It is recognized that availability analysis can be modified suitably, but in this case it offers no visible advantage.

## 3.6 KINETIC CONSTRAINTS OF SNG PROCESSES

The process in Figure 5 would have been excellent even if practical irreversibilities were to be included. Regrettably, no present available catalysts operate satisfactorily below 1000K. While higher temperatures give higher steam conversion, CO and $H_2$ are formed together with methane at temperatures above 800K. $H_2$ and CO can either be converted to $CH_4$ in a separate reactor, or alternatively, they can be selectively recycled. These alternatives will be discussed later. It is desirable to first understand the thermodynamic limitations imposed by the side reactions at high temperatures.

# Chapter 4

# EFFECT OF SIDE REACTIONS ON A CHAR GASIFIER FOR SNG

## 4.1 THE USE OF THERMODYNAMICS IN THE ANALYSIS OF KINETIC CONSTRAINTS

If CO and $H_2$ are formed together with $CH_4$ and $CO_2$, three independent chemical reactions (for example I,III and IV in Table 3) are sufficient for a complete description of the system in equilibrium. In a single chemical reaction, the change in free energy leads to equilibrium constraint, which is clearly a thermodynamic constraint. For example, if steam is reacted with carbon and all the additional compounds formed are only $CH_4$ and $CO_2$, the equilibrium concentration of $CH_4$ in a single isothermal reactor cannot be passed. In multiple chemical reactions thermodynamic analysis has a completely different implication. Thermodynamic constraints in reaction engineering often refer to kinetic constraints. Many organic compounds stable at 1000K may be formed under the gasifier conditions with a proper catalyst. The fact that it is assumed that the component space is six-dimensional, is a kinetic statement based on estimates of the magnitude of the reaction rates. It implies that no other species which affect the mass balance are formed. Unconstrained thermodynamics (which allows all possible reactions) makes sense above 1500K, where most organic compounds are unstable, the number of compounds still stable is small, and all reaction rates are fast.

Once the six-dimensional space is accepted, additional information can be obtained by a combination of thermodynamics and kinetics. Based on experience, and since it is correct in the context made [Shinnar and Kuo 1978; Exxon 1978], the assumption that the amount of methane formed is limited by the overall global equilibrium, leads to valuable design information.

Figure 6 shows the amount of $CH_4$, CO, $H_2$ and $CO_2$ formed by passing steam over carbon as a function of temperature at global equilibrium. Figure 7 compares the corresponding methane yield from Figure 2. It is noted that the methane yield is always lower for the three simultaneous reactions than for reaction I alone, though up to about 800K the yields are almost identical. The amount of methane formed at 68 atm., at global equilibrium, has a flat maximum of 0.22 mole around 800K and starts to decline significantly above 900K. The temperature of maximum $CH_4$ yield, which is the temperature at which CO and $H_2$ formation becomes significant, increases with increasing pressure. At very high pressures the yield of reaction I can be approached at any temperature. However, this is expensive and not practical. The base pressure for comparison was chosen as

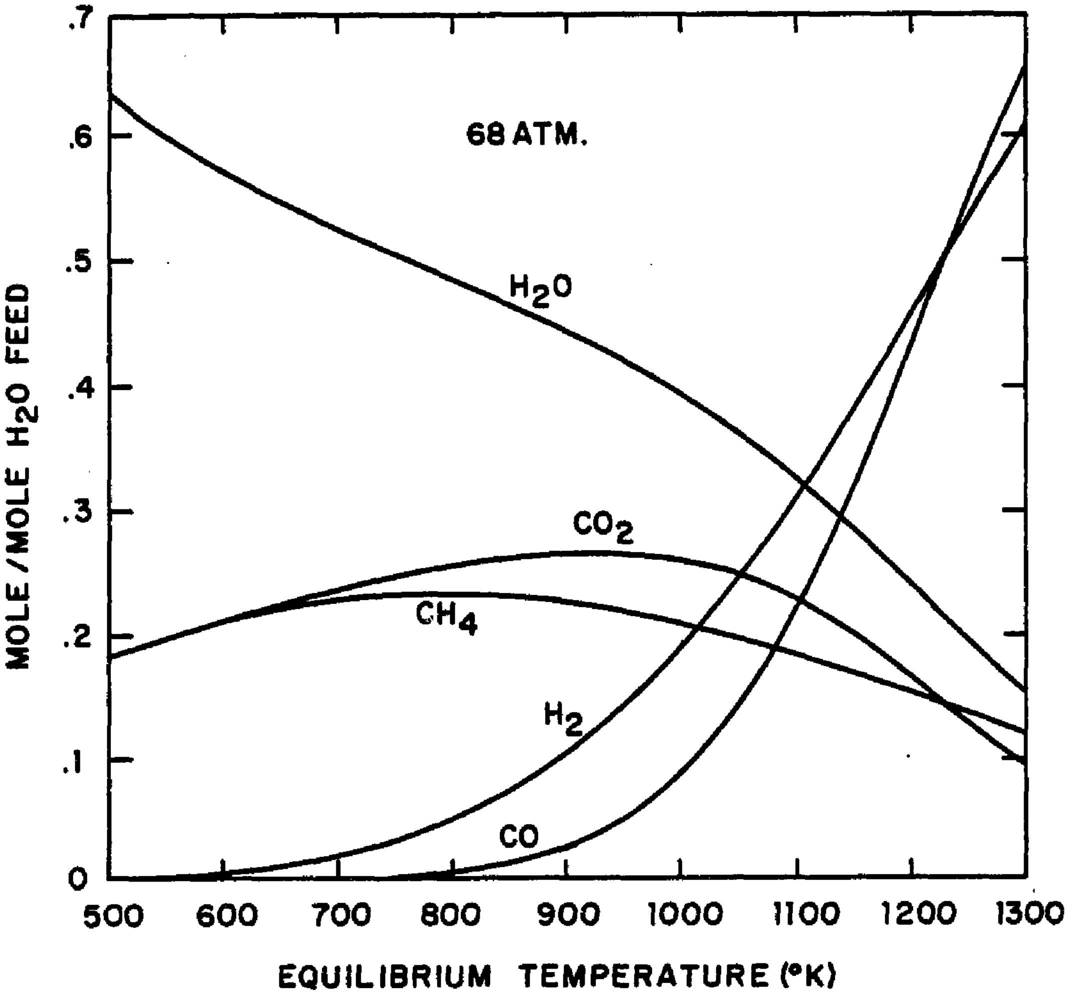


Figure 6: Product yield at equilibrium for steam-carbon reaction.

68 atm. (1000 psia), but the trends are similar at other pressures.

Despite an extensive search, there are no catalysts which operate below 1000K. Above 1000K a reactor with a catalyst can approach global equilibrium [Exxon 1978], and so can a reactor at high temperatures without a catalyst (above 1200-1250K). The question arises; is global equilibrium a sensible design constraint?. Thermodynamically, there is no reason why a catalyst that achieves the higher yield (curve A in Figure 7) at high temperatures cannot be found.

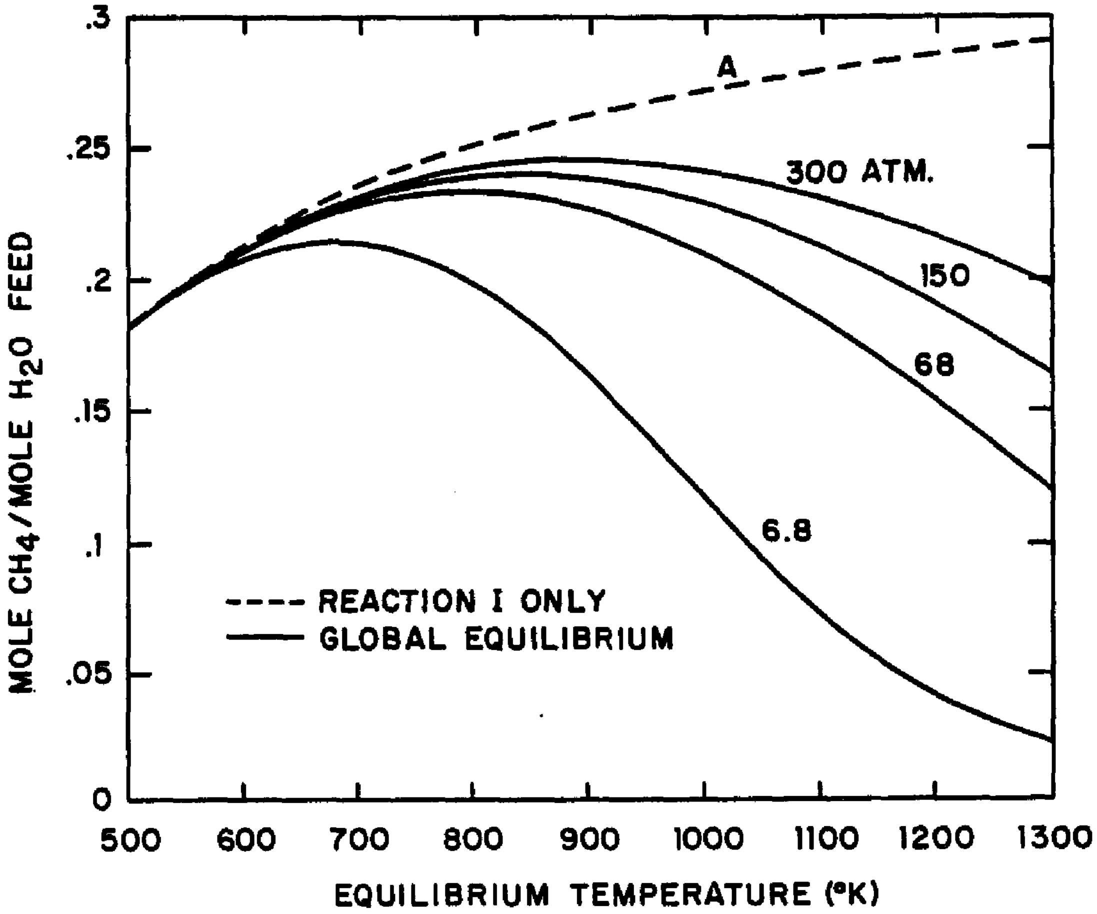


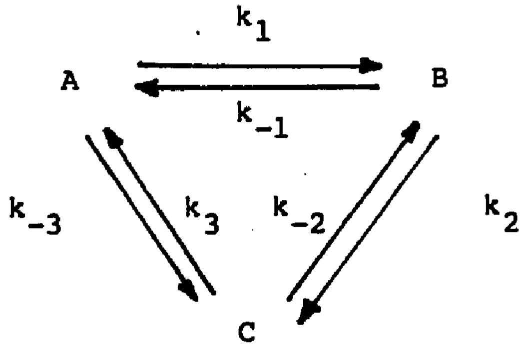
Figure 7: Methane yield at global equilibrium as a function of temperature and pressure.

## 4.2 REACTION PATHS AND THE PRINCIPLE OF DETAILED BALANCING

In general, there are two types of kinetic systems. In the first, the maximum yield of the desired product, achieved in an isothermal reactor, is a point on a kinetic trajectory in the component space. In the second, it is the global equilibrium which is the maximum point. Thermodynamics is here a useful tool, since it allows to distinguish between these two cases with a minimum knowledge of the kinetics of the system. The principle involved is explained next. Since the case dealt with is complex, it is preferred to start with a much simpler example which allows rigorous derivations.

### 4.2.1 Isothermal Linear System

Consider for example the monomolecular system [Faith and Vermeulen 1961; Aris 1969].



(14)

If the starting composition is pure A and if $k_{-3}$ is smaller than $k_1$, then, it can easily be seen that $c/a_o$ cannot exceed the global equilibrium, $c(equ.)/a_o$, or

$$c/a_o = \frac{K_1K_2}{1 + K_1 + K_1K_2} \qquad (15)$$

where $K_1=k_1/k_{-1}$ and $K_2=k_2/k_{-2}$ and $K_1K_2K_3=1$. However, if reaction $k_{-3}$ is large compared to $k_1$ and $k_2$, then $c/a_o$ can reach the equilibrium concentration of the single reaction A==C, $K_1K_2/1+K_1K_2$ which is larger than $K_1K_2/1+K_1+K_1K_2$.

The limitation of the concentration of C not being able to exceed the global equilibrium if $k_1>k_{-3}$, is due to the requirement of detailed balancing, or to the fact that $k_{-i}/k_i=1/K_i$ , where $K_i$ is the equilibrium constant of reaction i. This is a much more severe constraint than the demand of decreasing free energy along a reaction path, and it allows to delineate accesible subspaces in the stoichiometric component space [Wei and Prater 1962; Faith and Vermeulen 1961; Aris 1969; Krambeck 1970] without any prior knowledge of the rate constant [Faith and Vermeulen 1961]. An example is given in Figure 8 where $K_1=K_2=K_3=1$ was assumed for convenience. If pure A is the starting composition, then only those compositions in the area AFEGA are accessible by the above set of reactions in an isothermal reactor under the above conditions. If $k_1>k_{-3}$, then the accessible area reduces to AFEA, whereas if $k_1<k_{-3}$, the accessible composition space is AEGA. For a given set of reaction rates, the accessible composition is further limited, but the knowledge that $k_i$ is either significantly larger or smaller than $k_j$ leads to valuable design information. For a detail discussion of the kinetic constraints of chemical reactions see Shinnar and Feng (1982).

There is another case of interest. If $k_2$ is very large compared to $k_1$ and $k_{-3}$, then the reaction trajectory will always be close to the line AE. Neither B nor C can then exceed global equilibrium. This illustrates the two types of reactor design problems. In the first, the optimum outlet concentration is a global equilibrium at the outlet reactor temperature. This is true in this example if A is to be converted to a maximum yield of C and $k_1>k_{-3}$. However, if in the same example $k_{-3}>k_1$, and $k_2$ is not very large in comparison to $k_{-3}$, then the maximum yield of C is going to be a point on a kinetic trajectory. Global equilibrium is equivalent to a focal point on the stoichiometrically permissible reaction surface. In that case the optimum composition is not sensitive to reactor design, and it can be computed from thermodynamic properties of the compounds. In the second case, where the optimum concentration is a point in a trajectory, the optimum point is not only sensitive to reaction kinetics, and therefore,

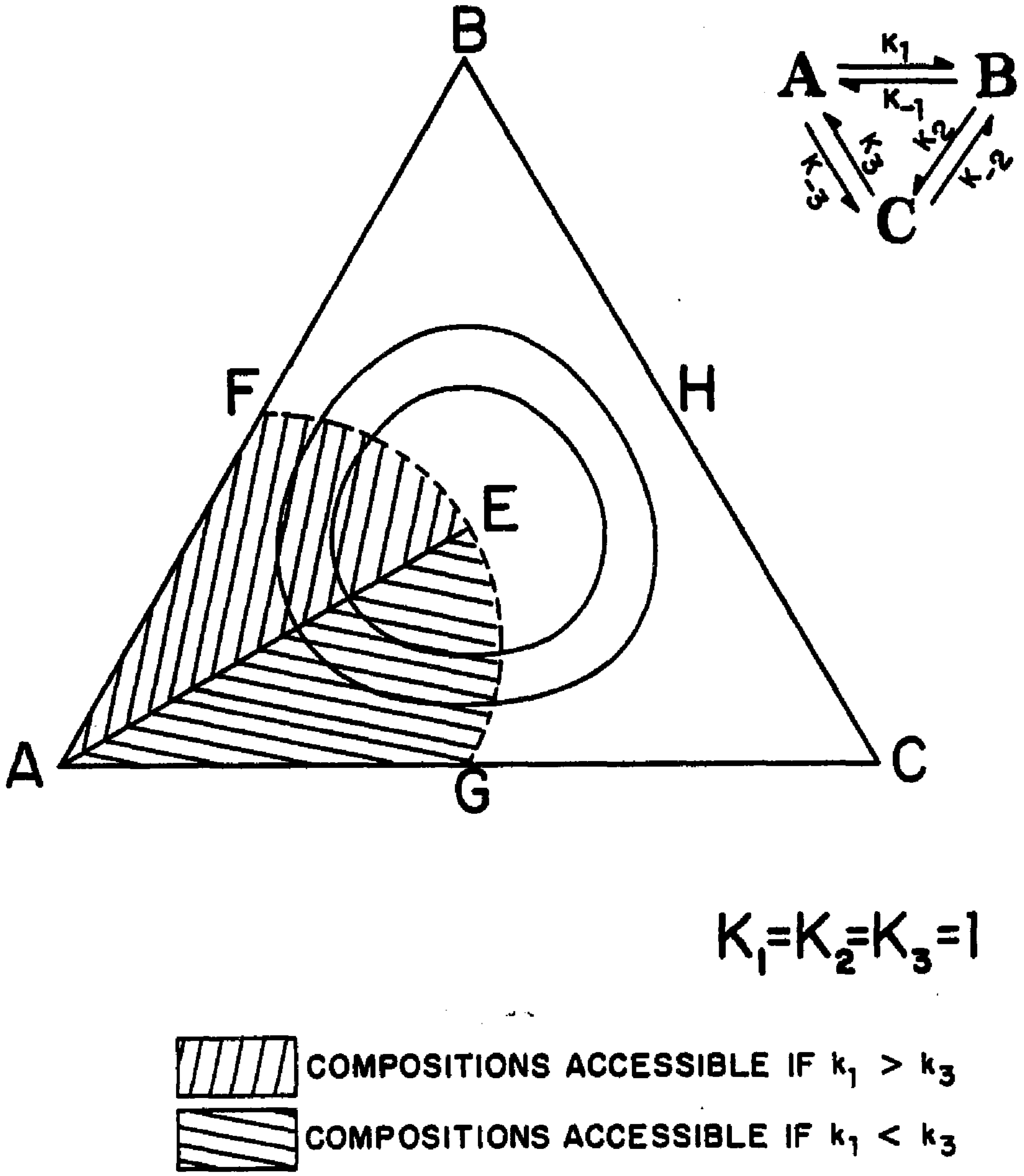


Figure 8: Accessible compositions for an isothermal linear three-component system.

to catalyst properties, but it is also more sensitive to mixing, and therefore, to reactor design.

The condition of $k_{-3}$ being very small compared with $k_1$ and $k_2$, allows, in design, to substitute thermodynamics for kinetics in order to get an approximate mass and heat balance. The only purpose for which kinetics is needed is to size the reactor. If on the other hand, all reactions have similar magnitudes, kinetics is really needed for design, as $c/a_o$ can exceed $c(equ.)/a_o$.

### 4.2.2 Non-Isothermal Linear System

This simple example can illustrate another important feature of the kinetics of SNG production. Assuming that the reaction $A \rightleftharpoons B$ is strongly endothermic, the reaction $B \rightleftharpoons C$ is exothermic, and the reaction $A \rightleftharpoons C$ is weakly endothermic. Furthermore, reaction $A \rightleftharpoons C$ is slow, and therefore, global equilibrium provides a constraint on the maximum C obtainable.

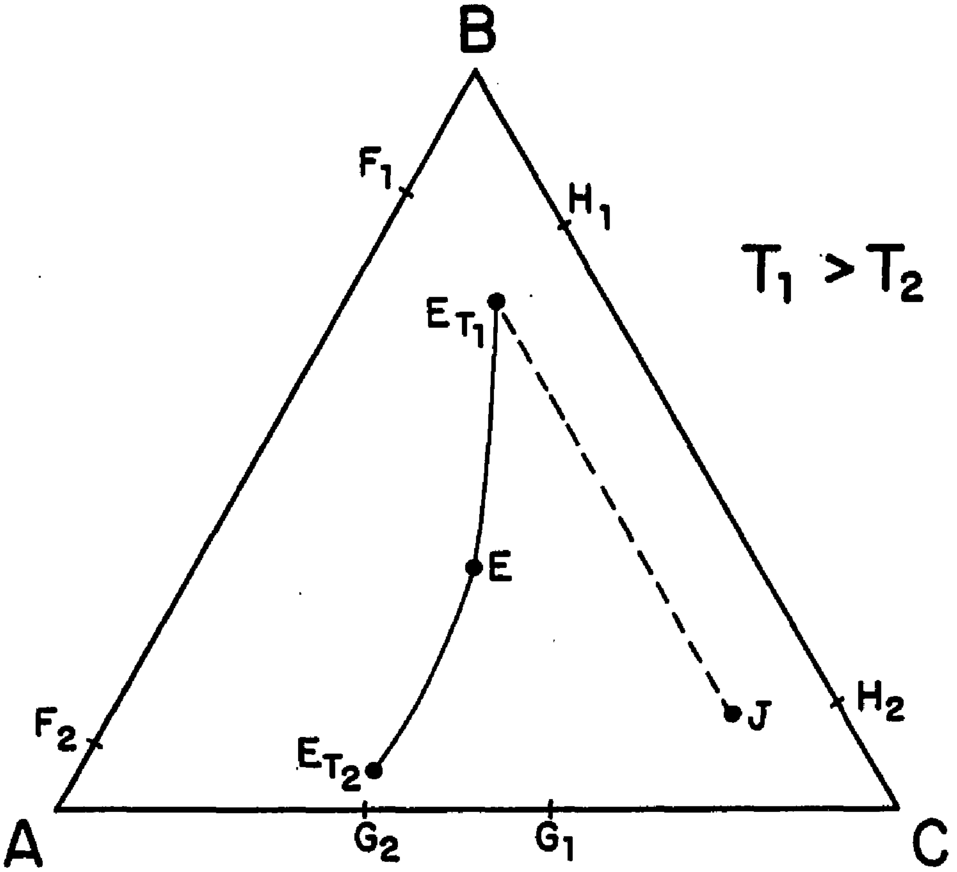
$K_1$ will increase and $K_2$ will decrease with increasing temperature. The changes of the points E,F,G and H in the temperature range $T_1$-$T_2$ are given in Figure 9. If the reaction is brought to equilibrium at a high temperature, $T_1$, and then cooled to a low temperature, $T_2$, the kinetic constraints change completely. The starting composition, for the second step, is $E_{T_1}$ which is not reachable from A at $T_2$. If $k_2$ is very large point J can be reached, for which $c/a_o$ can be larger than at any global equilibrium in the temperature range $T_1$-$T_2$. The concentration of C at point J is

$$(c/a_o)_J = \left[\frac{K_1 + K_1K_2}{1 + K_1 + K_1K_2}\right]_{T_1} \left[\frac{K_2}{1 + K_2}\right]_{T_2} \qquad (16)$$

$c/a_o$ in equation (16) can be larger than either $c/a_o$ at global equilibrium (Point E) which is $(K_1K_2/1+K_1+K_1K_2)_T$, or at equilibrium for reaction $A \rightleftharpoons C$, which is $(K_1K_2/1+K_1K_2)_T$. This depends on the changes of $K_1$ and $K_2$ in the temperature range $T_1$ - $T_2$. While in an isothermal reactor the side reaction forming B is always detrimental, the nonisothermal reactor can utilize B in a beneficial way to obtain a higher yield of C. A nonisothermal reactor permits trajectories which with a given set of reactions cannot be reached in isothermal reactors. The conditions for a final high yield of $c/a_o$ are in this case:

1. The yield of B in the first reactor must be large at $E_1$.
2. Finding a second temperature for which $(K_2)_{T_2}$ is large.
3. $k_2$ at $T_2$ must be large compared to $k_1$ and $k_3$.

For those conditions, limiting yields can be found solely from the thermodynamic properties of A,B and C. Again, only an approximate knowledge of the rate constants is used. For this system it is easy to distinguish experimentally if the



$A \overset{K_1}{\rightleftharpoons} B$ STRONGLY ENDOTHERMIC

$B \overset{K_2}{\rightleftharpoons} C$ EXOTHERMIC

(SLOW) $A \overset{K_3}{\rightleftharpoons} C$ WEAKLY ENDOTHERMIC

$(K_2)_{T_2}$ -LARGE

Figure 9: Non isothermal reaction path for reaction system in Figure 8.

optimal case is an equilibrium point and if a nonisothermal reactor improves the yield.

Assume that the catalyst operates in a temperature range $T_1$-$T_2$. For the three compounds (two dimensional) case, only one point on a kinetic trajectory is needed at each temperature. If c/b at this point is less than $c_{(equ.)}/b_{(equ.)}$ at E, then the system is a focal point system. If it is larger, the potential for an optimum along a kinetic trajectory exists. Therefore, additional points on the trajectory may be needed.

### 4.2.3 Char Gasification System

The linear example was brought because it allows rigorous analytical treatment. Similar results can be deduced for the char gasification system, though the calculations are more complex. Furthermore, the applicability of detailed balancing to this system has to be clarified. The main constraints on yields in the linear example were not due to free energy but due to the requirements of detailed balancing. Detailed balancing always applies close to equilibrium points whether the reaction is linear or not [Krambeck 1970]. For truely linear reactions it always applies, because the magnitude of the deviation from equilibrium cannot affect the properties of a linear system. For nonlinear reactions the following implication can be derived. Any single reaction $\sum \alpha_j A_j = 0$ cannot proceed if

$\prod[A_j]^{\alpha_j}=K_p$, where $A_j$ is the partial pressure of the compound $A_j$, and $_j$ is the stoichiometric coefficient of compound j in reaction i. That means that an individual reaction can only proceed if the free energy decreases along the path of the reaction's trajectory.

Thus, for example, if in the steam gasification system the concentration of CO, $H_2$, $CO_2$ and $H_2O$ are such that the shift reaction (VIII) itself is in equilibrium, then it cannot proceed along the shift reaction trajectory even if the individual concentrations of CO, $H_2$, $CO_2$ and $H_2O$ are far from the global equilibrium of the multicomponent system. The only way in which further shift can take place is if the concentration of one of the components is changed by one of the other reactions involved. This holds for catalytic reactions too. The above is true only if no other intermidiates are involved in substantial amounts, since the reaction can proceed along other pathways in a multi-component space.

The nonlinearity in steam gasification of carbon, allows a large number of possible reactions, and an exact analysis of the accessible compound space is much more complex. However, some strong similarities to the simple example in Figure 8 do exist. In an isothermal reactor the maximum yield of methane is at global equilibrium. Furthermore, a two stage nonisothermal reactor gives higher yields for very similar reasons. The main features of steam gasification for

SNG are thus very similar to the one given in Figure 9. There is no inherent constraint why global equilibrium should give maximum yield of methane. It is simply a property of present available catalysts which lead to trajectories that approach equilibrium from the undesired side (which is equivalent to the area AFEA in Figure 8).

The desired product is $CH_4$ but the only products formed directly from steam and char are CO and $H_2$. This can be seen from Figure 10, where typical experimental results from steam gasification of char impregnated with $K_2CO_3$ are plotted [Exxon 1978].

A plot of the trajectories requires a three dimensional plot, but in this specific case it can be simplified. In steam-carbon gasification, the number of hydrogen and oxygen atoms remains constant. Therefore, each trajectory can be described by two triangular diagrams representing the element balances. The trajectory of the experimental data approaches global equilibrium in a way that does not permit $CH_4$ to exceed global equilibrium. The trajectory is close to gas phase equilibrium (both methanation and shift reactions are fast compared to the steam-carbon reaction). Similar results can be derived from the knowledge of reaction rates. For the known catalysts, direct methane formation is very slow compared with CO and $H_2$ formation, and so methane formation must occur by methanation of CO and $H_2$.

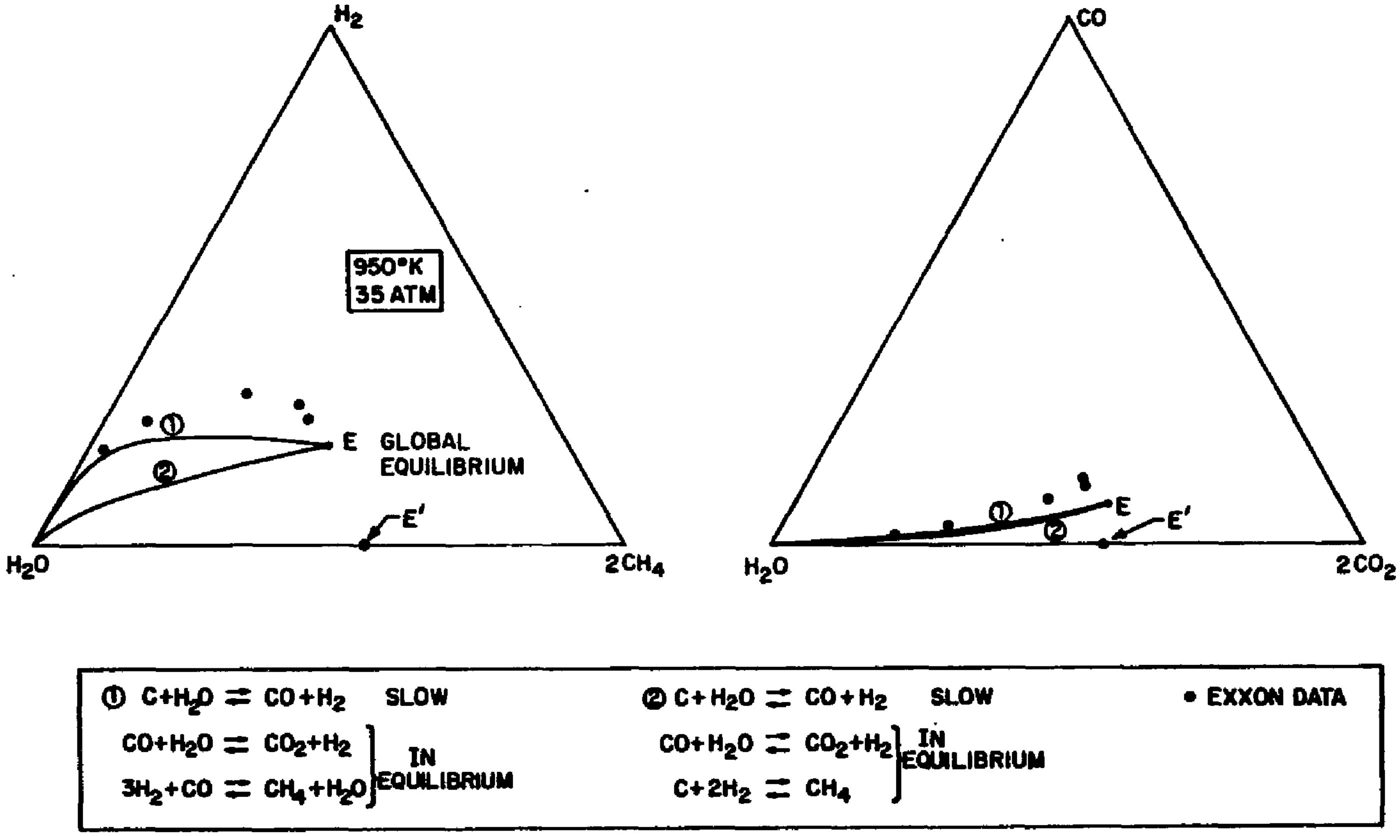


Figure 10: Kinetic trajectories of catalytic ($K_2CO_3$) steam gasification of char (data from Exxon 1978). E' - Equilibrium point for reaction I only.

Cabrera et al. (1981) reported direct methane formation from a steam-graphite reaction using various alkalioxides at 500-600K. The reaction was slow. Since at these temperatures the equilibrium concentration of CO and $H_2$ are negligible, it is hard to draw conclusions on the mechanism.

Blackwood and McGrory (1957) gasified char with steam at 1100K and 50 atm. and clearly observed direct methane formation. Based on their experiment, it was concluded that the kinetic mechanism leads to the overall reaction

$$1.5C + H_2O \longrightarrow 0.5CH_4 + CO \qquad (17)$$

(reaction V in Table 3), though one can also explain these data by assuming the occurance of reaction I. Blackwood and McGrory's choice of reaction V was not based on the overall data but rather on mechanistic arguments as to the elementary steps underlying the reaction. In that experiment direct methane formation was slow compared to CO and $H_2$ formation. If reaction V or I is slow compared to CO and $H_2$ formation, then the mechanism is irrelevant to the analysis. The maximum yield will be at global equilibrium. This is illustrated in Figure 11 where several hypothetical trajectories are given based on reactions (I,III,VIII) and (III,V,VIII). The temperature in Figure 11 was chosen to be 1200K since at high temperatures the potential of higher $CH_4$ yield over global equilibrium increases. It can be seen that in order for the methane yield to exceed global equilibrium, the reaction rate of rection I or V has to be

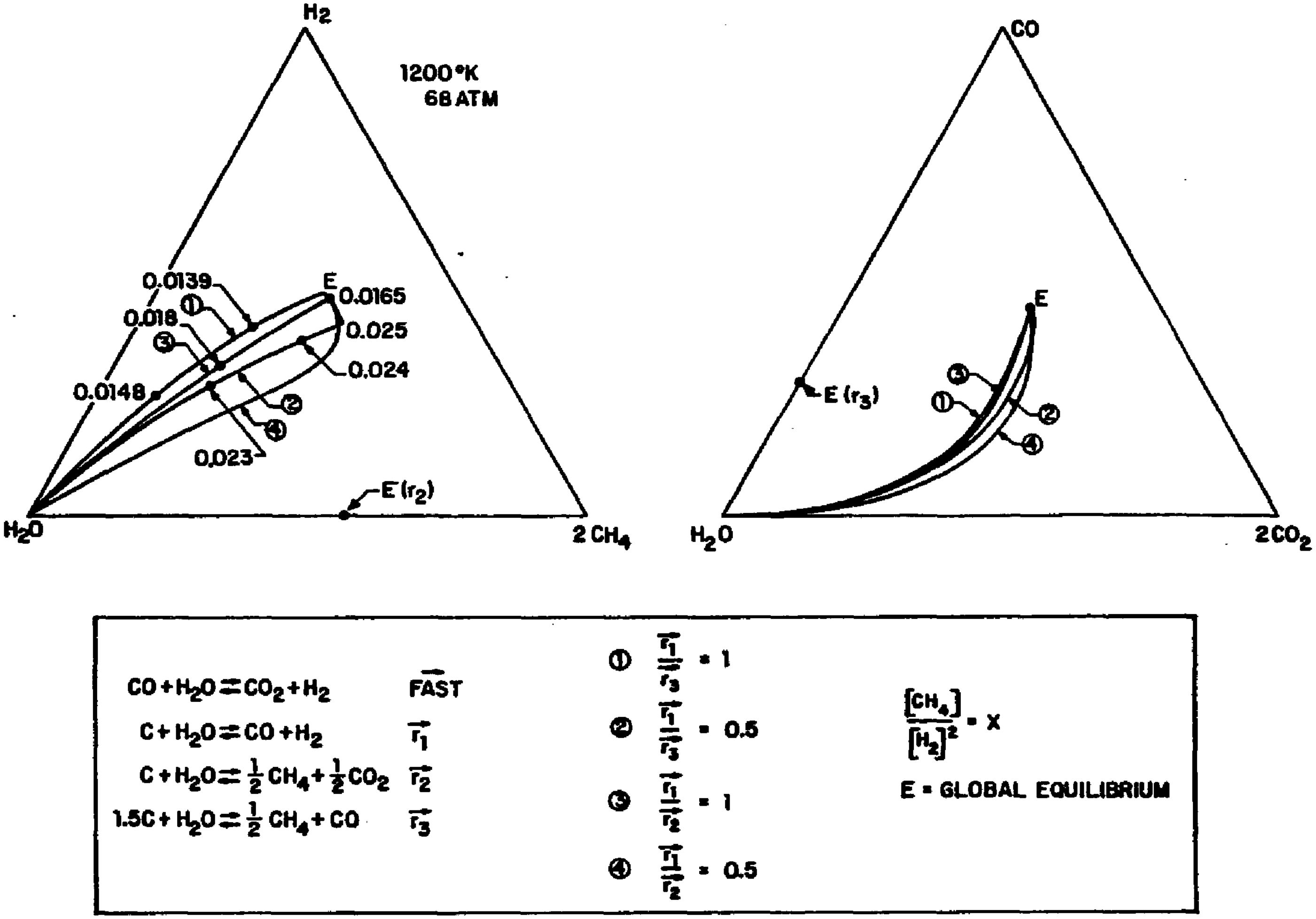


Figure 11: Hypothetical kinetic trajectories in steam gasification of carbon. $E(r_2)$, $E(r_3)$ - Equilibrium points for reactions 2 and 3 respectively.

at least 2 times higher than reaction III. The experiments indicate that without a catalyst, reaction III is faster than reaction I or V, and that a potassium catalyst accelerates reaction III more than reaction I. Most catalysts should also promote steam reforming of excess methane.

One can, however, ask how much would be the potential value of a catalyst that promotes reaction I or V. In this case, there is a big difference if the catalyst promotes reaction I or V. The maximum increase is much less dramatic for the seconed case, as can be seen from Figure 12. Reaction I is independent of pressure. At a temperature of 1100K it would allow a 50% higher yield than global equilibrium. It also has a low heat of reaction, an advantage which will be discussed later. Reaction V is strongly pressure dependent (see Figure 12). At 68 atm. and at temperatures below 1100K the maximum yield is less than global equilibrium. Only at 1200K does the methane yield approach that of reaction I. However, it is much more difficult to find a catalyst that operates selectively at high temperatures. At low pressures the maximum methane yield per mole steam of raction V exceeds that of reaction I at temperatures above 1000K. However, in the absence of a catalyst, reaction V is very slow at low pressures, and no catalyst is known to accelerate it in a selective way.

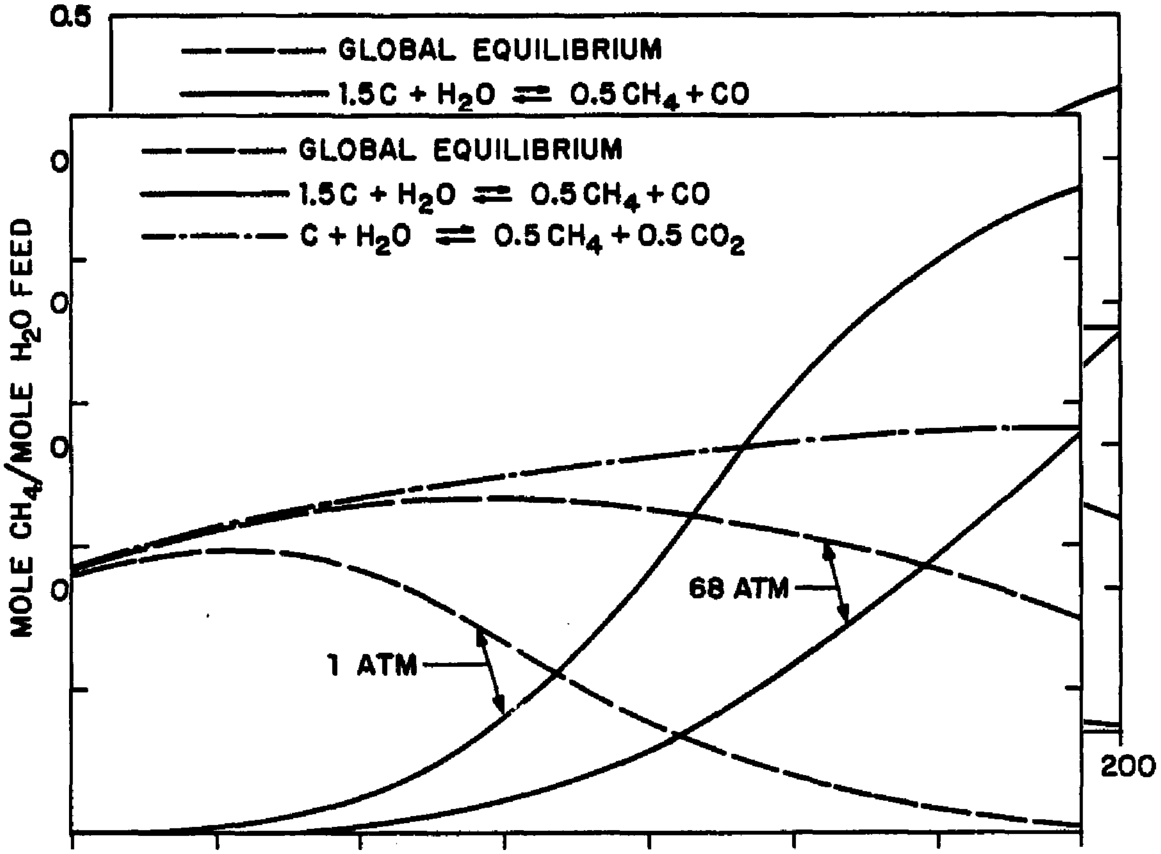


Figure 12: Methane yield in steam gasification of carbon as a function of temperature and pressure.

The trajectories in Figure 11 have one interesting property. At some points along the trajectory (and in some cases along the whole trajectory) the ratio of $[CH_4]/[H_2]^2$ exceeds the equilibrium ratio for reaction VI. Such a trajectory cannot be formed by the set of rections (III,VI,VIII,XI) without including direct methane formation.

While there are no complete trajectories reported, there are many individual data points observed that have this property [Squires 1961; Johnson 1974]. Based on this evidence, Squires concluded that the char has a higher free energy. Such a conclusion can only be justified if the free energy of the product's composition exceeds the free energy of the raw materials (steam and carbon). Some typical results quoted by Squires (1961) are given in Table 4. It is evident that the $CH_4$ yield is significantly lower than at global equilibrium, and that G is negative. High $[CH_4]/[H_2]^2$ ratios have only been observed in gasification of coals or chars, when both steam and char conversion were low. An alternative explanation will be discussed in the coal section. Here, it is sufficient to realize that with present catalysts the maximum $CH_4$ yield per mole of steam fed occurs, for carbon gasification, at global equilibrium, and therefore, global equilibrium is an optimal reactor condition.

## TABLE 4

Comparison of methane yield, in Char-Gasifiers, with computed equilibrium yield, assuming char to be graphitic carbon [May et al. 1958].

| Run # | 200 | 211A | 213A | 214 | 216 |
|---|---|---|---|---|---|
| T [$^{o}$F] | 1672 | 1672 | 1710 | 1764 | 1752 |
| P [psig] | 126 | 125 | 125 | 125 | 125 |
| $\frac{\text{mole inert (feed)}}{\text{mole } H_2O \text{ (feed)}}$ | 0.036 | 1.584 | 1.083 | 0.049 | 0.046 |
| $\frac{\text{mole } O_2 \text{ (feed)}}{\text{mole } H_2O \text{ (feed)}}$ | 0 | 0 | 0 | 0.238 | 0.111 |
| $K_p = \frac{Y_{CH_4}}{Y_{H_2}^2 P}$ | | | | | |
| Experimental | 0.042 | 0.035 | 0.04 | 0.037 | 0.039 |
| Equilibrium | 0.017 | 0.017 | 0.015 | 0.012 | 0.0126 |
| $\frac{\text{mole } CH_4 \text{ (product)}}{\text{mole } H_2O \text{ (feed)}}$ | | | | | |
| Experimental | 0.017 | 0.012 | 0.02 | 0.021 | 0.023 |
| Global Equilibrium | 0.058 | 0.036 | 0.036 | 0.024 | 0.033 |
| $\Delta$G(out-in) [Kcal] | -5.8 | -4.47 | -5.95 | -32.16 | -17.48 |

## 4.3 USE OF SIDE REACTIONS - NON-ISOTHERMAL TWO-STAGE REACTOR

Based on the simple example of a monomolecular system in Figure 9, one may now ask if a nonisothermal two-stage reactor can improve the conversion of steam. This can be seen in the example given in Figure 13. In the first reactor steam is brought to equilibrium over carbon at 1100K. The methane yield is given as point E. The product gas is then separated from the solid, cooled to 600K and passed over a shift-methanation catalyst at 600K. If the total gas mixture is brought to equilibrium in the gas phase, the equilibrium point (1) can be approached. Since in the gas phase this is a global equilibrium point, the trajectory is unimportant. The same composition can also be approached in the two-stage reactor without gas-solid separation, provided that at 600K all gas-solid reactions are very slow compared to the methanation and shift reactions. Available catalysts, such as nickel and iron, can achieve this step. The final composition at 600K will contain only traces of CO and $H_2$ at the equilibrium point, and has a much higher yield of methane per mole of steam than any isothermal reactor in Figure 6. The conventional SNG process uses a similar approach, though in the case of a Lurgi reactor, the high temperature stage does not necessarily approach global equilibrium, and $CO_2$ and $H_2O$ are removed together with $H_2S$ before methanation.

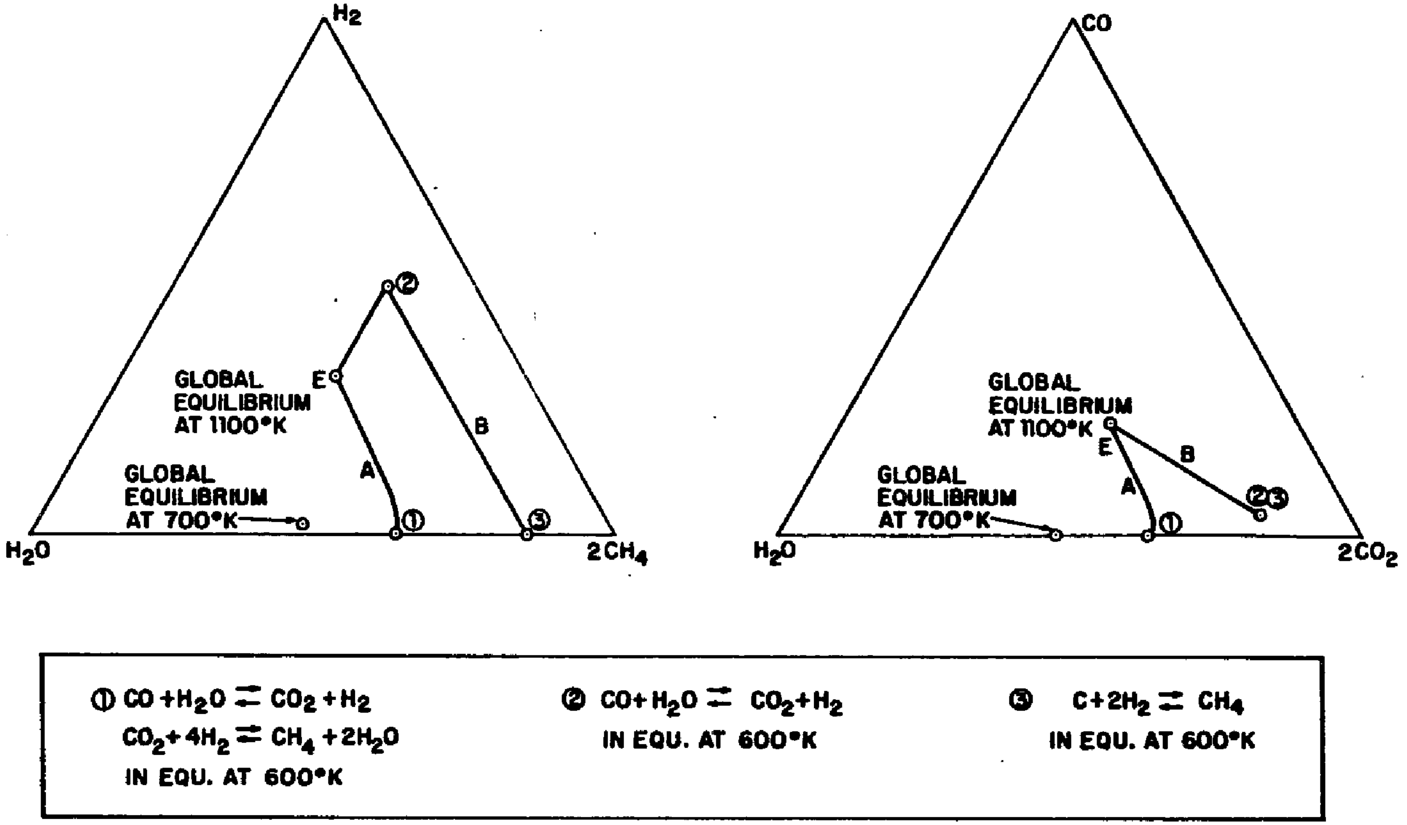


Figure 13: Kinetic trajectories for a two stage process at 68 atm..

There is another two-step route which can be superior with a proper catalyst. The same gas at 1100K is cooled to 600K, passed over a shift catalyst to shift equilibrium, (point (2) in Figure 13). The $CO_2$ and $H_2O$ are then removed, and the remaining $CH_4$ and $H_2$ mixture is passed over carbon at 600K. The equilibrium yield will be at point (3), which is superior to point (2). However, there is no known catalyst that can promote the hydrogasification reaction at low temperatures, and at higher temperatures the equilibrium conversion is low.

# Chapter 5

# DIFFERENT DESIGN ROUTES TO SNG - THERMODYNAMIC OPTIMIZATION

## 5.1 FOUR BASIC ROUTES

If it is acceptable that the maximum methane yield is limited by the global equilibrium, then there are several process options to produce pure $CH_4$ and $CO_2$, despite the CO and $H_2$ formation.

### 5.1.1 Gasification and Methanation - Two-Stage Process

Two schematic flow sheets are given in Figure 14. In the first version, the gas from the high temperature gasifier is directly methanated up to equilibrium at 700K in a second stage reactor. In the second version the steam is condensed, and the $CO_2$ removed before methanation. The basic principle of this approach was discussed in the previous section. Part of the excess steam can be used to shift the CO to increase $H_2/CO$ ratio. From the thermodynamic point of view there is no difference between 14(a) and 14(b). In reality, 14(a) is more efficient than 14(b), since cooling and reheating a gas always involves a thermal penalty. However, for coal, option 14(a) requires a sulfur resistant methanation catalyst.

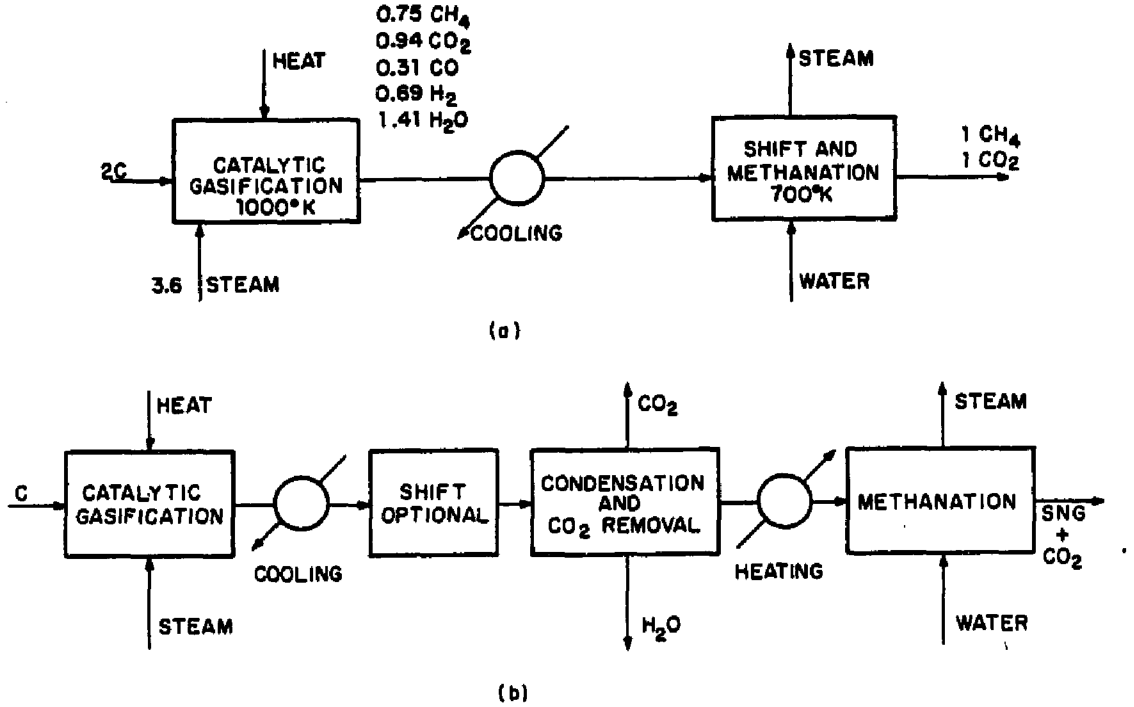


Figure 14: Schematic flowsheet of a two stage process.

The crucial point for high thermal efficiency is that equilibrium steam conversion is approached in the first reactor, and that no additional steam is used in the second reactor above the stoichiometric requirement to form a $H_2/CO$ ratio of unity. If pure steam is used as a feed in the first reactor, the $H_2/CO$ ratio is above unity up to about 1200K. However, a methanation catalyst which promotes the shift reaction is essential for high efficiency in this route, as the actual catalytic methanation requires an $H_2/CO$ ratio of 3 and also forms steam. In order to utilize the gas without prior shift, the catalyst has to be able to utilize steam formed by methanation to shift CO. One has to be careful in computing the steam requirements of this process. If the $H_2/CO$ ratio is above unity, degraded steam is formed in the methanation reactor, and it cannot be fully utilized. Steam conversion in the reactor is therefore an insufficient indicator of total steam requirements. The criteria should be the total steam fed into the first reactor per total methane formed at the exit of the second reactor.

### 5.1.2 Catalytic Gasification Process (Exxon)

While the two-stage process benefits from a catalyst, the main thrust in catalytic gasification at present is a recycle process in which the $CH_4$ and $CO_2$ are removed from the recycled gas. In Figure 15a a mass balance for this process is given at 1050K. The unconverted steam is condensed, and $CO_2$ is removed. Methane is cryogenically separated from CO and $H_2$, which are then recompressed and recycled to the reactor. The net result is similar to the ideal membrane process, but here, the CO and $H_2$ have to be separated and recompressed instead of just removing methane and $CO_2$. Compared with the two-stage process, (Figure 14) this route saves the methanation step. It also reduces the heat of reaction that has to be supplied to the gasifier.

However, energy-wise, this is a very inefficient membrane process. The theoretical losses are quite small, but in reality they are very significant and the success of the process hinges on the ability to find conditions that minimize recycle.

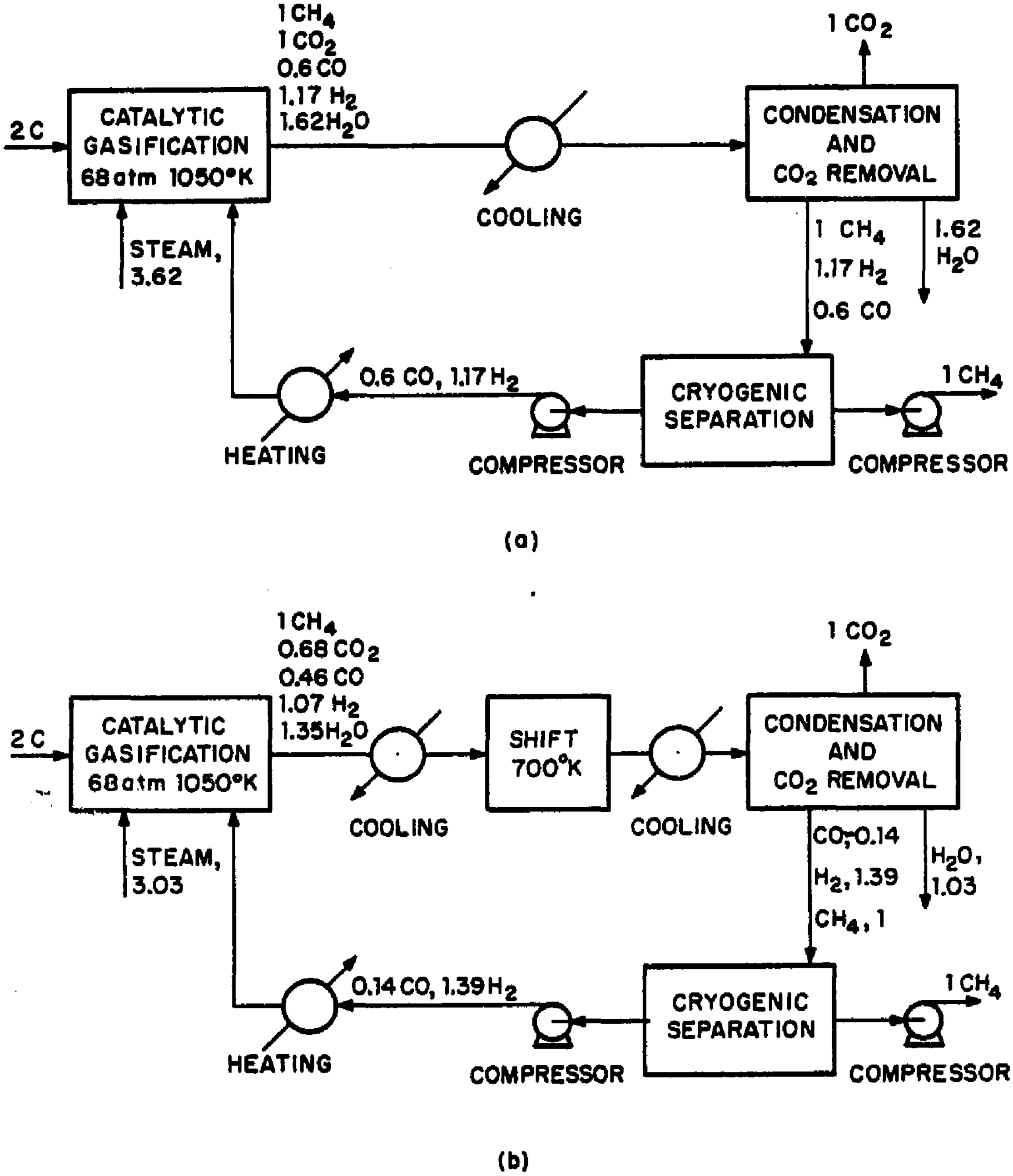


Figure 15: a) Schematic flowsheet for Exxon catalytic SNG process.

b) Schemetic flowsheet for Modified Exxon catalytic SNG process.

### 5.1.3 Modified Exxon Route

The analogy of the Exxon process with a semipermeable membrane suggests a significant improvment of the limiting thermal efficiency of the process (see Figure 15b). The product stream from the reactor still containes a large excess of unconverted steam, and it can be used to shift the CO in the product gas to $H_2$. The $CO_2$ and $CH_4$ are removed and the shifted stream is recycled to the reactor. This is equivalent to a membrane that preferentially removes $CO_2$ from the process, and therefore, drives it to higher conversion. The mass balance in Figure 15b shows that the modified process has higher steam conversion and a lower recycle ratio than the original process described previously. One can also interpret this route as an intelligent realization of hydrogasification.

### 5.1.4 Hydrogasification

The two-stage process can be modified by using the excess steam to shift the CO in the exit gas to $H_2$, remove $CO_2$ and $H_2O$, and use the $CH_4 - H_2$ mixture to gasify additional carbon. Path B in Figure 13 showed that this would give the highest steam utilization. To achieve close to complete conversion in the second reactor, a catalyst that promotes hydrogasification at 650K would have to be found. At present, the process has a lower limiting efficiency than the other routes discussed, and therefore, it will be discussed separately, after comparing the first three options mentioned.

## 5.2 COMPARING LIMITING THERMAL EFFICIENCIES

### 5.2.1 Steam Requirement

The theoretical steam requirements, as total fresh steam to the gasifier, are given in Figure 16. As expected, below 800K all routes have almost the same steam requirement since little amounts of CO and $H_2$ are formed. Above 1000K, the two-stage process starts to be significantly better than the Exxon process, whereas the modified Exxon process is better than both. It was claimed before that for the two-stage process, the optimum condition for maximum yield of methane in the high temperature stage, is global equilibrium. However, in noncatalytic gasifiers, methane yield is normally significantly less than the yield at equilibrium. The penalty of not reaching methanation equilibrium in the high temperature stage is indicated by curve IV in Figure 16. Curve IV shows the steam requirement for a two-stage reactor, in which CO, $H_2$, $CO_2$ and $H_2O$ are the only compounds formed at global equilibrium in the first stage. A significant penalty compared to the case with methane formation in the first stage is noted (curve I).

Figure 16 reflects the result of the previous section. By taking advantage of the side reactions and using a

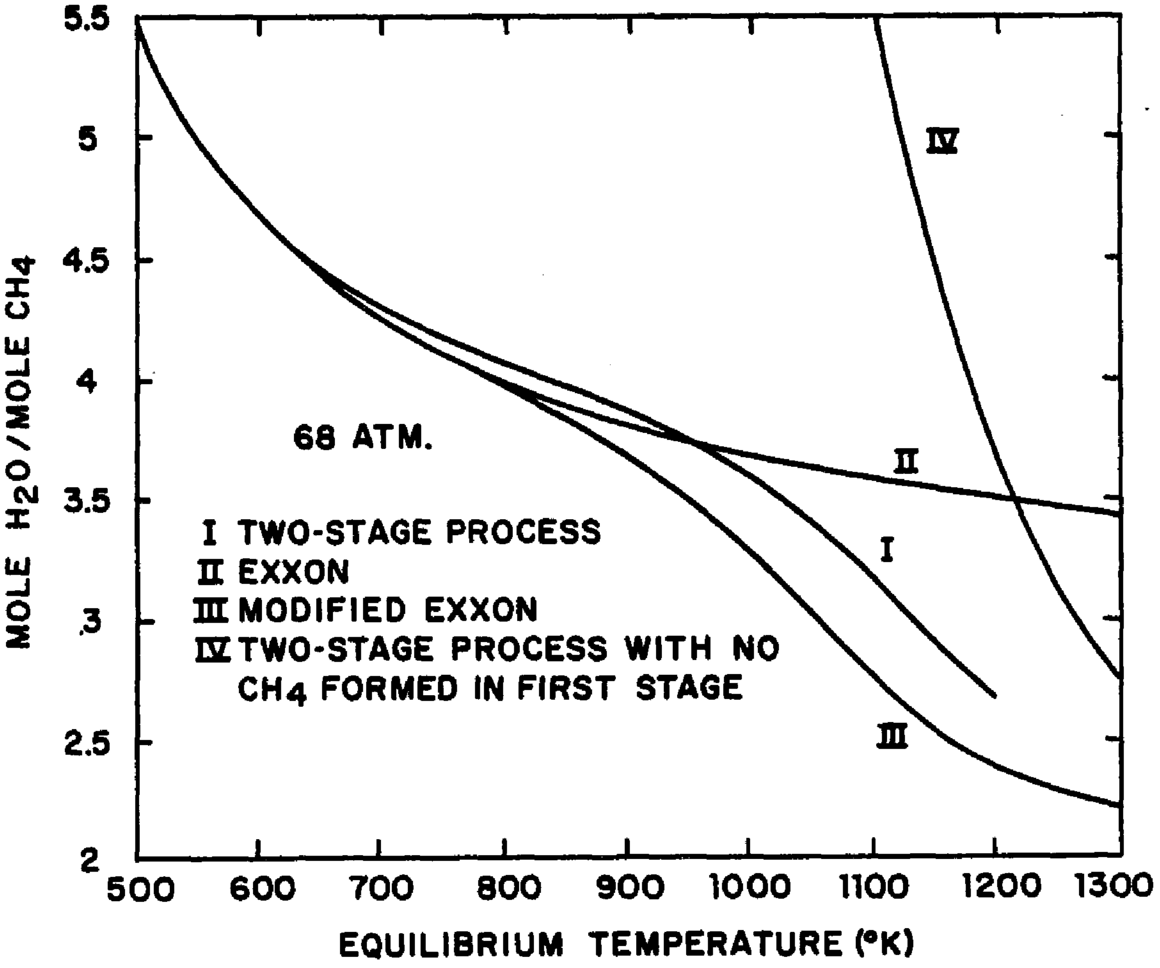


Figure 16: Steam requirements for the basic routes and a two stage process with no methane formation in the first stage, as a function of gasifier temperature.

nonisothermal route, steam requirement can be reduced significantly. The modified Exxon route is also a nonisothermal process, since it relies on achieving shift equilibrium at low temperatures. It even has a lower steam requirement than the two-stage process. The steam requirement of the Exxon process at high temperatures decreases with temperature only slightly, since the process does not benefit from the side reactions.

### 5.2.2 Heat of Reaction

Steam requirement is only one of the two key parameters determining thermal efficiency. Each one of the routes has an additional dominant parameter which is difficult to express in purely theoretical thermodynamic terms. For the two-stage process, it is the penalty of transferring heat to the reactor at high temperatures. For the Exxon and the modified Exxon processes, it is the practical energy requirement of the cryogenic separation.

Figure 17 shows the heat of reaction which is required to be supplied to the reactor, for the three processes. The Exxon process has the lowest heat requirement in the reactor and this heat is independent of temperature since only methane is formed. The heat requirement of the modified Exxon process increases slightly with temperature, but the requirement is low compared with the two-stage process.

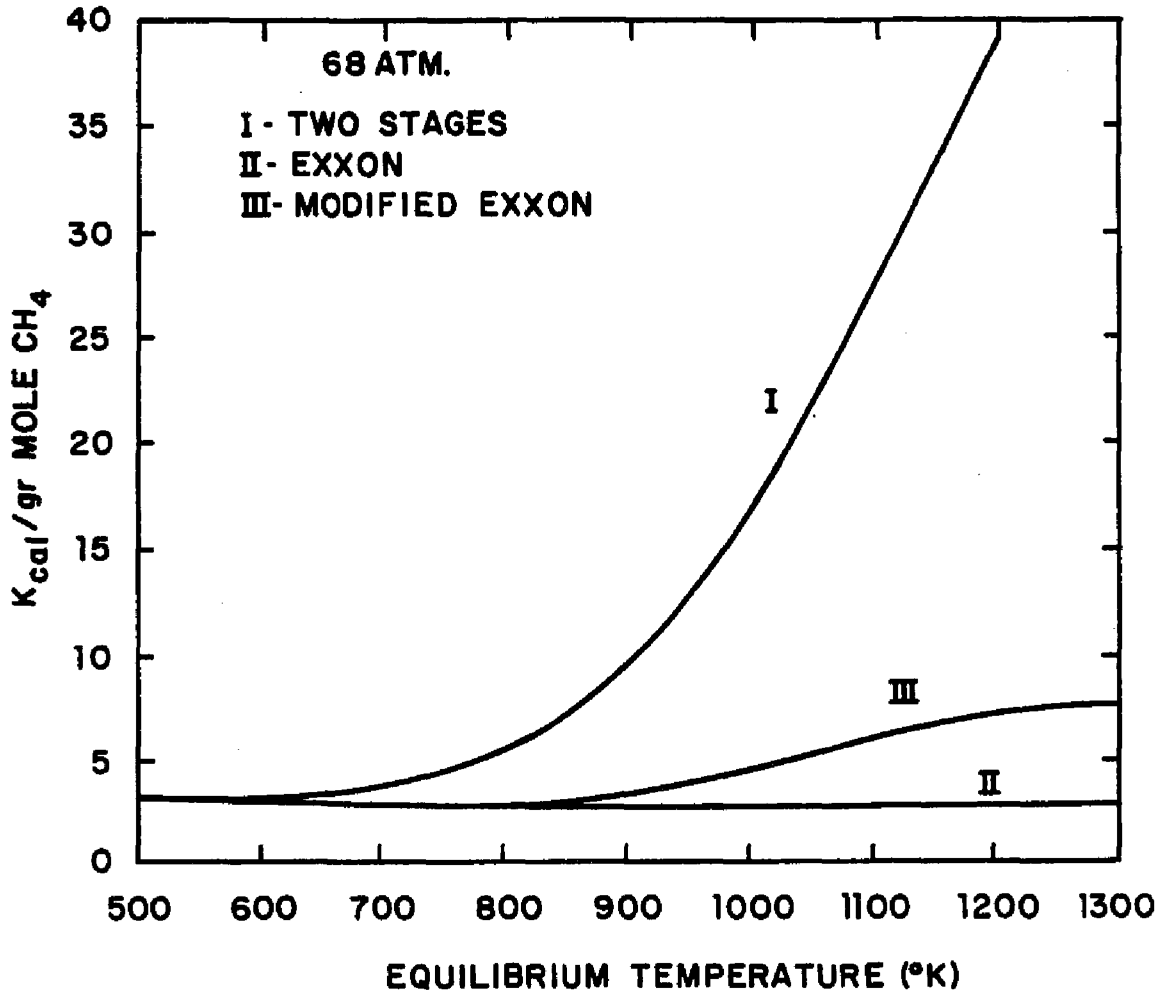


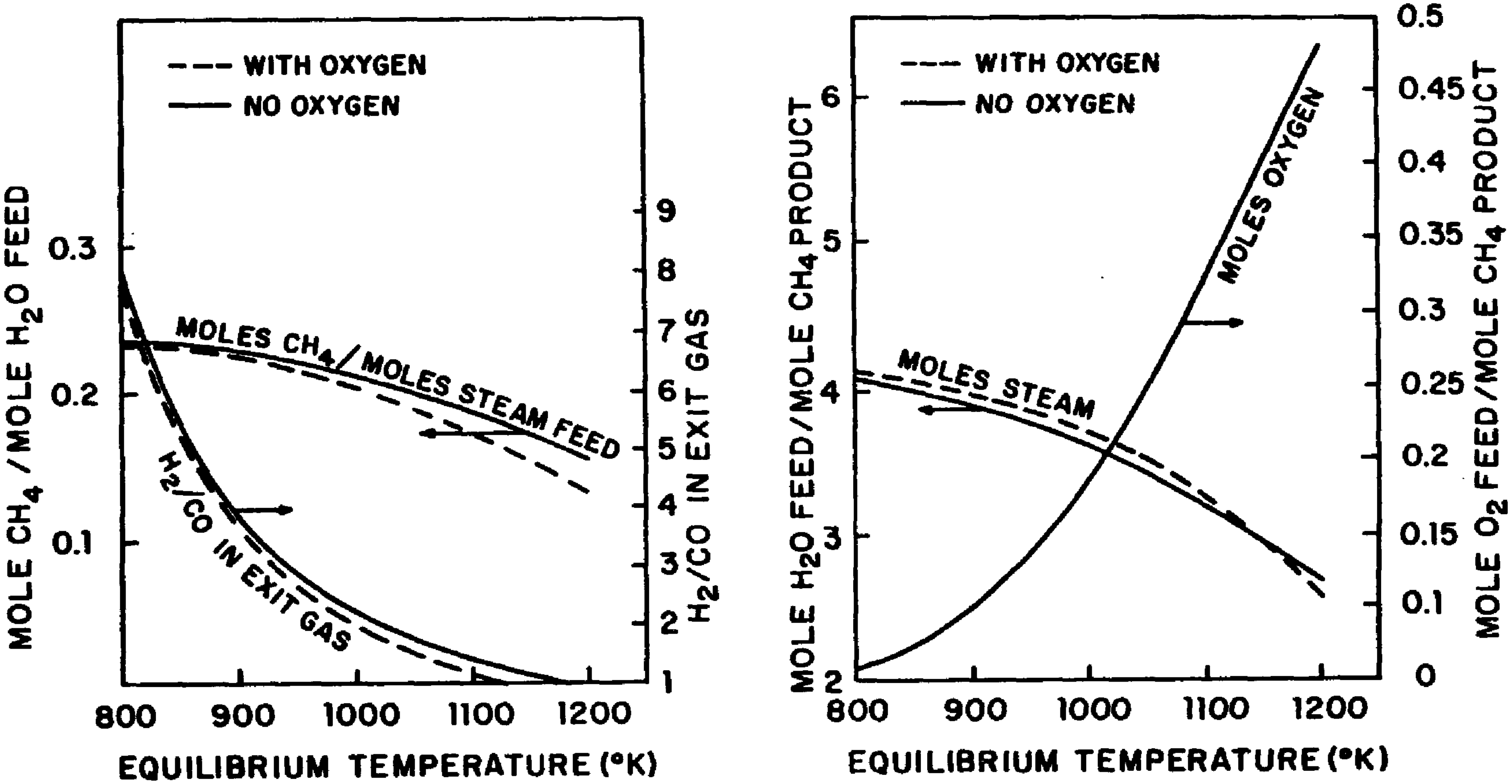
Figure 17: Reaction heat requirements for the gasifier in routes I, II and III.

The overall efficiency of transferring heat to a process in a heat exchanger, by combusting coal with air at atmospheric pressure, is between 85%-90%. The temperature is limited to below 1000K (1340F) by problems related to materials of constraction. In some opinions it would even be limited to 900K. It is also quite difficult and expensive to provide the necessary heat transfer surface in the gasifier. All processes presently under development use other means of supplying the heat required, such as:

1. Feeding oxygen directly into the gasifier or into a recycle stream.
2. Heating the feed or the recycle stream by combusting a clean gas (maximum temperature 1100K).
3. Circulating hot char or hot ash which are heated by combustion with pressurized air in a second reactor.

Interestingly, all three options have a very similar thermal efficiency of about 65% [Shinnar and Kuo 1978]. Therefore, it is sufficient to deal with the most common option which is feeding of oxygen directly to the gasifier. Feeding oxygen has a small additional penalty. It increases the $CO_2$ content in the gasifier, which in return reduces methane yield and steam conversion. This penalty is shown in Figure 18. It increases with temperature, but in the temperature range of interest, the penalty is small.

The fact that the heat of reaction is supplied to the gasifier at high temperature and regained at low temperature



(b) (a)

Figure 18: a) Steam and oxygen requirements for route I, supplying reaction heat inside the gasifier by combusting oxygen.
b) Impact of oxygen on $CH_4$ yield and $H_2$/CO ratio in the gasifier (route I).

is a severe penalty, which under present design constraints, is much larger than one would predict from straightforward thermodynamic analysis. However, once the data for this penalty is known, thermodynamic analysis can be used to compare different process options.

As was shown in Figure 5, the steam balance had a similar problem. There was a distinct difference between heat obtained above the boiling point of the high pressure steam and below it. Similarly, heat at high temperatures has a much higher penalty than equivalent heating value of coal. Availability analysis predicts correctly that the cost of heat of reaction should increase with temperature. However, there is one difference that design constraints impose on the heat balance of a plant. The cost of high temperature heat input is not a continuous function of temperature, but rather a step function. Furthermore, the cost is about 50% more than the availability of the heat used from combusting coal, and can be triple the availability value of the heat of reaction required. For approximate analysis, it might be preferable to represent the value of any heat flow in the plant in terms of step functions, such as given in Table 5. Both the temperature of the step and the penalties depend on the plant design and on the design constraints accepted by the designer. Table 5 is a strong oversimplification, and accurate values can only be obtained by detailed flowsheets.

## TABLE 5

## Multiplication factors for estimating heat values of input and output streams

Input Streams

| Temperature [°F] | Factor |
|---|---|
| >1200 | 1.5 |
| > 600 | 1.0 |
| < 600 | 0.5 |
| > 300 | |

Output Streams

| Temperature [°F] | Factor |
|---|---|
| >700 | 1.0 |
| <700 | 0.5 |
| >400 | |

### 5.2.3 Recycle Penalties

The two versions of the Exxon process have another penalty, which dominates their thermal efficiency and their design. The two versions require cryogenic separation of CO and $H_2$ from methane and recompression of the gases to gasifier's pressure. The cryogenic separation is energy-wise very inefficient and provides a heavy energy penalty.

Both the number of moles gas recycled and the energy requirements for the recyle are shown in Figure 19. In both routes the energy requirements are far larger than the requirements indicated by thermodynamics, and therefore, energy requirements based on practical experience are used. As can be seen from Figure 19 the modified Exxon process has a very significant advantage at high temperatures. Figure 19 shows one important feature of the separation process in the two Exxon routes. For low recycle, real energy requirement is almost independent of the CO and $H_2$ content, which is a typical feature of many practical separation processes.

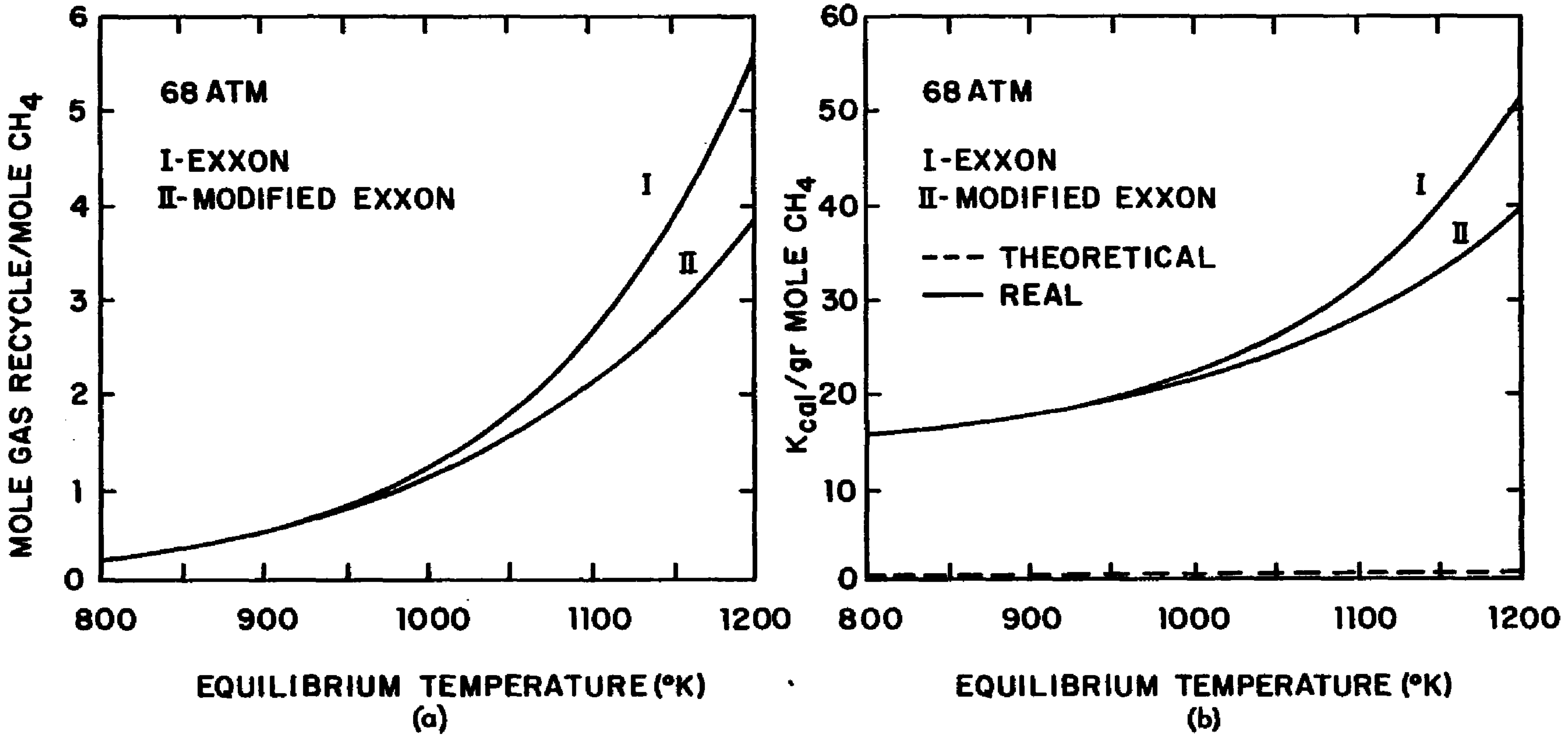


Figure 19: a) Recycle requirements for routes II and III as a function of gasifier temperature.
b) Energy requirements for cryogenic separation and recompression for routes II and III as a function of gasifier temperature (based on heat input to boiler in power plant).

### 5.2.4 Comparing the Routes - The Practical Advantage of the Two-Stage Process

The penalty for unconverted steam decreases with increasing temperatures. The penalty due to supplying heat of reaction in the two-stage process and due to recycling requirements in the two Exxon routes, increases with increasing temperature. Therefore, one should expect an optimum temperature for each of the three processes. Figure 20a shows the minimum total energy requirements of the three routes as a function of temperature. The total energy requirements include the basic requirements for all processes, namely, 2 moles of steam per one mole of methane, the heat of reaction, and the three main penalties of the processes:

1. Penalty due to incomplete steam conversion.
2. Penalty due to the heat of reaction.
3. Penalty due to the cryogenic separation process.

Since the penalties for recycle and oxygen separation are taken from practical experience, the same is done for the generation of steam. Two lines are shown for all processes. One for temperature range where indirect heat transfer might be possible. The other line includes the penalty of direct heat transfer at high temperatures.

The two-stage process is superior compared with the two Exxon processes. Since recycle separation has an inherently

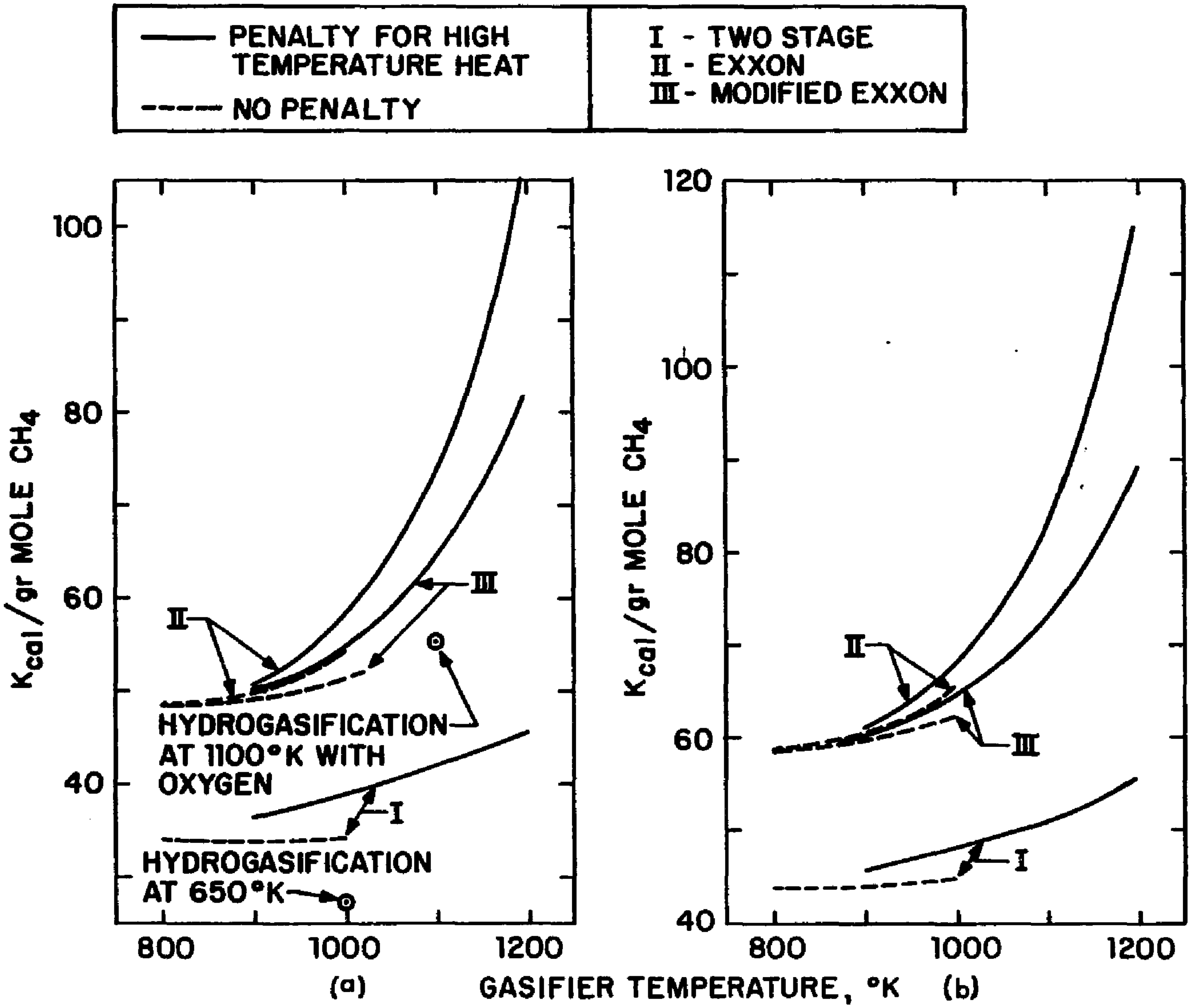


Figure 20: Minimum total process energy losses for the routes mentioned. a) Ideal flowsheet. b) Actual flowsheet.

large minimum penalty, it is preferable to operate the reactor at low temperatures, where the heat requirement as well as CO and $H_2$ content, are small. If a catalyst, which operates at low temperature could be found, the two-stage process would be clearly superior. There is no present process under development which uses indirect heat transfer to supply heat to the gasifier by combustion of coal. It will only make sense at temperatures below 900K, and there are no catalysts which operate well at that range of temperatures.

The main advantage of the two-stage and the modified Exxon processes over the original Exxon process is not in the small difference in energy requirement, but in the ability to operate at higher temperatures without a severe penalty. Operating at higher temperatures can either allow use of cheaper catalysts or use of smaller reactors due to higher reaction rates.

The catalytic two-stage process, as well as the modified Exxon process allow, with existing catalysts, significantly higher efficiencies than existing processes, which, due to process constraints, operate far from optimum conditions. However, all such processes involve similar compromises between the penalty, due to feed of oxygen (or other means of supplying the heat of reaction) and efficient steam utilization. Therefore, this approach is applicable to them, too.

Noncatalytic processes require higher temperatures in the first stage and in most cases have lower methane yield than the yield at global equilibrium. The penalty of lower methane formation can be estimated by looking at the limiting case with no methane formation in the first reactor. The penalty for supplying the heat of reaction is 40 Kcal/gr-mole methane versus, 10-20 Kcal for the catalytic two-stage gasification-methanation reactor with maximum methane formation in the first stage.

Figure 20a is based on a comparison of the main penalties, excess steam and separation requirements (oxygen for two-stage and cryogenic separation for the two Exxon processes). Figure 20b shows similar results based on actual flowsheeting. The overall results are very similar.

### 5.2.5 Hydrogasification

Till now hydrogasification was excluded from the discussion. It would have been the best route if a catalyst operating at 650K could be found for hydrogasification. Yet, present catalysts (or noncatalytic hydrogasification) require high temperatures above 1000K (and preferably above 1100K) to achieve reasonable gasification rates. At high temperatures the equilibrium is unfavorable, as can be seen from Figure 21, where the conversion of $H_2$ over carbon, as a function of temperature, is plotted. If the gas already contains methane, as it does for any gasifier operating

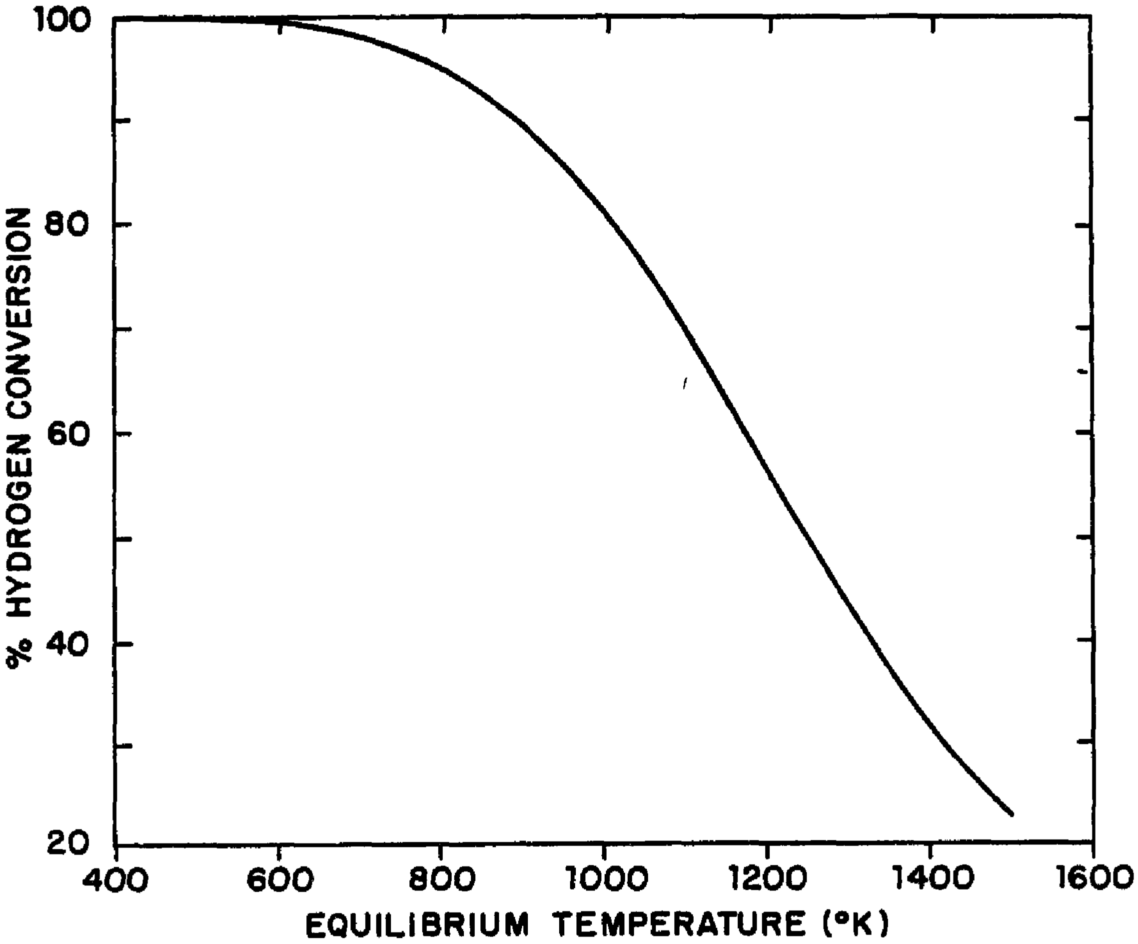


Figure 21: Conversion of $H_2$ over carbon in an hydrogasifier.

below 1300K, then conversion is further limited. To get a high hydrogen conversion, a cryogenic separator is needed. A possible process scheme is given in Figure 22. In this case an incremental 0.069 mole of $CH_4$ per mole steam fed is achieved, compared with the two-stage process at the same temperature (see Figure 14). The higher yield of $CH_4$ per mole $H_2O$ also reduces the penalty of supplying heat to the first reactor. However, this advantage is more than nullified by the large energy requirements of the cryogenic separator. In the two Exxon processes the need for an oxygen plant was eliminated and a cryogenic separator substituted. In this case both are needed. To illustrate that, Figure 20a shows the energy requirements for the two points, one for the hypothetical case where the hydrogasifier operates at 650K, and a second where both the steam gasifier and the hydrogen gasifier operate at 1100K. The second case is worse than the two-stage route. For certain coals, hydrogasification can still be attractive due to other process considerations, especially since many noncatalytic gasifiers operate far from the optimum conditions.

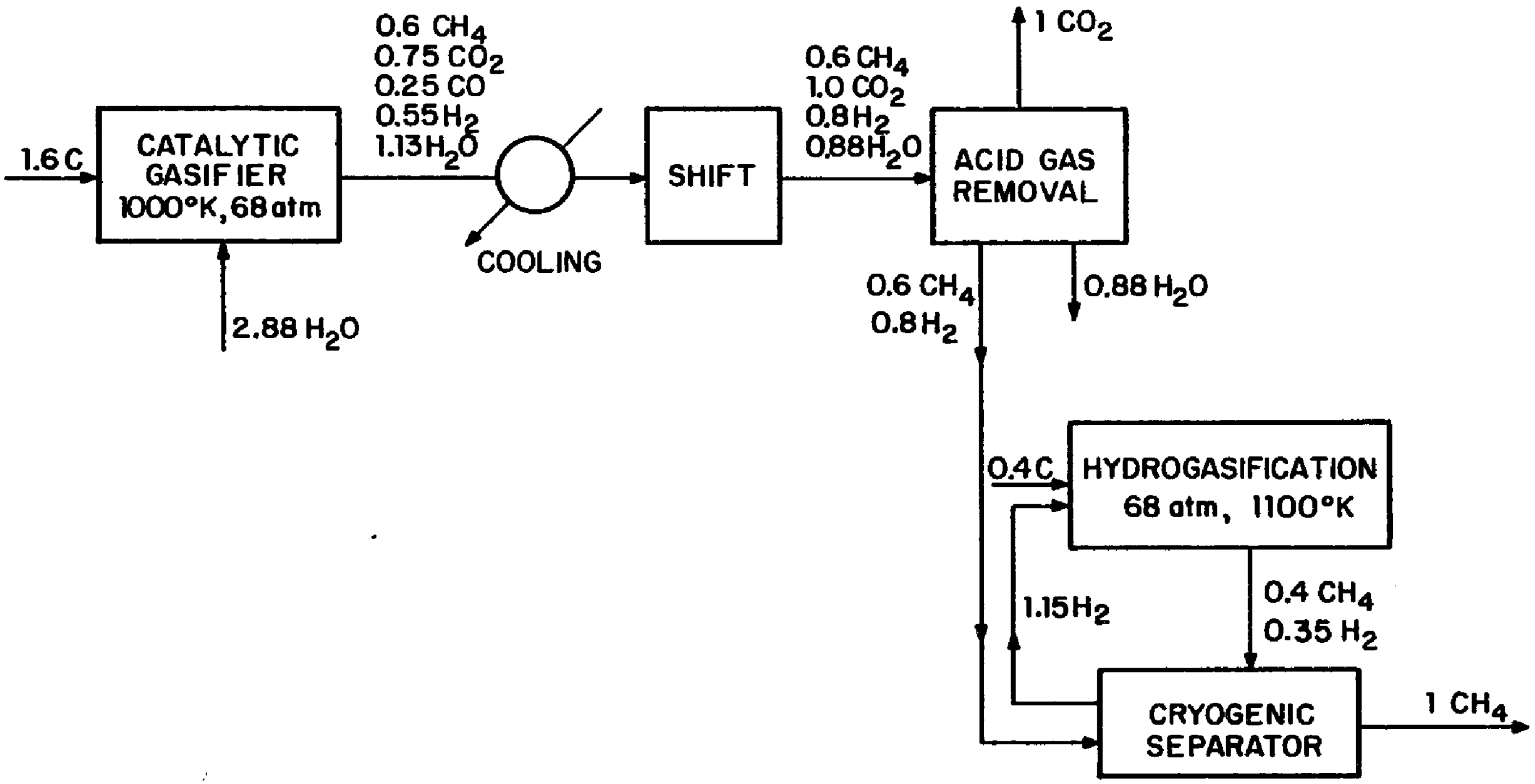


Figure 22: Schematic flowsheet for hydrogasification process.

### 5.2.6 Effect of Pressure

Until now all processes were considerd at a fixed pressure, 68 atm. It was noted before that the main parameters determining thermal efficiency, for the three routes under consideration, were the steam requirement, heat of reaction and recycle ratio for the two Exxon processes. Pressure has one further effect. If the methane is desired at 68 atm., lower operating pressures will require compression of the product. The equivalent of Figure 20 is shown in Figure 23, where the total minimum energy requirements for the three processes are compared as a function of pressure at 1000K.

For the Exxon process, the heat of reaction and the net steam requirement are independent of pressure. For the other routes, the heat of reaction decreases with pressure, but net steam requirement increases with increasing pressure. The recycle ratio for the two versions of the Exxon process decreases with increasing pressure. The advantage of low steam requirement at low pressures is negated by higher reaction heats, higher recycle ratios and by the requirement of product compression.

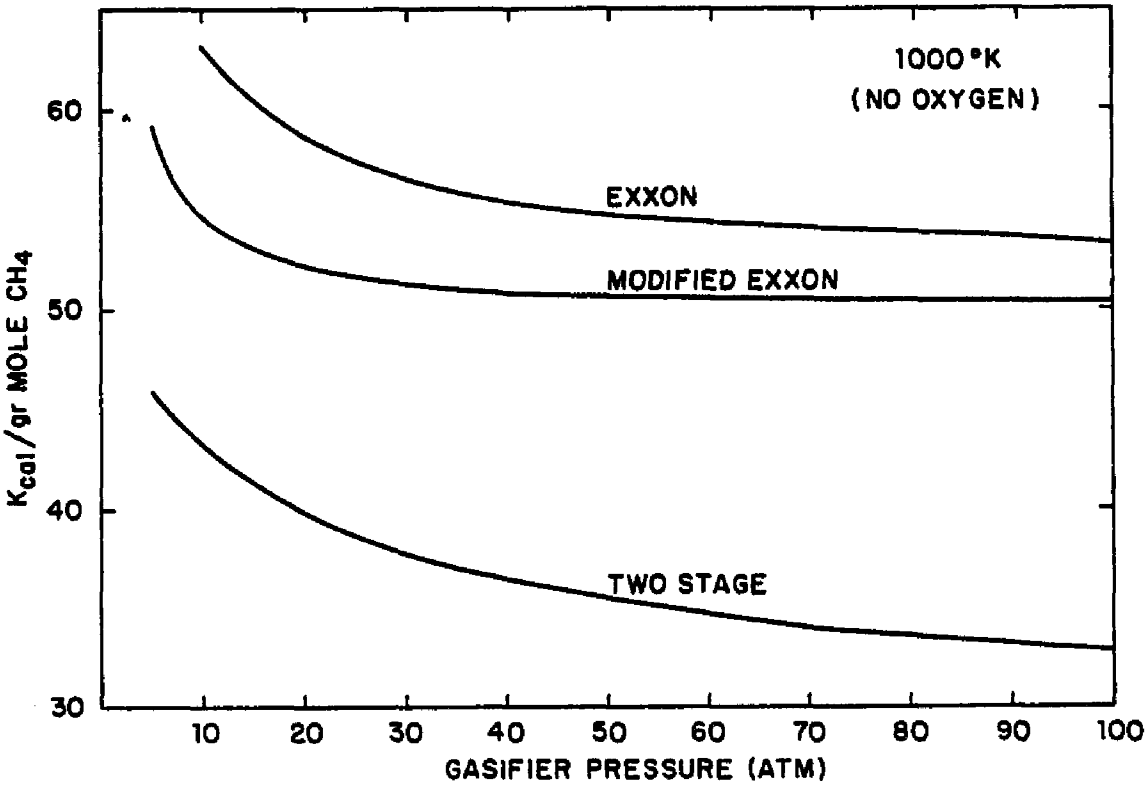


Figure 23: Minimum total energy losses as a function of pressure for the three routes (product at 68 atm.).

## Chapter 6

## REACTIONS WITH COAL

### 6.1 HYPOTHETICAL DIRECT REACTION WITH COAL

The results of the previous analysis of reactions with carbon are similar to the results of the reactions with coal and coal chars. The reason for the similarity is that in all gasifiers coal decomposes to char and volatiles faster than any direct reaction with steam or hydrogen. As will be shown later, char has similar properties to those of carbon, which justifies the previous emphasis on carbon.

Consider a hypotetical coal with the composition $CH_{0.8}O_{0.1}$ (typical Eastern coal). (Real coal also contain sulfur and nitrogen but it will be neglected in this analysis). The overall reaction of this coal is given in reaction XIII (Table 3). A reasonable estimate of the value of $\Delta G^o_{298}$ and $\Delta H^o_{298}$ can be made (see Appendix A).

$$1.738CH_{0.8}O_{0.1} + 1.304H_2O_{(g)} \longrightarrow CH_4 + 0.738CO_2$$

$$\Delta G^o{}_{298} = -10.46 - 1.738x\Delta G^o{}_{298}(\text{coal}) = -11.53 \text{ Kcal/gr-mole} \quad (18)$$

$$\Delta H^o{}_{298} = -11.93 - 1.738x\Delta H^o{}_{298}(\text{coal}) = -6.71 \text{ Kcal/gr-mole}$$

It is noted that the reaction has a negative $\Delta G^o_{298}$. Although the heat of vaporization for water is still needed, only 1.3 moles of steam per mole $CH_4$ are required (instead of 2 moles steam per mole $CH_4$ in the case of the reaction with carbon). In reality, despite the negative $\Delta G^o_{298}$, the process is only slightly better than for carbon, and the reason for that is the fact that the reaction

$$CH_{0.8}O_{0.1} \rightarrow \text{char} + \text{volatiles} \qquad (19)$$

is much faster than all other direct reactions of steam with coal. Thus, char and not coal is gasified.

Since coal decomposes to char rather fast above 700K (800F), a catalyst, operating below 650K (600F), is needed to prevent char formation. Such a catalyst can be a major achievement, but the present analysis is concerned only with known catalysts or known reactions. Therefore, the following analysis will take into account that coal devolatilizes first, and so char is the solid which is gasified.

## 6.2 THE EFFECT OF CHAR-GASIFICATION ON GLOBAL EQUILIBRIUM

As for coal, the thermodynamic properties of the char can only be estimated. An estimation based on different assumptions as for the structure of the char is presented in Appendix A. Since the estimates are approximate, a range of values is given for the heat of reaction and for the free energy of formation. The overall reaction of steam with char can be written as:

$$1.86CH_{0.3} + 1.72H_2O_{(g)} \longrightarrow CH_4 + 0.86CO_2$$

$$\Delta G^{o}_{298} = 0.76 - 1.86 \times \Delta G^{o}_{298}(\text{char}) = -2.03 \text{ to } -0.82 \text{ Kcal/gr-mole} \quad (20)$$

$$\Delta H^{o}_{298} = -12.5 - 1.86 \times \Delta G^{o}_{298}(\text{char}) = -10.6 \text{ to } -12.7 \text{ Kcal/gr-mole}$$

$\Delta G^{o}_{298}$ is negative at low temperatures, but at temperatures where reaction rates are appreciable, $\Delta G(T)$ is slightly positive. The equivalent equilibrium yields of Figure 6 are given in Figure 24, assuming again that char is the only solid compound and that $CH_4$, $H_2O$, $CO$, $CO_2$ and $H_2$ are the only compounds in the gas phase. At a temperature of 1000K, higher $CH_4$ yield than that of $CH_4$ yield at global equilibrium over carbon, can be thermodynamically achieved, but steam conversion is incomplete. Thus, conversion is still equilibrium constrained.

However, close to equilibrium, the assumption that only one type of char is formed in the solid phase is not realistic. It implies that any reverse reaction in the gas phase forms exactly the same char. The gas-solid reactions known to have reasonably large reaction rates are the Boudouart reaction $2CO \rightleftharpoons C+CO_2$ and methane decomposition reaction $CH_4 \rightleftharpoons C+2H_2$.

The conditions of carbon formation from synthesis gas and from methane have been studied extensively in conection with steam reforming and shift reaction [Rostrup-Nielsen 1972; Gruber 1975; Dent 1945]. At temperatures below 1000K the gas

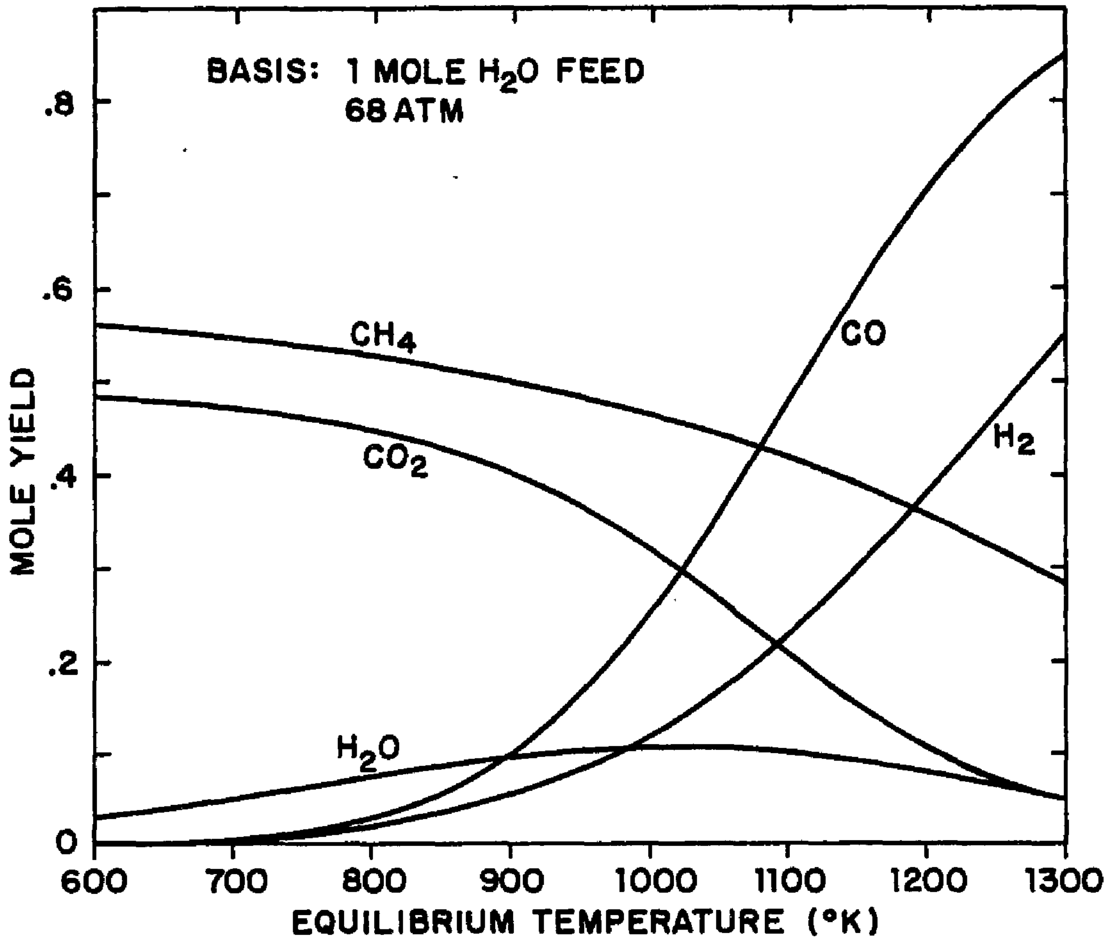


Figure 24: Estimate of product yield at equilibrium for steam-char reaction.

can sustain a sufficient supersaturation (gas phase concentrations which have higher ratios of $[CH_4]/[H_2]^2$ or $[CO]^2/[CO_2]$ than permissible at equilibrium over graphitic carbon) for long times. The permissible supersaturation depends on the catalyst. The carbon formed has a higher free energy of formation compared with graphite. At temperatures above 1000K, the free energy of the carbon formed is independent of the chemical composition of the catalyst, and is similar to that of graphite. The gas phase cannot sustain a supersaturation since carbon formes easily on any surface. Regrettably, there is little information available on the composition of the chars formed in these reaction which might contain small amounts of oxygen and hydrogen. The few available data on equilibrium over char, such as those of Exxon (1978), indicate that the properties of this char are fairly close to those of graphite. There is no evidence that either thermal or catalytic reactions can synthesize a complex char from CO, $H_2$, $CH_4$ and $CO_2$ in the time scale of the gas residence time in a gasifier.

This leads to two interesting conclusions:

1. If a complex char is brought to equilibrium with steam or hydrogen, the equilibrium mixture will contain carbons or simple chars which result from reactions such as methane and CO decomposition.

2. The reaction of a complex chemical structured char with steam or hydrogen, near equilibrium, is a two-step reaction involving an irreversible decomposition to carbon followed by reaction with steam or hydrogen.

The first conclusion results from the fact that $CH_4$ and CO decomposition have finite reaction rates forming simple chars at temperatures and at pressures of interest. The second conclusion results from the requirement of detailed balancing. As can be seen in Figure 24 steam conversion is incomplete. Therefore, the overall reaction is reversible and the forward reaction rate at the beginning is larger than the backward reaction by just one order of magnitude. If the formation of the char from the gas is very slow, the forward reaction near equilibrium, involving steam and char, must be slow too. The fact that coal and complex chars are not formed at reasonable reaction rates from either CO, $H_2$ or $CH_4$ implies that the forward reaction must have some irreversible steps in order to be fast. Irreversible in the sense that conversion in these steps is far from equilibrium, or that equilibrium conversion is so high that the ratio between backward and forward reaction is very large. In the latter case even a negligible rate for the backward reaction is consistent with a fast forward reaction.

Consider for example the case of reaction VI with the same char as in reaction (20).

$$CH_{0.3} + 1.85H_2 \rightarrow CH_4 \qquad (21)$$

Let assume that this char is significantly different from graphite. At 1100K and 68 atm. the conversion of $H_2$ at equilibrium is 83%. It is also known that at 1100K, the backward reaction of (21), or formation of this specific char from $CH_4$, is slow compared to formation of simple char from methane with properties similar to graphite. At equilibrium the forward and the backward reactions have equal reaction rates, and therefore, near equilibrium the forward reaction of reaction (21) must be slow compared to the hydrogasification of a graphitic carbon.

The partial pressure of pure hydrogen at 68 atm., far from equilibrium, is only 4 times larger than that at equilibrium. As the overall reaction rates of reaction (21) and reaction VI can both be considered in the same order, reaction (21) should still be very slow compared to hydrogasification of the char formed from decompositin of $CH_4$. If hydrogasification of this char is fast, far from equilibrium, then it must involve an irreversible step, different from reaction (21).

An irreversible step can be explained in the following way. Consider reaction (22) to represent a hypotetical overall devolatilization reaction of coal

$$CH_{0.8}O_{0.1} \rightarrow 0.7C + 0.2CH_4 + 0.1CO \qquad (22)$$

At 1000K the equilibrium pressure is $10^{10}$ atm. This is so much higher than standard pressures of gasification that the reaction can be truely irreversible and the coal completly disappears. At normal pressures (less than 1000 atm.) one can, therefore, never observe a net backward reaction, which will require a pressure greater than $10^{10}$ atm. to be observed. A very fast forward reaction is, therefore, consistent with the knowledge that the backward reaction is not observed. Reaction (22), at normal gasifier pressures, will go to completion, just as devolatilization of coal. It would be misleading to consider this an equilibrium, since for a solid-gas reaction, complete conversion can still be far from equilibrium. Any reaction that has a very high conversion can occur fast, despite the fact that the backward reaction is not observed. This is not true for reactions where conversion is strongly limited by equilibrium considerations.

Irreversible reaction can occur in gasification of devolatilized char. Consider for example the reaction

$$12CH_{0.3} + 0.2H_2 \longrightarrow CH_4 + 11C \qquad (23)$$

At 1100K and 68 atm. $K_p=10^8$ and the potential conversion is very high. The equilibrium partial pressure of hydrogen at 68 atm. is $10^{-5}$ atm. The ratio between this pressure and the initial pressure is $10^7$. If the rate of reaction (23) is considered to be first order, the reaction rate at equilibrium will be $10^7$ times slower than the initial rate. The rate of the forward reaction at equilibrium gives a good estimate for the backward reaction. A fast reaction rate of reaction (23) at 68 atm. will, therefore, be consistent with the fact that the backward reaction is too slow to be observed, as the formation of other chars from $CH_4$ is 10 times faster.

Reaction (23) is just a hypothetical overall reaction. A large number of such reactions are possible between char and hydrogen or steam (see Table 6). Such a mechanism would explain the results of Wen and Huebler (1965). According to this reference, hydrogen and devolatilized char were reacted in a bomb reactor at 975K and 137 atm. Initialy, the $CH_4$ concentration was high and the ratio of $[CH_4]/[H_2]^2$ exceeded equilibrium. The $CH_4$ concentration later decreased with time, and reached a final equilibrium value equal to that over graphite. In these experiments, char conversion was low. High char conversion could only be reached with large excess of $H_2$. At high char conversion the ratio $[CH_4]/[H_2]^2$ did not exceed $K_p$ for graphitic carbon. Initial high methane yields have been obsereved by other investigators, and it has been suggested that freshly formed char is more active. However, no case has been reported with almost complete char conversion and high ratio of $[CH_4]/[H_2]^2$ in either hydrogen or steam

## TABLE 6

### Equilibrium constant for reactions of char with hydrogen and steam

| | Equilibrium Constant | |
|---|---|---|
| | 1000°K | 1100°K |
| $C + 2H_2 \rightarrow CH_4$ | 0.089 | 0.035 |
| $CH_{0.3} + 1.85H_2 \rightarrow CH_4$ | 0.522 | 0.217 |
| $12H_{0.3} + 0.2H_2 \rightarrow CH_4 + 11C$ | $1.4\times10^{8}$ | $9.4\times10^{7}$ |
| $6.66CH_{0.3} + H_2 \rightarrow CH_4 + 5.66C$ | $1.1\times10^{4}$ | $6\times10^{3}$ |
| $C + H_2O \rightarrow CO + H_2$ | 2.5 | 11.0 |
| $CH_{0.3} + H_2O \rightarrow CO + 1.15H_2$ | 15.2 | 68.9 |
| $6.66CH_{0.3} + H_2O \rightarrow CH_4 + CO + 4.66C$ | $3\times10^{4}$ | $6.8\times10^{4}$ |

The numbers given in the table are upper bounds estimated on the basis that the free energy of formation of the char is $\Delta G^{o}_{1000K} = 3.5$ $\Delta G^{o}_{1100K} = 3.95$ Kcal/gr-mole.

gasification. A reaction mechanism similar to reaction (23) followed by gasification of char would explain the above experiments and be consistent with the overall knowledge of char gasification. A more detailed discussion of the effect of thermodynamic properties of coal and char on coal gasification, is given in Appendix B.

The example above illustrates another application of thermodynamic analysis in reaction engineering that merits wider application. The knowledge that a backward reaction is slow, coupled with an estimate of the equilibrium constant, allows to estimate which forward reactions are likely to occur.

The high irreversibility of reactions (22) and (23) was due to the fact that the primary coal or char formed another char with a lower free energy together with gaseous products. The exact nature of the process may be complex but there is no need to know it for estimating the likelihood of the overall reaction.

Very little is known about the nature and the extent of irreversible reactions of different chars. All that is known, is that in hydrogasification, it is possible to achieve much higer yields of methane per mole $H_2$ fed at low char conversion than at high char conversion [Wen and Huebler 1965], and that at high char conversion the equilibrium properties of the char are close to that of graphite for both steam and hydrogen gasification

[Blackwood and McGrory 1957; Johnson 1974]. Less is known about irreversible reactions between char and steam, but again, there is no evidence that high steam or char conversions can exceed that of graphite. It is also known that the properties of the char can change during gasification [Blackwood and McGrory 1957]. Regrettably, these effects have not been taken into account in kinetic studies of gasification rates, most of which have been carried out at low char conversion. The data are, therefore, questionable for design at high char and steam conversions. For this study this is no obstacle, but for real design, proper data will be highly desirable.

Much more is known about the devolatilization of coal [Anthony and Howard 1976; Solomon 1979; Zaharadnik and Grace 1974]. It is generally assumed that when coal devolatilizes, it first formes volatiles and char. The volatiles either decompose to char, gases and liquid products, or react with steam or hydrogen to form methane, CO and $H_2$.

The product distribution of devolatilization of coal is, therefore, a result of competing reactions (decomposition of volatiles versus their reaction with steam or hydrogen). It therefore, depends on pressure, temperature, rate of heating, and the composition of the gas in which the coal is devolatilized. These conditions can affect the overall efficiency of the process. Thermodynamics cannot give any information on relative rates. It can only provide bounds on likely product distributions. But once it is realized that gasification of coal is a two-step process, thermodynamic analysis provides guidlines for reactor design.

## 6.3 ADVANTAGE OF PRIOR-DEVOLATILIZATION

The advantage of prior devolatilization can be understood if it is realized that equilibrium composition is just a function of element balance, temperature and pressure. The results will be the same if instead of coal- char, $CH_4$ and $CO_2$ are fed to the gasifier. It is obvious that feeding the products to the gasifier will reduce conversion of steam. It was concluded in the case of the membrane process that it is preferable to remove products selectively from the reactor.

At global equilibrium over char, feeding coal without prior devolatilization is equivalent to feeding carbon, hydrogen and oxygen separately. The only way in which the coal chemical structure affects the reactor is in the heat requirements. If the conversion is incomplete, then it simply increases the ratios of H/C and O/C fed to the reactor. If conversion is limited, and unconverted char is removed from the reactor, both the composition of the char and the amount of the char removed are required to compute steam conversion at equilibrium. If char is gasified, it is enough to assume that the overall char composition does not change during the reaction and that the char has the same composition as does the char in the reactor. For computing the equilibrium yields in this case, only one gas-solid phase reaction is required (for example reaction III in Table 3). The results for two types of coal are given in Figures 25 and 26. The yields per mole steam fed are insensitive to conversion if conversion exceeds 90%.

In all the examples with coal, an ultimate conversion of 90% will be used. The unconverted char can be combusted in a fluidized bed boiler to raise steam. Thermodynamically, it is better to burn char instead of coal because the hydrogen in the coal is valuable; yet it requires the development of boilers which are able to handle the char. This does not mean that the $CH_4$ yield cannot exceed global equilibrium over graphite. The $CH_4$ yield from devolatilization (or reasonable initial reactions) exceeds the global equilibrium value at high temperatures. The problem is to achieve a high char conversion by steam carbon reaction without decomposing the $CH_4$ by either reaction VI or XI (steam reforming of methane). The latter is catalyzed by all catalysts that promote char gasification and also by many minerals contained in the ash. Designing a reactor in order to achieve a kinetic optimum between steam conversion and methane yield would be very difficult, as reaction rates vary from coal to coal due to the difference in ash composition and catalytic activity.

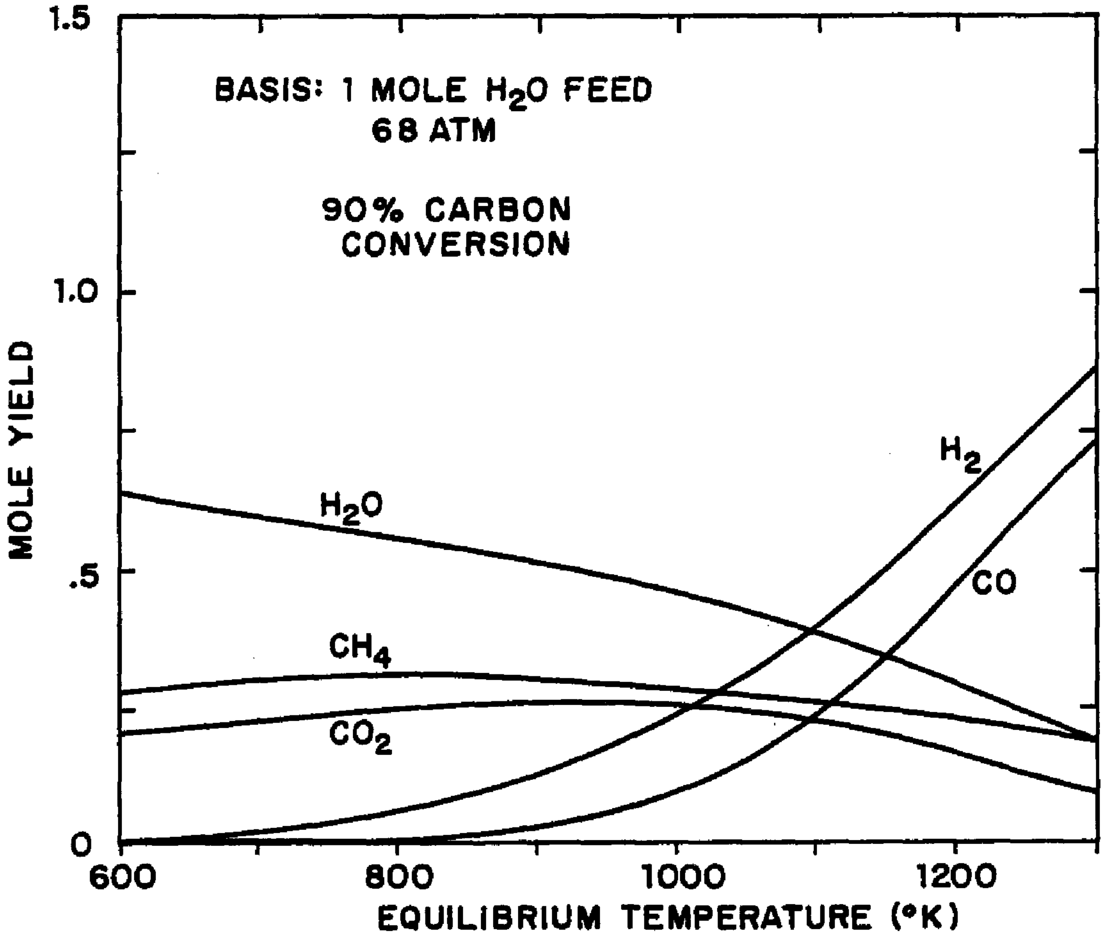


Figure 25: Real equilibrium yields for steam gasification of Eastern coal.

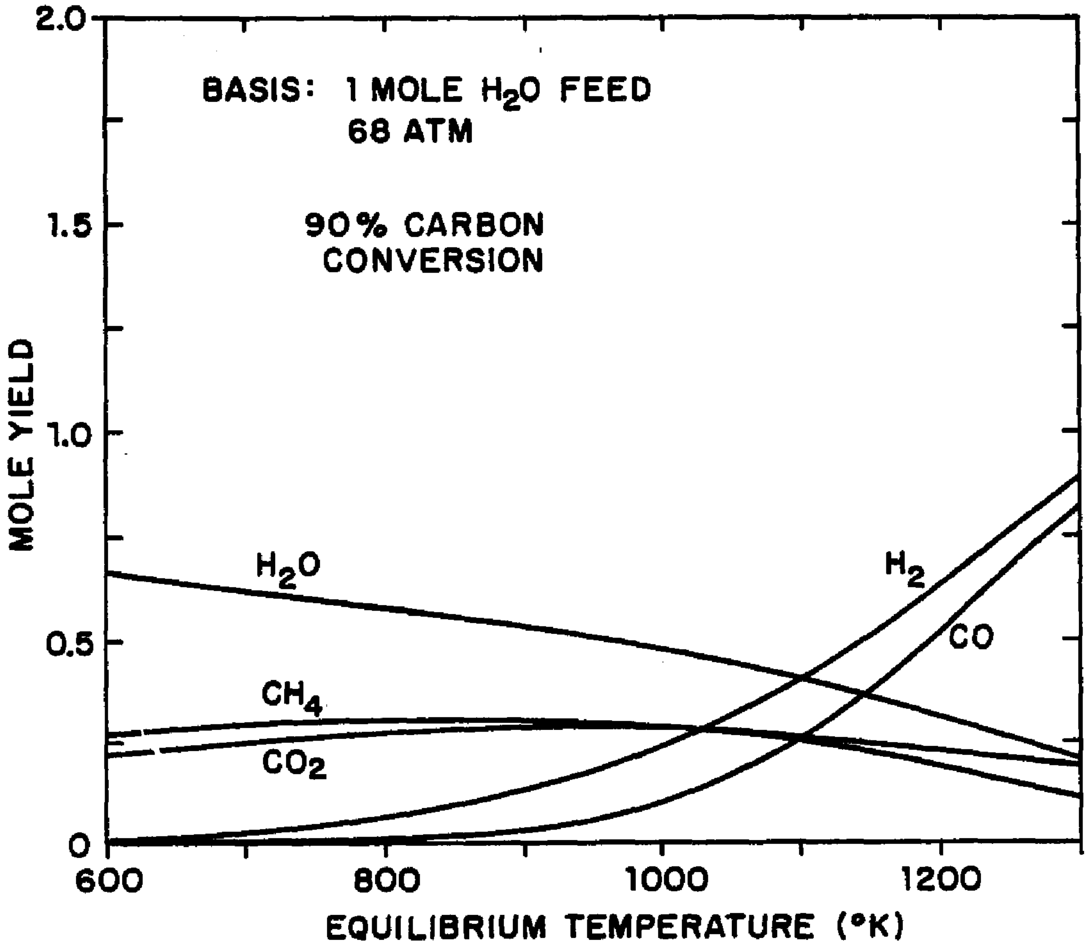


Figure 26: Real equilibrium yields for steam gasification of Western coal.

Anyway, a two-stage reactor with a separate devolatilization stage can have higher potential steam conversion and better overall thermal efficiency compared to such kinetic optimum even if it is achievable. Methane formation in a char gasifier always reduces steam and heat requirements (see Figure 16). All is needed to evaluate the potential of an optimal countercurrent gasifier, with a devolatilization stage, is a knowledge of equilibrium over carbon and an estimate for the products of the devolatilizer. The latter depend on the conditions in the devolatilizer as well as on the coal, but for this analysis an approximate estimate is enough. Typical devolatilization products for two coals are given [Yoon et al. 1977]:

Eastern coal

$$CH_{0.8}O_{0.1} \text{-->} 0.8CH_{0.3}+0.13CH_4+0.017CO_2+0.053CO+0.012H_2O+0.009H_2$$

Western coal

$$CH_{0.8}O_{0.2} \text{-->} 0.71CH_{0.3}+0.14CH_4+0.03CO_2+0.113CO+0.012H_2O+0.009H_2$$

What are the implications of these assumptions? Consider for example, the gasification-methanation route. In Figure 27 two versions of this process are given. In the first, (27a), coal is introduced directly into reactor 1 and the products are fed to reactor 2. In 27b the coal is first

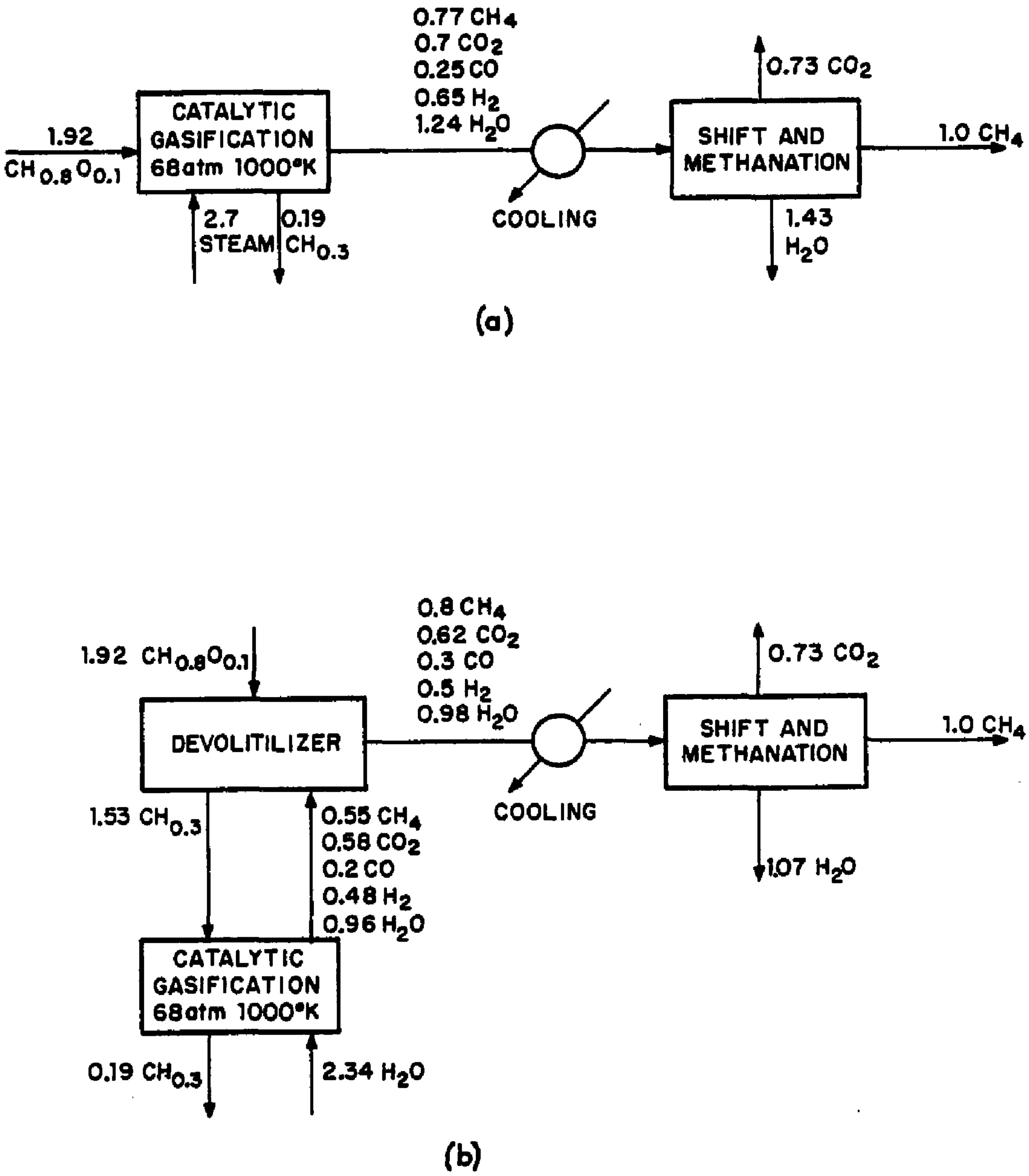


Figure 27: Schematic flowsheet for a two stage process.
a) Without prior devolatilization.
b) With prior devolatilization.

devolatilized and the products are fed to reactor 2. Since the example is at 1000K, steam requirements directly reflect energy requirements. A clear advantage for prior devolatilization can be noted. Since devolatilization is fast, it will have very little effect on the composition of the product gas, and it can be achieved by contacting the product gas from reactor 1 with the fresh coal.

Prior devolatilization has an additional advantage, which is neglected here. In both cases the coal is heat exchanged with the product gas. In practice, this is impossible without the occurance of devolatilization, and so, to prevent devolatilization, the coal has to be fed cold. Feeding the coal cold into the reactor increases the heat penalty by about 3-10 Kcal/gr-mole $CH_4$. This is a process constraint that affects the limiting efficiency.

Its disadvantage is that coal-pyrolysis generates tars and agglomerated compounds which may not be completely decomposed. This makes not only heat recovery difficult, but introduces byproducts, which in some cases, may be undesirable. One way to overcome this problem is to increase the residence time in the devolatilization stage, and choose the temperature such that all undesirable byproducts like tars and phenols are completely cracked, while the other gasification reactions are slow. This is neither a thermodynamic nor a kinetic constraint but relates to process development and cost considerations.

## 6.4 COMPARISON OF IDEALIZED LIMITING PROCESSES

In the previous section it was shown that the lowest steam and heat requirements are obtained in a countercurrent gasifier, in which the coal is devolatilized in a separate stage with the hot gas from the char-gasification zone. Therefore, the overall heat requirements strongly depend on the properties of the char-gasification stage. In that case, the results of Figure 20 are directly applicable to coal gasification, as the devolatilization zone can be added to any of the four processes mentioned.

Ideal process requirements for the two-stage process with or without prior devolatilization are given in Table 7. It is noted that the subbituminous coal has a small advantage over bituminous coal with prior devolatilization, and a disadvantage without it. In noncatalytic gasifiers subbituminous coals have an additional advantage due to higher reactivity, which allows them to approach equilibrium more closely.

In principle, the same approach can be used for the two Exxon processes. The coal fed can be devolatilized, and the combined product, from both the reactor and the devolatilization stage, sent to a cryogenic separator. Figure 28 shows simplified flowsheets for one typical coal. Here, as in the carbon case, the modified Exxon process has an advantage over the Exxon process. If the coal is fed without devolatilization, there is a significant penalty, as can be seen from Table 7.

# TABLE 7

## Comparison of steam, recycle and energy losses for various processes with coal

Basis: 1 mole $CH_4$

68 atm., 90% carbon conversion

EASTERN COAL

| Process | | Temperature °K | Steam [Mole] | Recycle [Mole] | Oxygen [Mole] | Heat Above 900°K [Kcal] | Total Heat [Kcal] | Efficiency $\eta_L$ % |
|---|---|---|---|---|---|---|---|---|
| Exxon | Straight Feed | 1000 | 2.7 | 1.08 | | 4.49 | 38.7 | 74.5 |
| Exxon | | 1030 | 2.67 | 1.35 | | 6.23 | 41.5 | 73.7 |
| Modified Exxon | | 1030 | 2.23 | 1.2 | | 7.25 | 37.9 | 74.8 |
| Two-Stage | | 1000 | 2.73 | | 0.18 | | 24.9 | 78.8 |
| Two-Stage | | 1100 | 2.31 | | 0.34 | | 31.2 | 76.8 |
| Exxon | Prior Devolatilization | 1000 | 2.5 | 1 | | -0.14 | 33.5 | 76 |
| Exxon | | 1030 | 2.48 | 1.23 | | 1.05 | 35.7 | 75.4 |
| Modified Exxon | | 1030 | 1.98 | 1.06 | | 2.28 | 31.6 | 76.7 |
| Two-Stage | | 1000 | 2.33 | | 0.11 | | 17.8 | 81.1 |
| Two-Stage | | 1100 | 2.0 | | 0.22 | | 21.5 | 79.9 |

WESTERN COAL

| Process | | Temperature °K | Steam [Mole] | Recycle [Mole] | Oxygen [Mole] | Heat Above 900°K [Kcal] | Total Heat [Kcal] | Efficiency $\eta_L$ % |
|---|---|---|---|---|---|---|---|---|
| Exxon | Straight Feed | 1000 | 2.74 | 1.12 | | 7.66 | 40.4 | 74.4 |
| Exxon | | 1030 | 2.71 | 1.41 | | 9.49 | 43.4 | 73.6 |
| Modified Exxon | | 1030 | 2.25 | 1.25 | | 10.62 | 39.6 | 74.7 |
| Two-Stage | | 1000 | 2.74 | | 0.22 | | 25.9 | 78.9 |
| Two-Stage | | 1100 | 2.27 | | 0.4 | | 32.5 | 76.8 |
| Exxon | Prior Devolatilization | 1000 | 2.47 | 1.11 | | -2.29 | 31 | 77.2 |
| Exxon | | 1030 | 2.45 | 1.34 | | -1.07 | 33.5 | 76.5 |
| Modified Exxon | | 1030 | 1.83 | 1.13 | | 0.5 | 28.6 | 78 |
| Two-Stage | | 1000 | 2.12 | | 0.1 | | 14.4 | 82.8 |
| Two-Stage | | 1100 | 1.8 | | 0.2 | | 17.6 | 81.7 |

In the two Exxon processes, prior devolatilization introduces an additional complexity. Devolatilization formes CO and $H_2$. If these are fed back to the gasifier they will increase recycle and reduce steam conversion. The obvious choice is to methanate part of the gasifier product in a separate reactor. One can then reduce the recycle by 30%. While this can affect design and cost significantly, it has only a small impact on the ideal and limiting efficiency. The heat of methanation evolved in the reactor, at total recycle, reduces the amount of high temperature heat that has to be supplied to the fed streams, and compensates for the losses due to the larger recycle.

The two stage process has a small significant advantage over the two Exxon routes at all temperatures. This small advantage can disappear if other process penalties are taken into account, but this advantage presists even if the temperature of the two-stage process is increased to 1100K, which allows much smaller reactor sizes. A small reactor size can also be achieved by the proposed modification of the Exxon process (shifting the exit gases before recycling).

Table 7 clearly indicates the strong advantage of the proposed modified Exxon process. It allows an increase of reactor temperature without any penalty in thermal efficiency, maintaining the same recycle and improving steam conversion. (This will reduce one of the main present

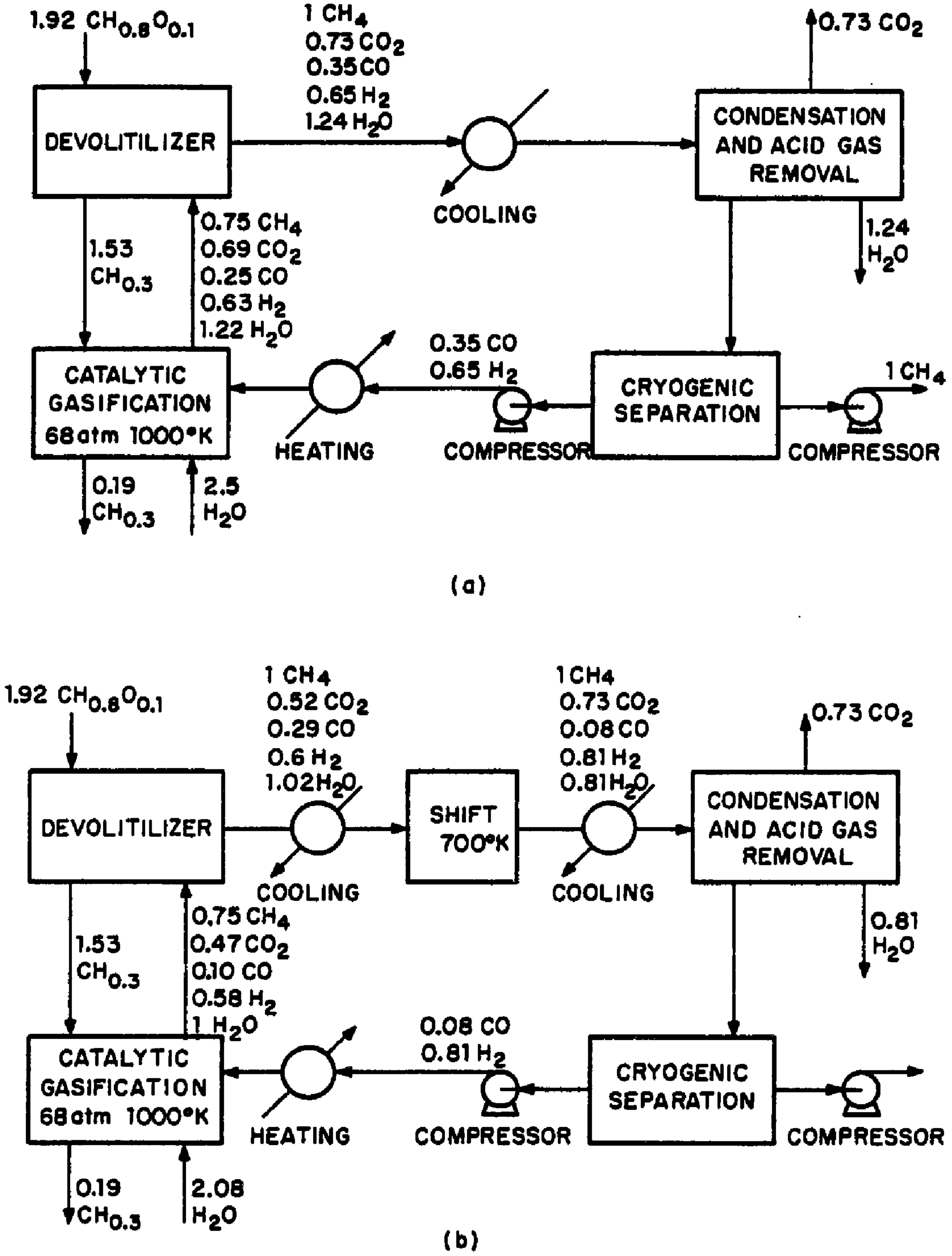


Figure 28: a) Schematic flowsheet of Exxon process with prior devolatilization.
b) Schematic flowsheet of Modified Exxon process with prior devolatilization.

disadvantages of the Exxon process which has a very large rector size, and merits closer examination in terms of actual process preformance).

## Chapter 7

# COMPARISON OF IDEAL AND REAL PROCESS REQUIREMENTS

In all processes, high thermal efficiency requires that all fed streams should enter the reaction zone as hot as they can be heated without penalty. Steam can be indirectly heated up to 950-1000K by combusting coal. The coal can be heat exchanged with product gas in a countercurrent moving bed (or in a countercurrent multistage fluid bed) gasifier. Both steps are essential for minimizing heat requirements at high temperatures. Table 7 indicates theoretical limiting efficiencies which are close to 80%. In practice, 65% is about the highest efficiency achieved. The limiting efficiency does not include the energy requirement for $CO_2$ removal nor process requirements and losses for heating and cooling, nor does it include the heat required for catalyst recovery. However, there is still a strong potential for improvement as can be seen by comparing the process penalty of present gasifiers with the ideal process in Table 7. Table 8 shows the total steam and oxygen requirements per mole $CH_4$ final product for several gasifiers. It is noted that present noncatalytic processes have almost double the steam and oxygen requirements. Each mole excess steam has a penalty of 10 Kcal, and each mole of excess oxygen used has apenalty of 40 Kcal. There is, therefore, a considerable range for improvement. It is noted that in a Lurgi gasifier, Eastern coal has a significant penalty compared to a typical Western coal. This is not due to any thermodynamic or kinetic reasons of the type described before, but due to an additional process constraint specific to moving bed gasifiers.

Since the reaction of char with oxygen is much faster than its reaction with steam, the gasifier cannot operate with optimal steam to oxygen ratios or highly preheated steam. Operation at these conditions will lead to a maximum temperature in the range of ash agglomeration. To overcome this problem, the Lurgi gasifier uses excess steam to lower the temperature. The amount of excess steam required to cool the combustion zone depends on the reactivity of the coal, as the endothermic gasification reaction contributes to the cooling. Western coal has here a significant advantage due to its higher reactivity. A slagger gasifier overcomes this problem by using excess oxygen which leads to a molten slag. The reactivity of the coal is, therefore, less important. In principle, fluid bed gasifiers should be able to overcome this penalty, but none of the presently reported gasifiers, for SNG production, has yet achieved this. The previous results indicate that a well designed catalytic gasifier can lead to significant improvement in thermal efficiency, provided that implementing the catalyst itself does not involve a significant thermal penalty.

## TABLE 8

### Process requirements for various gasifiers (mole/mole $CH_4$ final product)

**Eastern Coal**

| | Lurgi<br>Dry Ash | Slagger | Ideal two-stage<br>1100°K | 1100°K |
|---|---|---|---|---|
| Pressure [atm] | 25 | 30 | 25 | 68 |
| Steam [mole] | 5.7 | 2.8 | 1.74 | 2.0 |
| Oxygen [mole] | 0.67 | 0.58 | 0.29 | 0.22 |

**Western Coal**

| | Lurgi<br>Dry Ash | Ideal two-stage<br>1100°K | 1100°K |
|---|---|---|---|
| Pressure [atm] | 25 | 25 | 68 |
| Steam [mole] | 3.5 | 1.57 | 1.8 |
| Oxygen [mole] | 0.45 | 0.27 | 0.2 |

Steam for practical shift requirement to a $H_2/CO$ ratio of 1:1 included.

## Chapter 8

## SUMMARY AND DISCUSSION (PART I)

Part I presents an analysis of the thermodynamic constraints encountered by the developer in designing an SNG process with present technology, and suggests directions for further research and development. The results can be summarized as follows:

There are three factors that dominate the thermal efficiency of SNG processes from coal.

1. The conversion of steam in the gasifier. Recovery of steam from a steam-gas mixture is inefficient and expensive and therefore, steam utilization is a dominant factor.
2. Transferring heat to a reactor at high temperature (>900K) by combustion of coal involves a significant penalty (0.5 Kcal per Kcal supplied). The common way of using oxygen inside the reactor is as efficient as any of the other routes suggested till now. It is, therefore, important to minimize the high temperature heat requirement of the reactor.
3. Separation processes in a gas phase have very low efficiencies as compared to their theoretical efficiencies, and have to be minimized.

These constraints are not inherent results of the first and second law of thermodynamics, but rather thermodynamic consequences of available technology. All chemical processes involve irreversible losses in available energy inside the reactor. In SNG production these losses are small. However, the thermodynamic efficiency of the process is a consequence of the kinetic paths as well as process constraints that dominate reactor preformance.

The best hypothetical process, which will be consistent with the overall state of technology, will be the development of a cheap catalyst that can directly react coal with steam, at a temperature of 600K, at a reasonably high pressure.

No such catalysts are presently known, and the best process with presently available catalysts, is the one described in Figure 27b. Gasification occurs in a two-stage countercurrent reactor in which coal is devolatilized by the product gases from the primary gasification zone. Steam and oxygen are reacted with the char (formed in the first zone), and brought to equilibrium. The gases are then methanated and cleaned (or cleaned and methanated). Such a system can have a significantly better thermal efficiency than present processes (over 70% (LHV) versus 62% for present processes).

To achieve maximum efficiency it is important that:

1. Methane formation is maximized in the char gasification zone. Direct methane formation from char

and steam has a low heat of reaction, whereas CO and $H_2$ formation, which is the primary reaction with present catalysts, is highly endothermic. Catalysts which form methane by a direct reaction can have significant advantages. With present catalysts, global equilibrium gives the highest achievable methane yield per mole steam fed. This yield decreases with temperature, whereas overall steam conversion increases with temperature. Therefore, reactor heat requirements increase with temperature and the penalty more than negates the benefit of increased steam conversion. The optimum conditions require the reduction of reactor temperature as much as possible. In that sense, SNG production is different from syngas production for which higher temperatures are advantageous [Shinnar and Kuo 1978]. However, the penalty of increasing the temperature by 100C is still relatively small.

2. In order to minimize heat requirements in the reactor, all feed streams should be preheated as high as can possibly be achieved by heat transfer from coal combustion.
3. It is important that the coal is devolatilized before it is fed to the gasification zone, under conditions that maximize $CH_4$ and CO formation. Tars formed should be cracked in the devolatilizer. If the coal

is fed directly, as in a one stage fluid bed or cocurrent gasifier, the free energy of the coal is not utilized. $CH_4$ formed by methanation in the gasifier is further limited due to equilibrium constraints. Proper devolatilization is, therefore, essential for all gasifiers, unless a real low temperature catalyst can be developed.

4. Methanation of CO and $H_2$ should be carried out without additional steam. The unconverted steam from the gasifier can be used to shift the product gas, but the use of additional steam will involve a penalty in thermal efficiency. The methanator should operate at conditions of $H_2/CO$ ratio close to 1.

The present Exxon process, the only catalytic process under large scale development in the U.S., prevents CO and $H_2$ formation by separating them cryogenically from the methane, and recycling them to the reactor. This reduces the heat requirement of the reactor and eliminates the need for oxygen. Here, instead of the penalty for cryogenic separation of air, a similar penalty is required for the cryogenic separation of $CH_4$ from CO and $H_2$. The energy requirement for the separation of the recycled gas increases with temperature more steeply (Figure 19) than the oxygen required in the two-stage process. These facts force the Exxon process to operate at the lowest feasible temperature. The ability to operate at a 100C higher temperature, with the same thermal efficiency, is a significant advantage for a two-stage catalytic process (using oxygen and steam in the first stage and methanation in the second), and leads to smaller reactors or can allow the use of cheaper catalysts.

The efficiency of the Exxon catalytic SNG process can be significantly improved if the product gas is shifted with its own unconverted steam before the separation. This process modification reduces both recycle and steam requirements by preferentially removing $CO_2$ from the system, and can lead to a significant improvement of the present catalytic gasification process. The modified process permites operation of the gasifier at a higher temperature (an increase of about 30C to 50C) without any significant penalty in recyle requirement. It also leads to higher steam conversion. Operation at a higher temperature can significantly reduce the large size reactor of the present gasification process which is the main disadvantage of this route.

The literature contains some claims that the equilibrium methane yield is a strong function of char properties. However, no such data exist to justify these claims. The preceding chapters contain a thorough discussion of the thermodynamic constraints of methane formation, and present the argument that the equilibrium constant of methane over char is very close to that over graphitic carbon. This argument is based on experimental data. The experimental results used to indicate higher equilibrium constants for chars are also explained.

The analysis deals with catalytic gasifiers using known catalysts. Catalytic gasification gives the highest thermal efficiencies, at least for idealized processes. It also indicates how much the present processes can be improved by either optimizing their process conditions or by using catalysts. The analysis provides a guideline for such improvements.

Part I demonstrates that thermodynamic analysis can be a powerful tool in process development. It is especially useful in understanding the effect of kinetic properties of a catalyst (or a noncatalytic process) on the maximum conversion that can be achieved.

# PART II

## USE OF NUCLEAR ENERGY IN PRODUCTION OF SNG AND HYDROGEN FROM COAL

A differential economic anylysis of production of hydrogen via electrolysis of water, versus steam reforming of methane, using a High Temperature Nuclear Reactor.

# Chapter 9

# INTRODUCTION (PART II)

Use of nuclear energy in production of synthetic fuels from coal has recieved a varying amount of attention in recent years. It can be attractive for the long range future as it will allow the streching of coal reserves. There are several ways in which nuclear energy can be used in the production of synthetic fuels from coal:

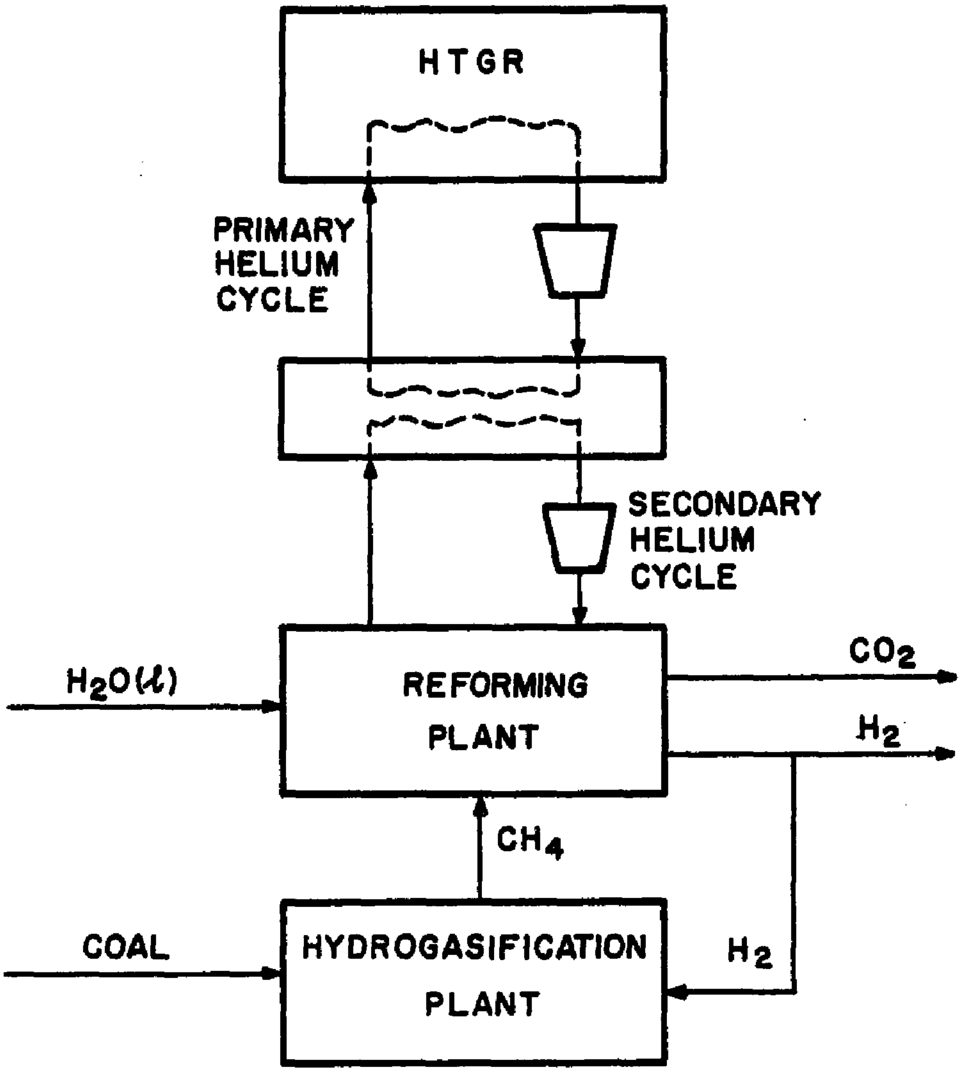
1. Electricity and steam generated by nuclear reactor to replace a coal fired boiler in a power plant.
2. Electricity from a nuclear reactor to generate hydrogen via electrolysis.
3. A High Temperature Nuclear Reactor (HTGR) to supply process heat.

The use of electricity is an available and economic option today, but the main limitation is the availability of nuclear generated electricity. The use of steam generated by nuclear heat is a more difficult problem since the nuclear reactor has to be physically close to the steam user, and involves potential problems of contamination and safety. However, the amount of steam and electricity that can be used in most synthetic fuel plants to save coal input, is limited to less than 15%. The process normally has large amounts of waste heat generated which have to be effectively utilized.

Generation of hydrogen using nuclear generated electricity is not economical at the present cost of coal, but can be attractive in the long run, as it can replace a large fraction of the coal input needed (60-70%). In fact, almost all presently known petroleum fuels and chemicals can be generated from hydrogen and $CO_2$, without a need for fossil fuels.

The third option recieves probably the most attention in the limited research effort that exists in this field, mainly in Europe [Kugeler 1980]. This evaluation focuses on one specific process, namely, production of hydrogen by reforming methane, using high temperature heat generated by an high temperature nuclear reactor. The methane itself is the product of reaction of coal with hydrogen in a hydrogasifier. A simplified scheme is given in Figure 29. Such a scheme might be part of a SNG plant (see Figure 30), or might be considerd on its own. The overall process in Figure 30 is at present under development in West Germany [Kugeler 1980] but a similar scheme was proposed by Stone and Webster (1972).

This scheme was chosen for the comparison as it is probably the most advanced of its class and is claimed to be the most promising. It is also a very illuminating case for understanding the potential role of nuclear energy in coal gasification.



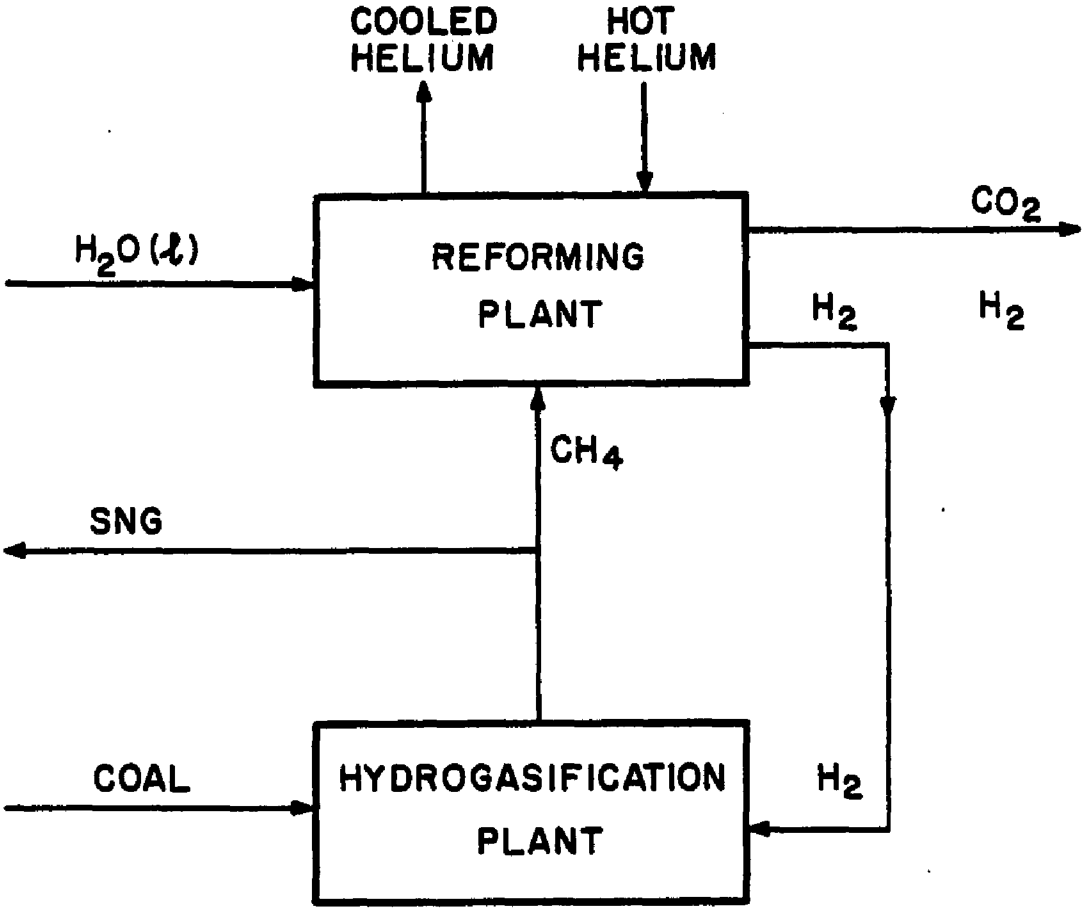
OVERALL REACTIONS

REFORMING PLANT: $CH_4 + 2H_2O \xrightarrow{\text{NUCLEAR HEAT}} 4H_2 + CO_2$

HYDROGASIFICATION PLANT: $C + 2H_2 \longrightarrow CH_4$

NET REACTION: $C + 2H_2O \longrightarrow 2H_2 + CO_2$

Figure 29: Schematic diagram of $H_2$ production from coal using nuclear heat.



**OVERALL REACTIONS**

REFORMING PLANT: $CH_4 + 2H_2O \xrightarrow{\text{NUCLEAR HEAT}} 4H_2 + CO_2$

HYDROGASIFICATION PLANT: $2C + 4H_2 \longrightarrow 2CH_4$

---

NET REACTION: $2C + 2H_2O \longrightarrow CH_4 + CO_2$

Figure 30: Schematic diagram of SNG from coal using nuclear heat.

## Chapter 10

# METHOD AND SCOPE OF EVALUATION

The approach to the economic evaluation has been discussed in detail in two previous publications [Shinnar 1978; Shinnar, Shapira and Zakai 1981]. Instead of preparing conventional flow sheets and cost estimates, the method focuses on evaluating the inherent advantages of the proposed technology, and tries to quantify directly any potential advantage over existing technology.

The choice of a proper comparison is, therefore, of utmost importance. The overall process described in Figure 30 can also be achieved without a nuclear reactor by generating the hydrogen from coal using the scheme in Figure 31a, which is a commercial process. Hydrogen can also be utilized from electrolysis of water (Figure 31b). Therefore, the comparison will focus on comparing hydrogen production as in Figure 29 with:

1. Hydrogen from coal.
2. Hydrogen from electolysis using electricity generated in a nuclear reactor.

The comparison is focused on hydrogen production, despite the fact that the proposed processes for using heat from an HTGR are intended for synthetic natural gas (SNG). The

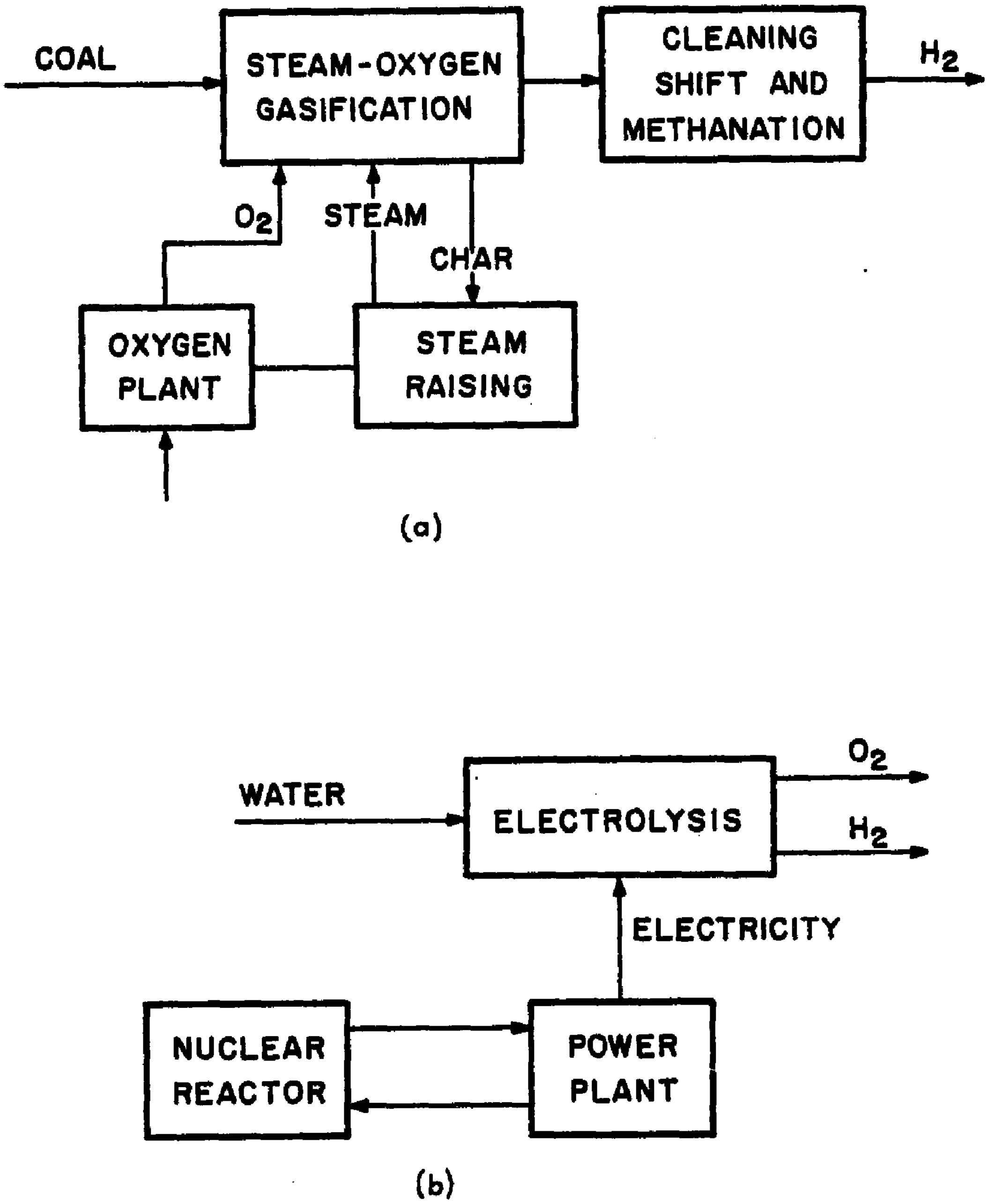


Figure 31: a) Schematic diagram for conventional coal-to-$H_2$ process.

b) Schematic diagram for electrolytic generation of $H_2$ process.

scheme in Figure 30 includes the hydrogen process from Figure 29. The hydrogen from the two alternative processes can be used to produce SNG in an identical hydrogasifier. Since the hydrogasification step is shared by all these processes it can be eliminated from the comparison. If possible, elimination of identical steps is always advisable in this type of process comparison.

An important decision, regarding the two alternative base cases, has to be made. Should numbers based on commercially available technology be used, or should they be based on advanced technology from bench scale or pilot plant. If a new process can be commercialized in a short time, commercially available technology is an important base case since it is not sure that the competing advanced technologies will really be commercialized. This analysis does not deal with a near future technology, but with a process which involves a long range government sponsored research effort. The goal here is to evaluate which technologies are more promising, and therefore, advanced technology demonstrated in pilot plants, is the proper choice.

The only parts of the processes under comparison, for which no reliable data is available are:

1. The hydrogasifier.
2. The high temperature nuclear reactor (HTGR).
3. The reformer heated with nuclear heat.

However, it will be shown that the conclusions are not affected by their uncertainties.

There is a considerable amount of literature regarding the HTGR, and a reasonably large demonsatration plant for elecricity generation has been operated. However, it is difficult to obtain reliable cost estimates on a comparative basis with either conventional nuclear energy or synfuel technology. It will be assumed that the cost of a HTGR is at least competitive with conventional nuclear energy for electricity generation and if it is cheaper, the advantage will apply equally well to the generation of electricity as well as to the supply of nuclear heat.

The reason for using two base cases is as follows: None of the two routes involving nuclear energy is competitive at present. Therefore, they have to be compared with a case based on coal only. They will only become competitive if the price of coal rises significantly. In the latter case, electrolysis provides an alternative that has some a priori advantages over the use of nuclear heat:

1. Electrolysis is more flexible and can use a variety of non-fossil electricity sources.
2. Electrolysis can replace a large fraction of the coal.
3. Electrolysis has a significant advantage in terms of safety and scale. The nuclear reactor can be far away from the electrolysis plant, and its scale is

not limited by the energy requirements of the process, since electricity is a salable, transportable commodity.

In order for the steam-reforming case to be attractive compared to electrolysis, it must have very significant advantages in terms of cost, to justify the development and the incremental safety risks.

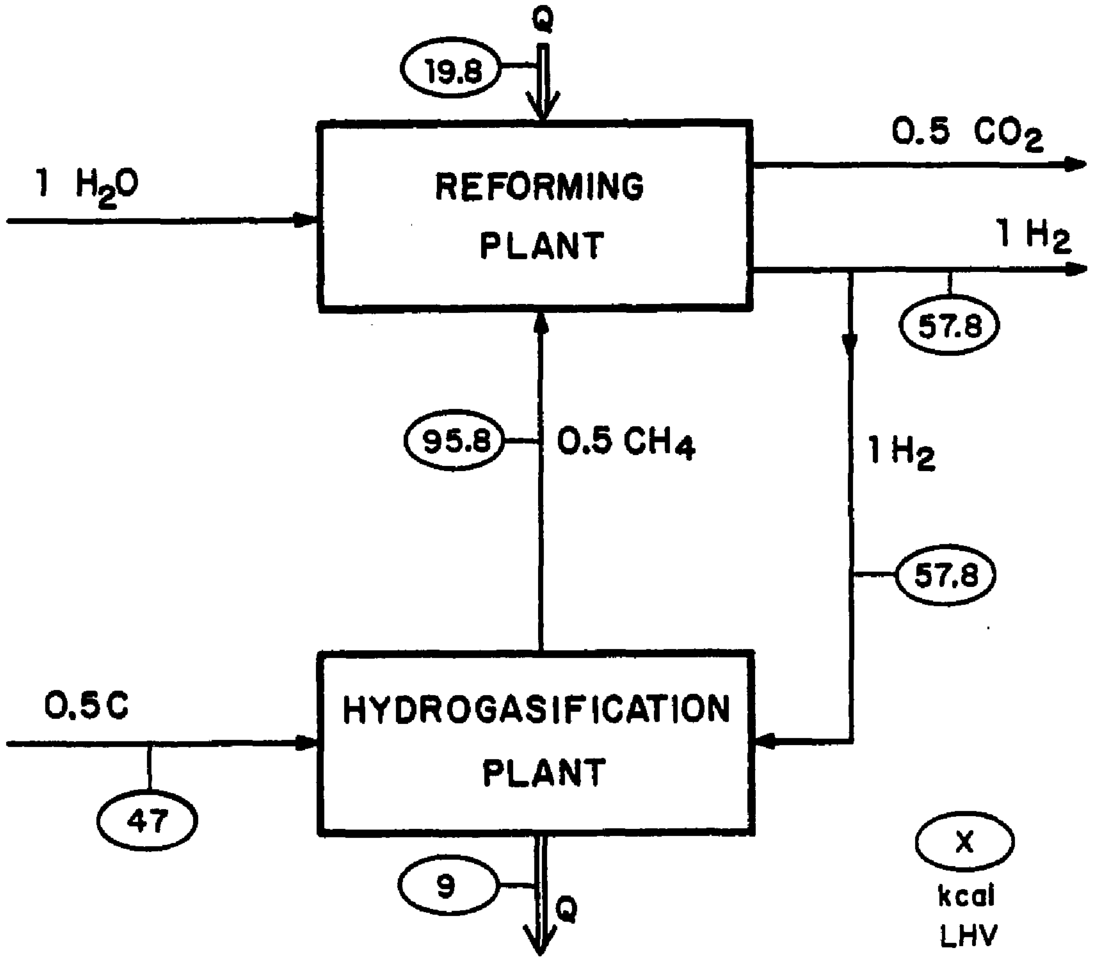
## Chapter 11

## PRELIMINARY ANALYSIS

In order to be able to focus on the important features of a new process, it is always advisable to try to understand its goals. In this evaluation, the product is identical in all the schemes. The two possible goals for the new process are:

1. Cheaper investment cost.
2. Replacing coal with nuclear energy.

The flowsheet in Figure 29, including the nuclear reactor, will require a larger investment than a conventional hydrogen plant. The steam reforming route in Figure 29 contains a steam reformer which is similar in its design to a conventional steam reformer, and its cost should also be similar. However, its size is much larger. In Figure 32 a simplified mass and energy balance for route 1, using carbon (32a) or coal (32b) as a feed, is given. The mass balance is based on one gr-mole hydrogen. It is noted that for the carbon case, half the hydrogen produced in the steam reforming section has to be recycled to generate the total hydrogen required. Therefore, a steam reformer, twice as big as the one in a standard steam reforming plant from SNG, is required to produce one net unit of hydrogen. This



REFORMING PLANT: $0.5\,CH_4 + H_2O \longrightarrow 2H_2 + 0.5\,CO_2$

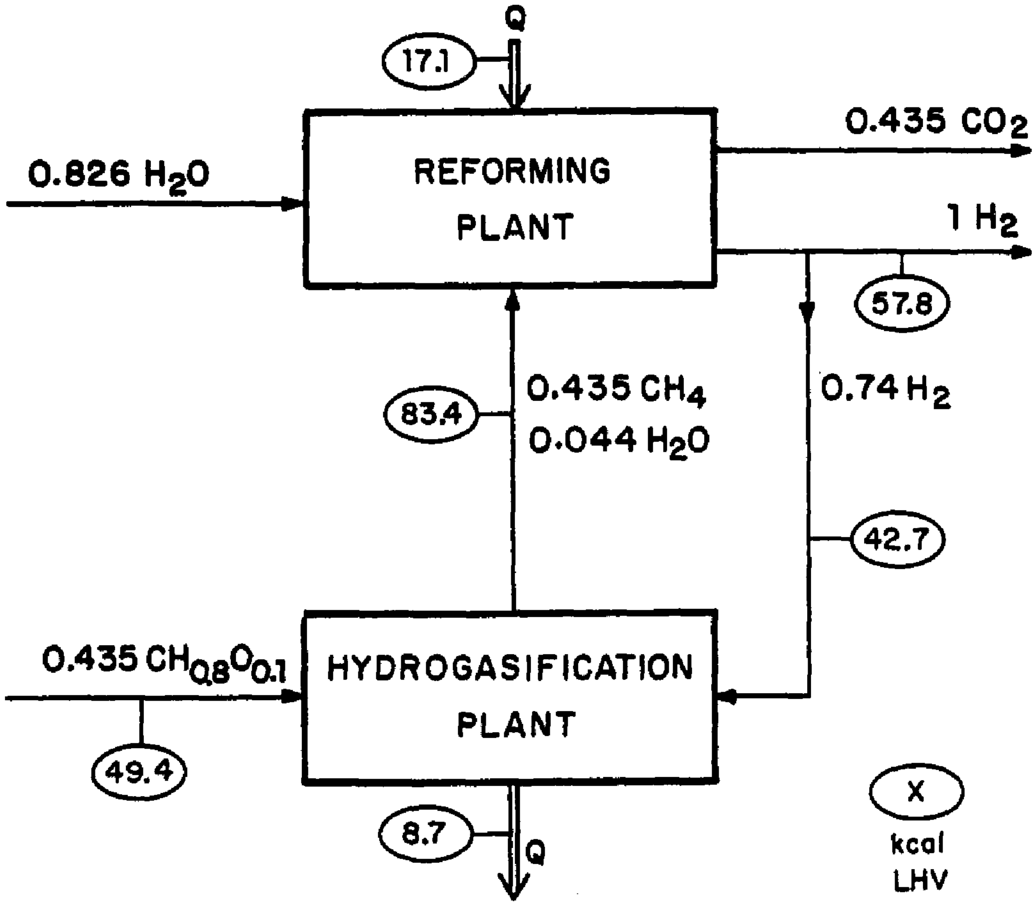
HYDROGASIFICATION PLANT: $0.5\,C + H_2 \longrightarrow 0.5\,CH_4$

---

NET REACTION: $0.5\,C + H_2O \longrightarrow H_2 + 0.5\,CO_2$

(a)

Figure 32: Stoichiometric balance for reforming route.
a) Carbon feed b) Eastern coal feed.



REFORMING PLANT:

$$0.435\ CH_4 + 0.87 H_2O \longrightarrow 1.74 H_2 + 0.435 CO_2$$

HYDROGASIFICATION PLANT:

$$0.435 CH_{0.8}O_{0.1} + 0.74 H_2O \longrightarrow 0.435 CH_4 + 0.044 H_2O$$

---

NET REACTION:

$$0.435 CH_{0.8}O_{0.1} + 0.826 H_2O \longrightarrow H_2 + 0.435 CO_2$$

(b)

is an inherent disadvantage of this type of scheme resulting from the stoichiometry. For coal, the disadvantage slightly reduces (see Figure 32b), but for this analysis, a factor of 2 is a satisfactory rough estimate.

Most of the elements of the hydrogen process in Figure 29 are almost identical to well-known processes. Therefore, a rough estimate of their cost can be achieved by looking at the cost of comparable industrial processes [Shinnar 1978; Shinnar, Shapira and Zakai 1981]. A summary of cost estimates for various processes is given by Corneil (1977). Adjasted figures for 1980 dollars are repeated in Table 9. The numbers in Table 9 are based on the production of 1 MMBTU $H_2$/day in a large plant.

Table 9 shows that a hydrogen plant from coal costs about three times as much as a hydrogen plant from methane. The steam reforming scheme (Figure 32) needs the equivalent of two hydrogen plants from methane in order to obtain similar hydrogen output as one coal-to-hydrogen plant. Therefore, the cost of one hydrogen plant from methane is left, to allow for the cost of the hydrogasification complex. It is unlikely that the large hydrogasification complex required will be cheaper than one steam reforming plant, but even then, the overall savings will be negligible. Therefore, the non-nuclear part of the proposed process (Figure 29)

## TABLE 9

Investment cost for various processes
1980 dollars per MMBTU daily capacity (LHV)

| Process | Investment |
|---|---|
| $H_2$ from methane | 2000 |
| $H_2$ from coal | 6000 |
| SNG from water and coal | 5500-6500 |
| Electrolysis of water | 2500-4000 |
| HTGR | 4500 |

will require approximately the same investment as a conventional coal-to-hydrogen plant. All that is left is the second goal which can be achieved by both the steam reforming route as well as electrolysis. Electrolysis has the advantage of a larger potential for saving coal since all the hydrogen is produced with no use of coal. Therefore, for comparison, an estimate of the nuclear reactor's size which is required to replace a unit of coal, is needed for each process.

The fact that the use of a HTGR cannot lead to any investment saving in the hydrogen plant itself, simplifies the analysis. The cost of saving coal is approximately proportional to the size of the nuclear reactor required to save a unit of coal. The potential attractiveness of the process, compared to electrolysis, depends then on the thermal efficiency. Therefore, the focal problem of the analysis is whether the use of HTGR-reforming scheme replaces coal more efficiently than electrolysis. The accompanying next question is what magnitude of advantage is one looking for. This determines the required accuracy of the estimates. Since this is a management decision, and it depends on the size of the future market, the expense involved in development and many other factors, it is assumed here that an advantage of 20% in the size of the nuclear reactor will be sufficient. Nevertheless, one can also ask for a much larger advantage to compensate for safety problems of the HTGR-reforming scheme.

# Chapter 12

# THE EFFECT OF THERMODYNAMIC AND PROCESS CONSTRAINTS ON THERMAL EFFICIENCY

## 12.1 OVERALL REACTION

The overall reaction in a coal-to-hydrogen plant is exactly the same as in the proposed HTGR-steam reforming scheme. For carbon:

$$0.5C + H_2O_{(1)} \longrightarrow 0.5CO_2 + H_2 \qquad (24)$$
$$\Delta H^{o}_{298} = 21.29\ \text{Kcal} \qquad \Delta G^{o}_{298} = 9.56\ \text{Kcal}$$

and for coal:

$$0.435CH_{0.8}O_{0.1} + 0.826H_2O_{(1)} \longrightarrow 0.435CO_2 + H_2 \qquad (25)$$
$$\Delta H^{o}_{298} = 16.82\ \text{Kcal} \qquad \Delta G^{o}_{298} = 5.55\ \text{Kcal}$$

On the other hand for electrolysis on the same basis:

$$H_2O_{(1)} \longrightarrow H_2 + 0.5O_2 \qquad (26)$$
$$\Delta H^{o}_{298} = 68.3\ \text{Kcal} \qquad \Delta G^{o}_{298} = 56.7\ \text{Kcal}$$

In reactions (24) and (25), the amount of free energy generated in the process is very small compared to the available free energy of the product (56.7 Kcal/gr-mole $H_2$), 17% in reaction (24) and 10% in reaction (25). Actually, the overall SNG plant has a loss in free energy despite the use of the HTGR.

$$1.74CH_{0.8}O_{0.1} + 1.3H_2O_{(1)} \longrightarrow CH_4 + 0.74CO_2 \qquad (27)$$
$$\Delta H^o_{298} = 6.5 \text{ Kcal} \quad \Delta G^o_{298} = -9.3 \text{ Kcal}$$

The nuclear reactor does not create an incremental amount of free energy. All it does is replacing coal that is used for process inefficiencies. This loss of coal is a price paid for the convenience of using synthetic fuels (or SNG in this case).

On the other hand, the use of hydrogen generated by electrolysis of water to produce SNG increases the net free energy available as a clean fossil fuel. For carbon:

$$C + 2H_2O_{(1)} \longrightarrow CH_4 + O_2 \qquad (28)$$
$$\Delta H^o_{298} = 118.7 \text{ Kcal} \quad \Delta G^o_{298} = 101.1 \text{ Kcal}$$

and for coal:

$$CH_{0.8}O_{0.1} + 1.6H_2O_{(1)} \longrightarrow CH_4 + 0.85O_2 \qquad (29)$$
$$\Delta H^o_{298} = 94.4 \text{ Kcal} \quad \Delta G^o_{298} = 78 \text{ Kcal}$$

An additional advantage of the electrolysis scheme is the release of oxygen to the atmosphere instead of carbon dioxide.

## 12.2 OVERALL PROCESS EFFICIENCY FOR HTGR-ELECTROLYSIS ROUTE

The hydrogen production scheme in Figure 29 has a small increase in free energy generated by the nuclear reactor. Since the energy losses in generating this free energy are quite large, the potential efficiency of this process is small. It is convenient, here, to define an efficiency of generating free energy from heat in a chemical process as:

$$\eta_G = \frac{\Delta G^o_{298}}{\sum q_i} < \frac{\Delta G^o_{298}}{\Delta H^o_{298}} \qquad (30)$$

where $\sum q_i$ is the total amount of heat introduced into the process [Shinnar, Shapira and Zakai 1981]. Since the increase in free energy is achieved by supplying heat to the system from a heat source at $T_R$, the efficiency is limited by the Carnot principle.

$$\eta_G \leqslant 1 - T_o / T_R \qquad (31)$$

Funk (1976), therefore, defines a relative efficiency

$$\eta_{\Delta G} = \frac{\eta_G}{1 - T_o / T_R} \qquad (32)$$

which indicates how much does the efficiency of the process deviate from the Carnot efficiency. The deviation of the system here is quite large. For carbon, (reaction (24)) $\eta_{\Delta G} < 0.6$, and for Eastern coal (reaction (25)) $\eta_{\Delta G} < 0.44$. The Carnot efficiency at 1700F is equal to 75%.

The theoretical limit on efficiency of 44% applies to any route based on coal. Since real efficiencies have to be lower, it presents a strong disadvantage for the process in terms of thermodynamic constraints. $\eta_{\Delta G}$ would have increased if a heat source, with a lower top temperature, could have been used. However, process constraints determine the minimum top temperature of the heat source which can be used.

On the other hand, the thermal efficiency of electricity generation in an HTGR should be about 47% which is equivalent to $\eta_{\Delta G}=0.62$ (or 62% of the Carnot efficiency). If the efficiency of the electrolysis plant is included, an upper practical limit on thermal efficiency will be 40% ($\eta_{\Delta G}=0.53$). Even if a lower efficiency for electrolysis is used, the practical value of $\eta_{\Delta G}$, using the same nuclear HTGR, will be higher than the stoichiometric limit for utilization of nuclear heat in production of hydrogen from coal.

Generating hydrogen by electrolysis has, therefore, an inherent thermodynamic advantage for synthetic fuels from coal, compared to the application of high temperature process heat. This applies to all potential applications of high temperature heat from an HTGR in synthetic fuels, independent of the process or the flowsheet.

The proposed process has a disadvantage in terms of $\eta_{\Delta G}$. However, efficiency can be looked at in a different way. In practice, the energy requirements of a coal-to-hydrogen plant are about 55 Kcal/gr-mole coal compared to 38.7 Kcal/gr-mole in reaction (25). Much of this coal can be saved in the steam reforming route. This saving can be looked at as a way of increasing the availability of fossil fuels. In that case both routes have to be compared on the same basis, with careful look at the sources of potential losses.

## 12.3 EFFICIENCIES REQUIRED FOR NEW PROCESSES

A reasonable value for thermal efficiency in a Shell-Koppers hydrogen plant or a Texaco process using bituminous coal is about 65% [Shinnar and Kuo 1979; Corneil 1977]. It means that for every Kcal of $H_2$ (LHV) 1.54 Kcal of coal are required as total feed to the plant.

In an electrolysis plant, with 85% thermal efficiency for the electrolysis process and 47% for the HTGR-electricity plant, 2.5 Kcal of nuclear heat are needed for every Kcal of hydrogen produced. An additional 0.11 Kcal are needed for compressing the hydrogen to the same pressure as in the coal plant (300 psig) (using 70% compressor efficiency). A total of 2.61 Kcal for every Kcal of hydrogen is needed in the electrolysis plant. Comparing it to the coal-to-hydrogen plant, 1.54 Kcal of coal are saved at the cost of 2.61 Kcal of nuclear heat, or 1.69 Kcal of nuclear heat per each Kcal of coal saved.

The steam reforming route is analyzed by examining Figure 32. In this case only 0.81 Kcal of carbon are needed for every Kcal hydrogen produced. Therefore, the maximum amount of carbon that can be saved is 0.73 Kcal, or 47% of the coal saved in the electrolysis route. In order for this process to be much better than electrolysis, it has to require significantly less than 0.73x1.69 or 1.234 Kcal nuclear heat per Kcal hydrogen produced. Considering 20% as a significant advantage, the proposed process has to realistically achieve a total energy required from the nuclear reactor of 0.98 Kcal per Kcal hydrogen produced. By substituting coal for carbon, stoichiometry requires an input of 0.86 Kcal coal. The maximum saving is, therefore, 0.68 Kcal of coal. This saving has to be achieved by 0.92 Kcal of nuclear heat. The overall stoichiometric heat requirements in Figure 32 are significantly below that number. However, practical heat requirements are much larger. In the following, it will be shown that the inherent process constraints of the process in Figure 29 make such an achievement very unlikely.

## 12.4 PROCESS CONSTRAINTS OF HYDROGEN GENERATION USING NUCLEAR HEAT

Examining the stoichimetry of the steam reforming route, 0.5 gr-mole C reacted give 1 gr-mole net $H_2$ with a lower heating value (LHV) of 57.8 Kcal. According to the previous requirement, the process can only afford

57.8x0.98=56.65 Kcal of nuclear heat per gr-mole $H_2$ produced. The inherent process constraints make it unachievable. The reaction of the process is as follows:

| | | $\Delta H^{o}_{298}$ [Kcal] | $\Delta G^{o}_{298}$ [Kcal] | |
|---|---|---|---|---|
| A. | $0.5CH_4 + H_2O_{(1)} \rightarrow 0.5CO_2 + 2H_2$ | 30.23 | 15.63 | (33) |
| B. | $0.5C + H_2 \rightarrow 0.5CH_4$ | -8.84 | -6.07 | |
| | $0.5C + H_2O \rightarrow 0.5CO_2 + H_2$ | 21.29 | 9.56 | |

($\Delta H^{o}_{298}$ includes the heat required for the formation of the stoichiometric amount of steam). It is noted that step A needs a higher $\Delta H^{o}_{298}$ than the overall reaction. Furthermore, more free energy than needed is created and it should be recovered in the hydrogasifier (step B). In practice, with present envisioned technology, this recovery can not be accomplished.

A hydrogasifier, as presently envisioned, will need compression of the feed and recycle of unconverted hydrogen after separation. Thus, it will require an addition of energy above that recovered from the heat of reaction. Therefore, the energy requirement of step A provides a theoretical lower limit for the process. However, step A as written, assumes complete conversion. Since the top temperature is limited due to material limitations, complete conversion is impossible. The process has to operate with excess steam, both to protect the catalyst and to obtain conversion to hydrogen.

The minimum steam requirements are obtained if the reaction is carried out in two steps. In the high temperature step the reaction is:

$$\text{A.1} \quad 0.5CH_4 + 0.5H_2O_{(g)} \dashrightarrow 0.5CO + 1.5H_2 \qquad (34)$$

$$\Delta H^o_{298} = 24.6 \text{ Kcal} \quad \Delta G^o_{298} = 17.0 \text{ Kcal}$$

followed by an exothermic low temperature shift reaction:

$$\text{A.2} \quad 0.5CO + 0.5H_2O_{(g)} \dashrightarrow 0.5CO_2 + 0.5H_2 \qquad (35)$$

$$\Delta H^o_{298} = -4.9 \text{ Kcal} \quad \Delta G^o_{298} = -3.4 \text{ Kcal}$$

The formation of steam from liquid water has to be added to the scheme:

$$H_2O_{(1)} \dashrightarrow H_2O_{(q)} \qquad (36)$$

$$\Delta H^o_{298} = 10.52 \text{ Kcal} \quad \Delta G^o_{298} = 2.05 \text{ Kcal}$$

The heat needed for steam raising plus the heat of reaction required in A.1 (35.12 Kcal) is larger than the heat required for the one step hydrogen production (reaction (33)). But, as this heat can be recovered in the shift reactor and can be used to raise steam, it does not limit the thermal efficiency. However, the process is limited not only by the maximum temperature of A.1, due to material constraints, but also by the minimum temperature of A.2. The latter is fixed by the kinetics of the available catalyst of the shift reaction, and is assumed here to be 450F.

Both limitations determine the maximum conversion of the steam at equilibrium in each reaction, and therefore, the minimum excess steam required. Figure 33 shows the minimum total steam requirements as a function of temperature. Since the minimum steam requirements are a function of methane conversion, the results are given for two typical methane conversions - 89% and 65%. A conversion of 89% leads, after $CO_2$ removal, to a hydrogen purity of 97% in the final product gas, whereas 65% is equivalent to an 88% hydrogen purity. (The CO conversion is kept fixed at 100%). For complition, Figure 34 shows steam requirements as a function of $CH_4$ conversion. Both figures are based on net hydrogen produced. It can be seen that if methane conversion is lower, steam requirements decrease. However, the energy requirements of the hydrogasifier will increase, since the $CH_4$ limits the conversion and increases the recycle.

At 1550F with 89% methane conversion, the steam required is 4.94 moles steam per 1 mole of $CH_4$ converted, of which only 2 moles are converted (see reaction (38)). Thus, 2.94 moles steam have to be condensed below 450F (after shift) from a stream containing 50% inerts.

As mentioned in Part I, condensing steam from a diluted stream below 450F is not only expensive but also leads to significant losses in thermal efficiency. While part of the

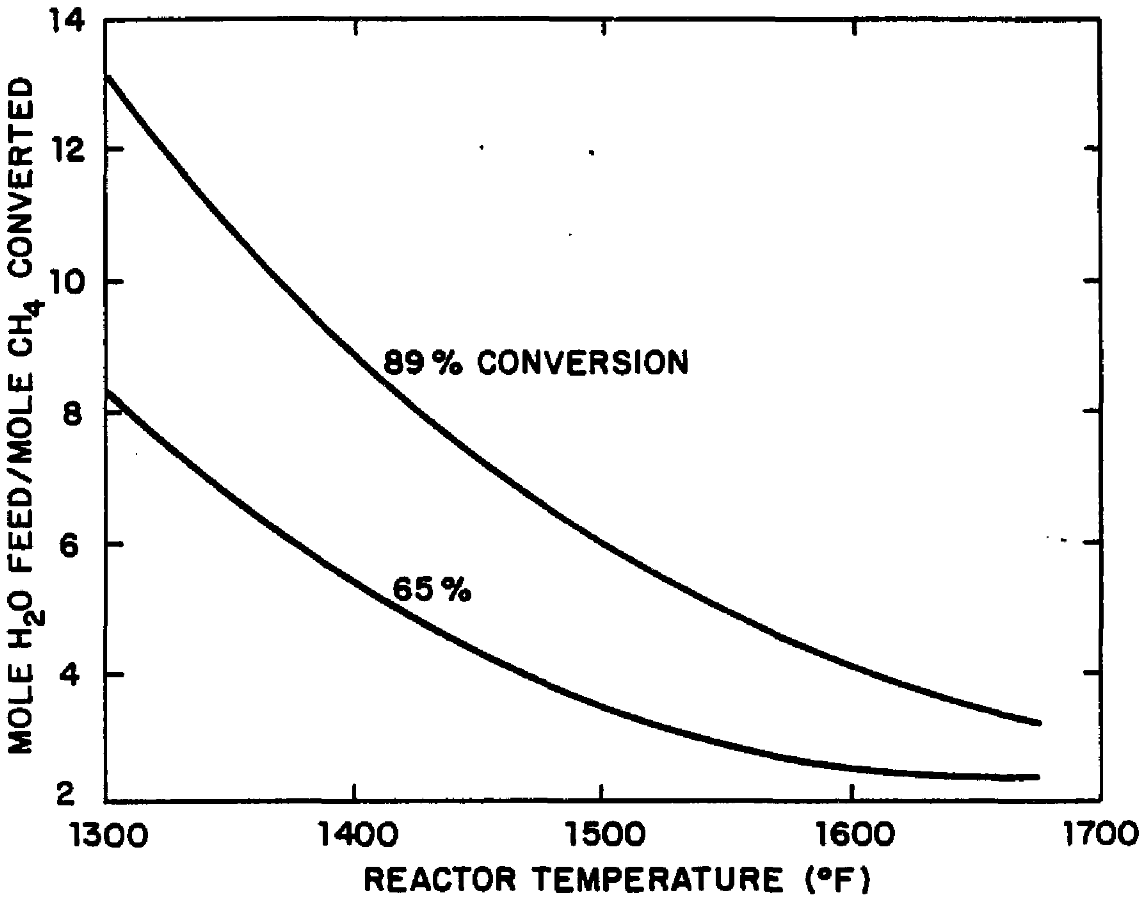


Figure 33: Minimum steam requirements as a function of temperature for reforming.

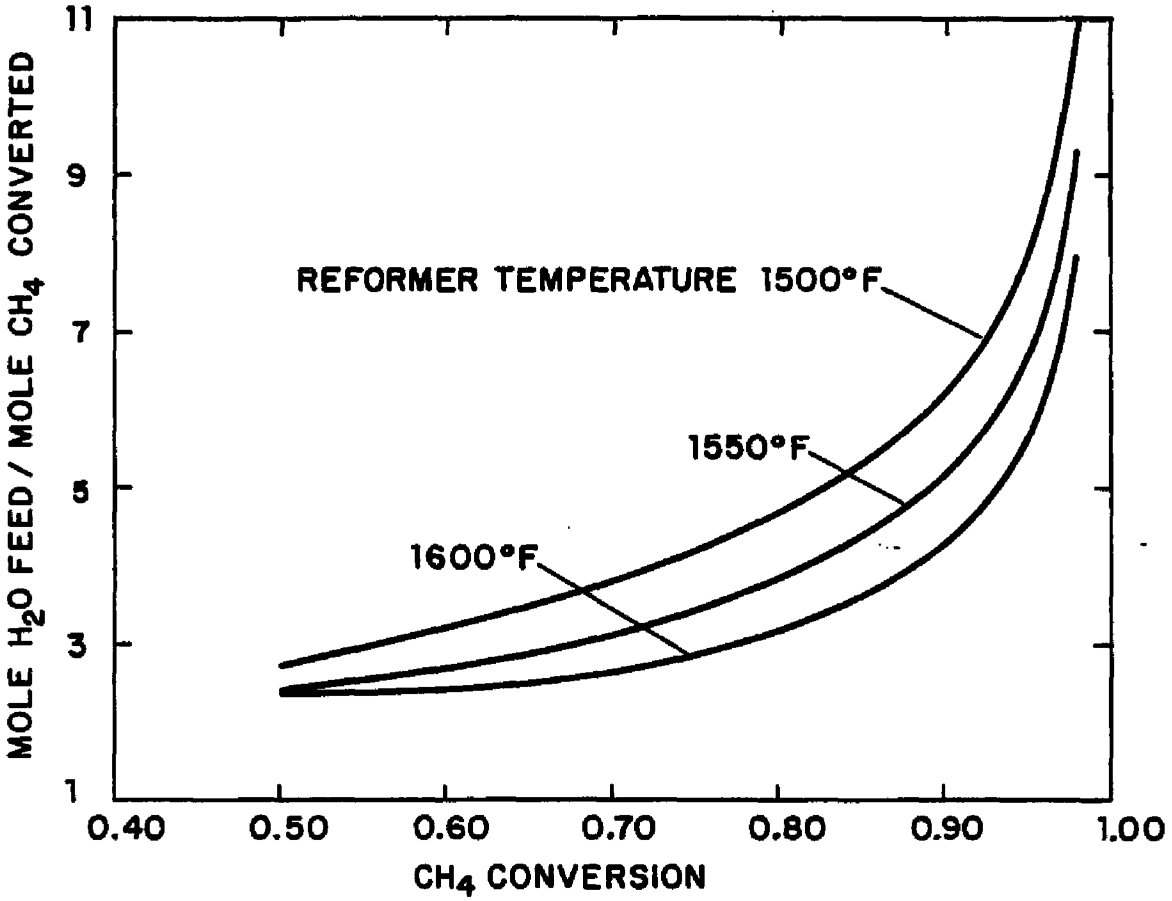


Figure 34: Minimum steam requirements as a function of conversion for reforming.

heat can still be used to compensate for practical losses, it does not change the fact that the minimum theoretical energy requirements of the process have to be increased by the heat of vaporization for the excess steam required. Therefore, the minimum heat requirements of step A are 44.73 Kcal which means that $\eta_{\Delta G}$ for carbon-to-hydrogen process is limited to less than 9.56/44.73=0.21 versus an achievable value of 0.53 for electrolysis.

In computing the efficiency for electricity generation, the heat from the HTGR is used directly. Using the HTGR heat for supplying high temperature process heat, requires an additional helium cycle [Shinnar, Shapira and Zakai 1981]. The net efficiency of this heat transfer loop will be at best 90%. This results in a minimum heat requirement of 44.73/0.9=49.7 Kcal of the 56.64 Kcal allowed for the entire process. Still, $CO_2$ removal, losses in the hydrogasifier, losses for heating and cooling, have not been accounted for.

## Chapter 13

## COMPARING PRACTICAL EFFICIENCIES

Even though the theoretical minimum energy requirements are already close to the goal set, practical energy requirements will be compared. Good estimate of the realistic minimum energy requirements can be achieved without any detailed flowsheeting of the process. The steam reforming of methane to produce hydrogen is a well developed procees, and since it is one of the steps in the overall process analyzed here, it can serve as a basis for comparison. The heat of reaction as well as steam and all process requirements are supplied by burning methane. At present technology, the thermal efficiency in terms of LHV is 72%. This efficiency is defined in terms of the heating value of the total product gas:

$$\frac{\text{LHV of product gas } (97\%\ H_2,\ 3\%\ CH_4)}{\text{LHV of methane to reactor + LHV of methane to furnace}} = 0.72$$

The computation here is based on 0.5 mole $CH_4$ converted, which, in returns, produces 2 moles $H_2$. The numbers are summarized in Figure 35. The unconverted $CH_4$ is equal to 2x0.03/0.97=0.062 moles. Therefore, the total methane fed to the reactor is 0.562 moles. The LHV of the total product gas is the LHV of 2 moles $H_2$ or 2x57.8=115.6 Kcal plus that of 0.062 moles $CH_4$ or 11.9 Kcal for a total of 127.5 Kcal. The total $CH_4$ requirements, at 72% efficiency, are then 177 Kcal, of which 0.562x191.76=107.77 Kcal are fed to the reactor and 69.23 Kcal to the furnace. Therefore, the heat that can be replaced by the nuclear heat is 69.23 Kcal/1 gr-mole net hydrogen produced. The 69.23 Kcal include the efficiency of the furnace (90% in terms of LHV). Using the HTGR will have the same overall heat requirements since the losses in the heat transfer loops will be approximatly the same as the losses in the furnace [Shinnar, Shapira and Zakai 1981].

The required heat is much above the 56.64 Kcal which was set as the goal. Even if the efficiency of the process would have been 75%, the losses would have been 62.23 Kcal, still high above the goal. Efficiency can be increased by lowering conversion, but the potential improvement is small. Lower conversion will reduce the heat requirement per mole methane reformed, but then, energy for separation of unconverted $CH_4$ from the $H_2$ has to be added, which makes it unattractive. Also, the net energy requirements of the hydrogasification process have to be added to the 69.23 Kcal.

The minimum energy losses of a hydrogasifier are found by preforming an energy balance around an optimistic adiabatic hydrogasifier, using the method of Shinnar and Kuo (1979).

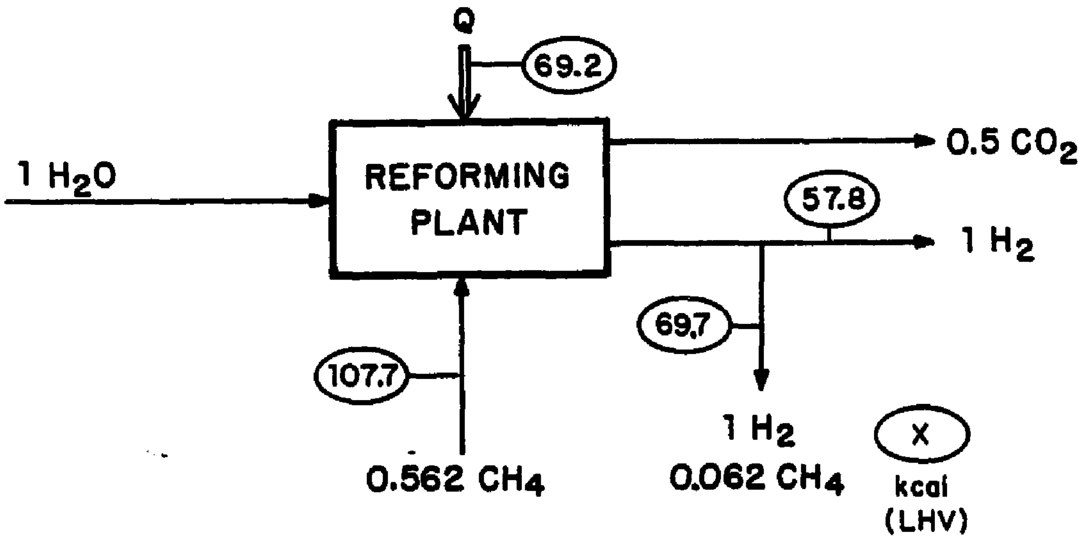
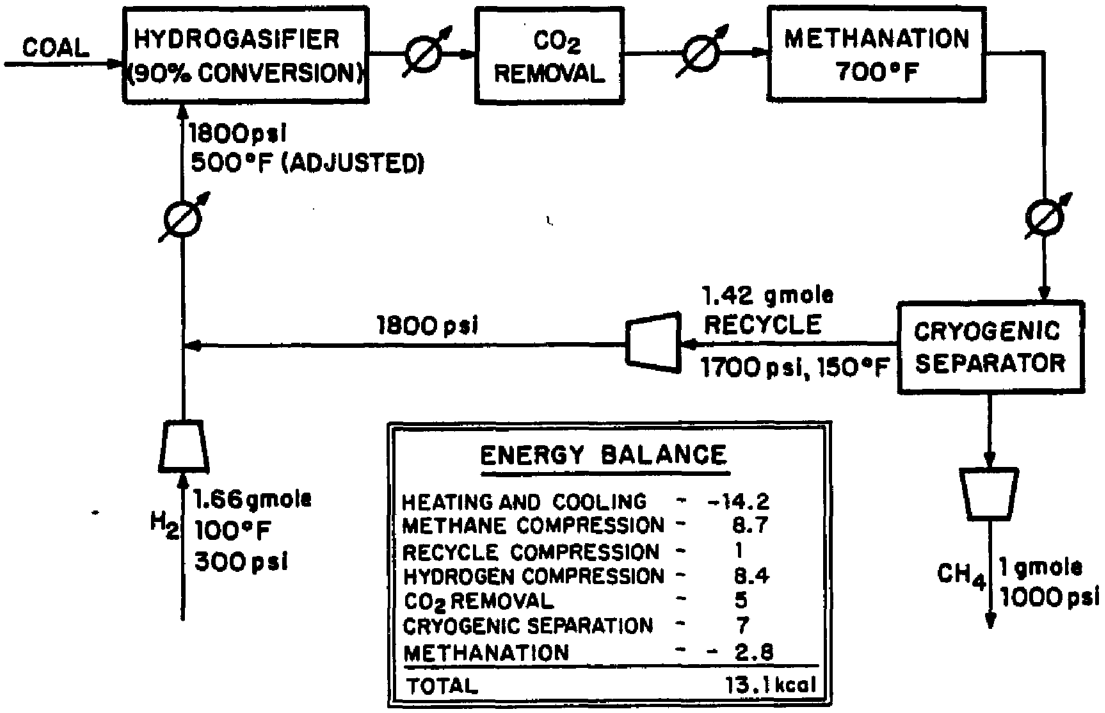


Figure 35: Energy balance for steam-reforming of methane.

In Figure 35 the product was assumed to be pure $H_2$, separated from the $CH_4$-containing product of the steam reformer, by cryogenic separation. In a real flowsheet one would probably settle for a lower purity. Since this stream would contain $CH_4$ it would affect the mass balance, but the net results, in terms of thermal efficiency, would be identical.

The simplified flow sheet is given in Figure 36. The hydrogasifier is fed with coal and operates at 1800 psi. Gas phase equilibrium is assumed at 1700F. The main penalties are the $CO_2$ removal (Rectisol), the cryogenic separation which requires excessive compression and the compression of the $H_2$ into the reactor. The net requirements, in addition to the heat of reaction released, are about 13 Kcal/gr-mole $CH_4$. The real energy requirements are higher since it is hard to approach equilibrium in a hydrogasifier. Furthermore, it is very difficult to approach 100% conversion in a hydrogasifier. Present pilot plants operate with less than 60% conversion, and use the char as a fuel for the hydrogen plant. An optimistic limit would be 95% carbon conversion. The char can be burned in a boiler to provide part of the energy for the hydrogasification complex.

By using coal instead of carbon in the analysis, the numbers in Figure 35 are further modified but the net result does not change. It was shown (Figure 32b) that hydrogen production from coal requires a smaller recycle, as part of the hydrogen is produced from the coal. For each net mole of $H_2$ produced only 0.74 moles have to be recycled to the hydrogasifier, and the amount depends on the hydrogen and oxygen content of the coal. Thus, the total feed to the reformer (Figure 35) is reduced by 15%. However, in Figure 32b, the LHV of the stoichiometric coal increases by



ENERGY BALANCE

| | |
|---|---|
| HEATING AND COOLING - | -14.2 |
| METHANE COMPRESSION - | 8.7 |
| RECYCLE COMPRESSION - | 1 |
| HYDROGEN COMPRESSION - | 8.4 |
| $CO_2$ REMOVAL - | 5 |
| CRYOGENIC SEPARATION - | 7 |
| METHANATION - | - 2.8 |
| TOTAL | 13.1 kcal |

Figure 36: Flowsheet and energy balance for hydrogasification process.

5% over that of the carbon case. If the conversion is only 95%, the coal required increases to 52 Kcal/gr-mole $H_2$. Then, only 60.3 Kcal/gr-mole $H_2$ can be saved, or 13% less than in the simplified case of pure carbon. A detailed energy balance is given in Figure 37. The numbers given are not actual estimates for the steam reforming process but reasonable lower bounds. Actual energy requirements can be higher.

Since the comparison is made with electrolysis, the energy balance in Figure 37 is repeated, based on 1 Kcal of net $H_2$ produced and is shown in Figure 38a. It is noted that the steam reforming process requires a total energy input of 1.1 Kcal and saves only 0.54 Kcal of coal compared to the coal-to-hydrogen process. Therefore, the ratio of nuclear heat to coal saved is 2.04. the case of electrolysis. It is clear from the above that the inherent process constraints are such that the proposed process has no chance to lead to substantial improvements over electrolysis, based on the ratio of nuclear heat required per unit coal saved.

It is clear that the more coal is saved, the lower will the overall efficiency be. For a given production rate, the process in Figure 29 needs only 42% of the nuclear heat compared to electrolysis. But this is misleading. A higher saving in coal can be achieved using a combination of a conventional coal-to-hydrogen plant and an electrolysis

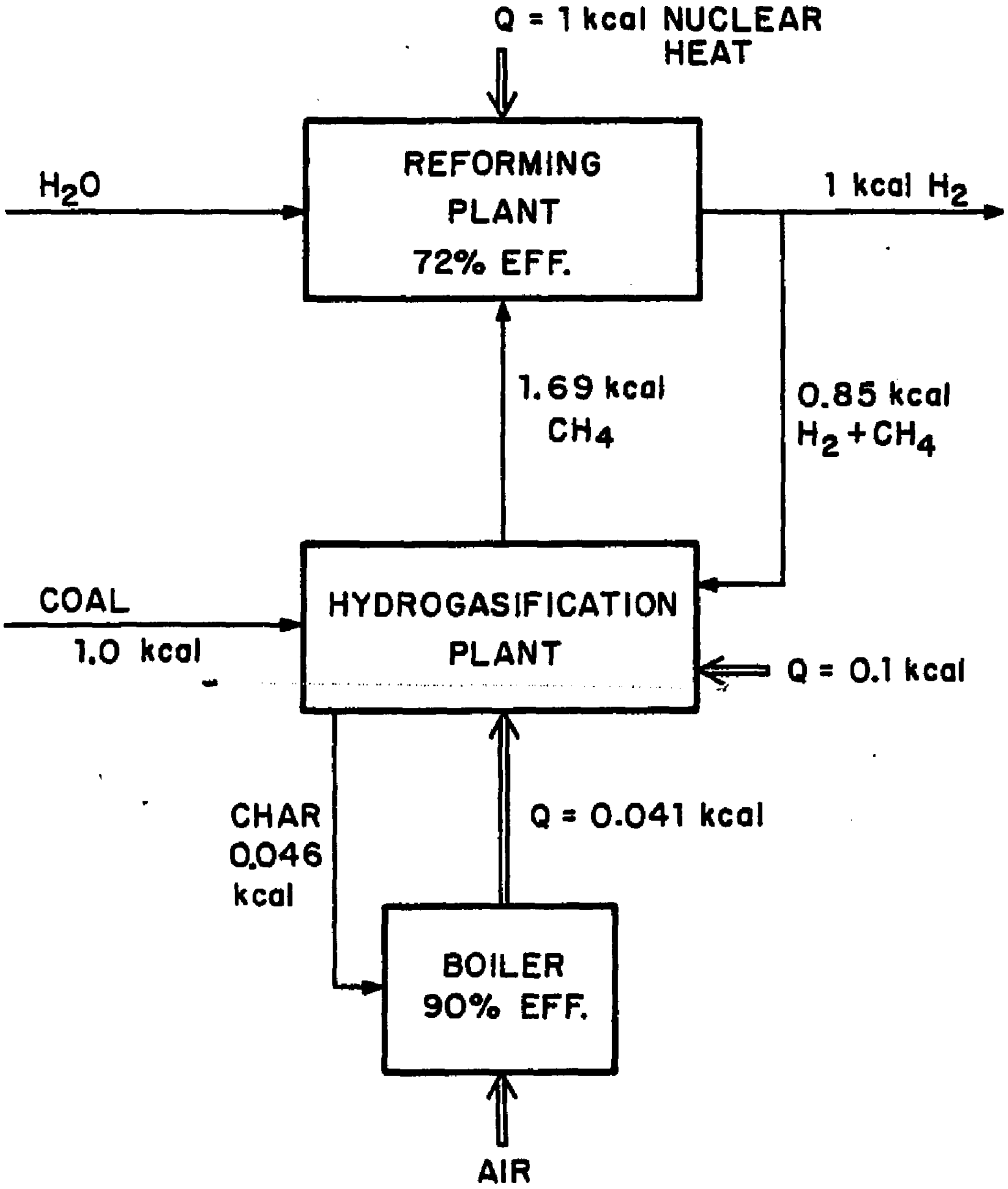
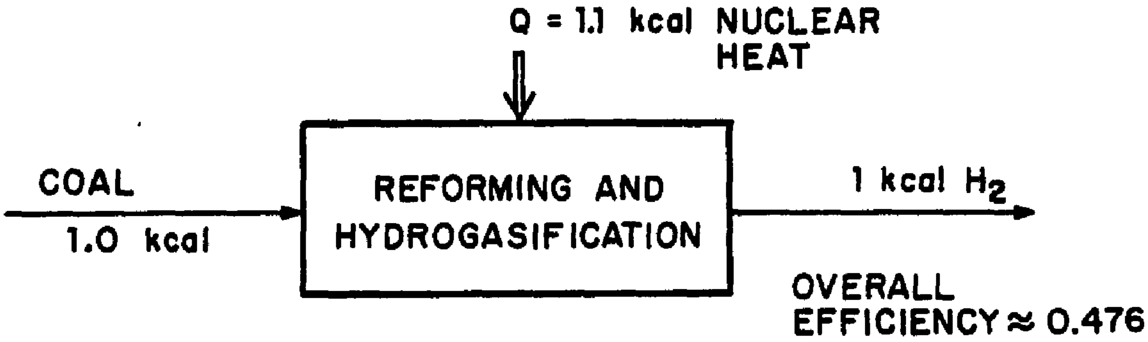


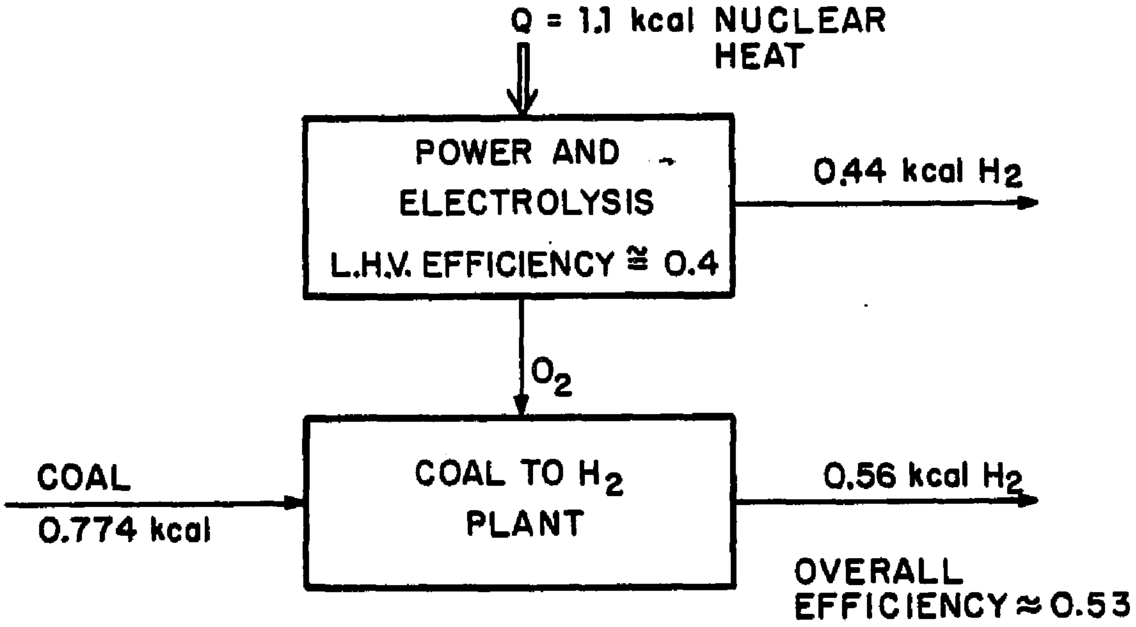
Figure 37: Energy balance for reforming using nuclear heat.

plant (see Figure 38b). Here, the combined process is allowed to use the same amount of nuclear heat which is required to produce 1 Kcal of $H_2$ via the steam reforming route (Figure 38a). Based on the privious optimistic estimates, this value is 1.1 Kcal requiring in addition 1 Kcal of coal. The electrolysis plant produces the hydrogen with an efficiency of 0.47x0.85 or 40% yielding 1.1x0.4 or 0.44 Kcal of $H_2$ and oxygen for the coal-to-hydrogen plant. In order to produce the balance of 0.56 Kcal $H_2$, the coal-to-hydrogen plant will require 0.56/0.65 or 0.86 Kcal of coal, including the energy required for the oxygen plant. However, a big fraction of the energy required for the conventional coal-to-hydrogen process is the oxygen plant. About 10% of the coal can be saved by using oxygen from electrolysis. Therefore, the coal needed is only 0.774 Kcal compared to 1 Kcal required in the steam reforming route. Thus, the route in Figure 38b has an interesting potential for a synergistic effect as it saves more coal for the same amount of nuclear heat. In the previous analysis, no energy credit was given to the oxygen formed by electrolysis, which penalized electrolysis in an unfair way.

One reason for the disadvantage of the steam reforming route is based on the flowsheet itself. 1.7-2 moles of hydrogen have to be generated for each net mole hydrogen produced, and then part of the free energy generated in the hydrogasifier is lost. It is this double work that makes



(a) REFORMING ROUTE



(b) COMBINED ELECTROLYSIS AND COAL TO $H_2$

Figure 38: Energy balance for reforming and combined coal to $H_2$-electrolysis routes.

reforming of methane unattractive in a coal-to-SNG plant, and reduces the thermal efficiency.

How sensitive is the analysis to the assumptions made? The results are not sensitive to the assumed efficiency of the coal-to-hydrogen plant, since reducing it will affect both electrolysis and steam reforming. However, the results are sensitive to the assumptions concerning the efficiency of electrolysis. Present commercial efficiencies for electrolysis are below 70%. Assuming an efficiency of 70% for electrolysis, the permitted energy for steam reforming becomes 69 Kcal/gr-mole $H_2$, approximately equal to the lower limit for it. However, efficiencies of 85% have already been achieved in pilot plants, and in cells for space applications [Nuttall 1980], whereas the efficiencies in Figure 37 are based on projections. Furthermore, when the energy credit for the oxygen produced by electrolysis is included (about 12 Kcal/gr-mole $H_2$) the efficiency of hydrogen production raises from 70% to 85%. The disadvantage of the nuclear steam reforming is, therefore, much larger than assumed here.

# Chapter 14

# CAPITAL INVESTMENT

It is very difficult to obtain reliable costs for an HTGR, as one faces the tendency to underestimate costs in new developments. It is hard to imagine that it will lead to significant cost savings compared to a standard nuclear reactor, though it might have other advantages such as safety. In a standard nuclear reactor the cost of the reactor itself is a small fraction of the total power station cost. Shielding and other expenses related to safety, cost more than the nuclear reactor itself. Therefore, it will be assumed that the HTGR will be competitive in cost with the conventional light water reactor for electricity generation. It is also assumed that the cost of KW(e) installed capacity is $900 (1980 dollars), excluding interest during construction.

If electricity generation is eliminated, and the HTGR is used for heat only, a double helium loop is inserted (see Figure 29) to transfer the heat. The heat transfer surfaces will increase significantly since the temperature gradients are smaller, and the heat transfer coefficient for steam generation is much higher than for helium. Additional power is also needed to pump the gas through the heat exchangers.

Most probably the coal plant will be located at some distance from the reactor so the process will have additional energy losses. Optimistically, it can be assumed that the heat transfer costs are equal, but the turbine for electricity generation is saved. That means that, at best, about $125/KW(e) installed are saved, though the heat case can, in practice, be more expensive. To simplify matters the $125/KW(e) installed investment for the turbine generator is included in the investment of the electrolysis plant itself. The HTGR will then have the same cost based on primary heat delivered, or $4500 per MMBTU per day primary heat.

Table 10 shows an estimate of the investments for different processes. The absolute numbers are not very reliable in terms of rapid inflation, but the comperative costs should be reasonably good. Scale effects in coal plants are large but should not upset the conclusions. If the inherent problems of handling coal are disregarded, (these problems are common to all synthetic fuel plants from coal and are included in the plant cost for coal), a large size coal-to-hydrogen plant should cost about 2.0 to 2.5 times the cost of a steam reforming of methane plant.

At present concepts of hydrogasification only 50-55% of the coal is gasified. The remaining char is used for hydrogen production. As 25% of the coal is devolatilized, the hydrogasifier actually gasifies only 25-30% of the

## Investment and feed requirements for the three processes (1980 $/MMBTU $H_2$/Day)

| Hydrogen from coal | | Hydrogen from electrolysis using nuclear heat | | Hydrogen from steam reforming of methane using nuclear heat | |
|---|---|---|---|---|---|
| Section | Investment [$] | Section | Investment [$] | Section | Investment [$] |
| Coal handling; drying, grinding | 600 | | | Coal handling; drying, grinding | 400 |
| Offsites | 200 | Offsites | 200 | Offsites | 200 |
| Gasifier | 1200-1500 | Electrolysis plant | 2500-4000 | Hydrogasifier (1.38 MMBTU $CH_4$/Day) | 2500-5000 |
| Shift | 600-800 | Electricity generation (turbine generator only) | | Methane reformer (1.67 MMBTU $H_2$/Day) | 3400 |
| $H_2$, $CO_2$ removal | 1000-1200 | | 1800 | | |
| Oxygen plant | 1000-1200 | Nuclear reactor | 11700 | Nuclear reactor | 4900 |
| Steam + Power | 800-1000 | | | | |
| Total | 5400-6500 | | 16200-17700 | | 11400-13900 |
| Coal feed (MMBTU/Day) | 1.54 | | --- | | 1.0 |
| Incremental Investment [$] | | | 10800-11200 | | 6000-7400 |
| Incremental Investment/Coal saved ($/MMBTU/Day) | | | 7000-7300 | | 11100-13700 |

carbon. If 95% conversion is required, the kinetics of the process require an increase in the gasifier size by a factor of 3. This penalty applies to the hydrogasifier in the SNG process (Figure 30), which gets the hydrogen from the hydrogen process. If the hydrogen is obtained from coal, the option of reducing the conversion and gasifying the unconverted char for hydrogen is available. The coal-to hydrogen process in this evaluation was not credited with this advantage, nor was it quantified since the results made this unnecessary.

In the absence of data it is hard to estimate the cost of the hydrogasifier, but a minimum cost can be obtained. The cost will include the whole hydrogasification complex: Rectisol, cryogenic separation, heat recovery, compression etc. In a SNG process, using a hydrogasifier, this should be about 30-40% of the total cost. If it is assumed that the whole plant for SNG will have approximatlely the same cost as a SNG plant from Western coal using a Lurgi type gasifier ($6000/MMBTU/day, see Table 10), the hydrogasification complex will then cost 0.3x1.69x$6000=$3000 (lower bound). The factor of 1.69 is used here as 1.69 MMBTU of methane have to be generated in the hydrogasifier for every MMBTU of $H_2$. Since the hydrogasifier is required to be three times larger in size, compared to that in a SNG plant, the cost might increase to $5000.

It is noted from Table 10 that there is no chance that such a proposed hydrogen process will have a significantly cheaper investment cost compared to a coal-to-hydrogen plant.

If on the other hand, the total hydrogen plant's cost is considered, the HTGR-steam reforming route has an investment advantage over the electrolysis route. This is the same illusion as was referred to in the section on thermal efficiency. Less coal is saved and therefore, it requires less nuclear energy. If the numbers are based on a constant nuclear heat input, a parallel coal-to-hydrogen plant and an electrolysis plant can be considered (see Figure 38b). The total investment will now be lower, because the coal plant saves its oxygen plant, as well as the steam plant associated with it. (A coal gasifier requires about 0.35 mole $O_2$ per mole $H_2$ and the oxygen plant, including incremental offsites, is about 25% of the investment of a coal-to-hydrogen plant.) The economics of this case is summarized in Table 11. As only differences are considered, the cost of the nuclear plant is not included since it has the same size as the one for the reforming route. The investment for the hydrogen production plants is $4250-5370 for the combined plant vs. $6500-9000 estimated in Table 10 for the reforming route. The proposed route has, therefore, an inherent disadvantage in investment required.

## TABLE 11

## Investment cost for combined coal to $H_2$ and electrolysis plant

| | Investment<br>1980 \$/MMBTU of $H_2$ per Day |
|---|---|
| $H_2$ from coal<br>(0.56 MMBTU $H_2$/Day) | 2270-2730 |
| Electrolysis plant<br>(0.44 MMBTU $H_2$/Day) | 1980-2640 |
| Total investment | 4250-5370 |

| | |
|---|---|
| Coal required (MMBTU/Day) | 0.774 |
| Nuclear energy required (MMBTU/Day) | 1.1 |
| Incremental investment (\$) | 3750 |
| Incremental investment/coal saved (\$/MMBTU/Day) | 4900 |

From the approximate analysis, a required increase in thermal efficiency of 20%, for substituting nuclear heat for coal, was derived. This was based on the assumption that the investment in the non-nuclear section is equal. The more detailed analysis shows that this is a too optimistic assumption, and a larger improvement is required.

# Chapter 15

# ECONOMICS

It was shown before that all that can be achieved by a nuclear reactor is substitution of nuclear energy for coal. Direct use of nuclear heat increases the cost of the process itself. Electrolysis has the potential to achieve a lower investment compared to a coal-to-hydrogen plant, but the savings are small compared to the cost of a nuclear reactor.

The question arises: is it attractive today to substitute nuclear heat or energy for coal in a hydrogen plant, synthetic fuel plant or a power plant? It is not very attractive, especially if it is compared to the possibility of substituting nuclear energy for coal in electricity generation. One unit of heat from the HTGR replaces 1/1.69=0.59 units of coal in a coal-to-hydrogen plant. Assuming the efficiency of generating electricity from coal in a power plant, with a scrubber, to be 37%, then the same 1 unit of heat from the HTGR generating electricity with an efficiency of 47%, is able to replace 0.47/0.37=1.27 units of coal, or twice the coal replaced by either electrolysis or by direct use of nuclear heat.

The incremental investment for saving one MMBTU of coal per day is $7200 for $H_2$ from electrolysis, whereas the incremental investment for saving coal in electricity generation is negligible. (If interest during construction is neglected, the capital cost of a nuclear power plant and a coal combustion power plant are very close.) At standard utility accounting, \$7200 translates into capital and operating charges of $8x10^{-4}x7200=\$5.7$ per MMBTU coal, to which the full cost of the nuclear fuel has to be added. If the nuclear fuel cost of \$1.5 (¢0.5/KWh) is added, it ends up with a cost of \$7.2 per MMBTU coal saved. While this might become attractive in the near future, it is still much less attractive than generation of electricity. The penalty of using nuclear energy for purposes other than generating electricity is typical of all such users. At present, electricity is sold for the equivalent of \$12 per MMBTU electricity or \$6 per MMBTU of heat generated from an HTGR. If it is converted to hydrogen, at present, the product sells at a much cheaper price per MMBTU than electricity. If that hydrogen is used as fuel, the price still drops, as the cost of high quality fuels is still only \$6-7 per MMBTU. Many energy sources which are attractive for electricity generation lose their attractiveness if the electricity is converted to a fuel or hydrogen. Some may dispute here the cost of nuclear fuel as it does not include any costs related to the fuel cycle, such as waste disposal, etc. The real cost of nuclear fuel is not of interest in this analysis as it affects all nuclear applications equally.

## Chapter 16

# SUMMARY AND DISCUSSION (PART II)

The results can be summarized as follows:

1. Use of high temperature heat in the production of hydrogen from coal is less attractive than the use of the same heat to generate electricity and split water into $H_2$ and $O_2$. It is, under the most optimistic assumptions, slightly more expensive per unit of coal saved, and has less potential for saving coal. It also suffers from inherent thermodynamic disadvantages.
2. Neither hydrogen from electrolysis, nor from direct use of nuclear heat is attractive in the near future, but it can become attractive as coal becomes expensive and scarce.
3. If an HTGR will become attractive in cost for supplying nuclear heat, it will become even more attractive as a source for electricity generation.

These conclusions are similar to those reached by Shinnar, Shapira and Zakai (1981) for generation of hydrogen from an HTGR, using thermochemical or hybrid cycles.

From a policy point of view, this has some interesting consequences. Development of the HTGR is justified only if it leads to either cheaper electricity or better safety in electricity generation. Conclusion 1 implies that if one wants to prepare for the long range future, where hydrogen from non-fossil sources becomes important for synthetic fuel production, one should concentrate on developing better plants for electrolysis. This can be done totally uncoupled from any development of nuclear reactors.

# Appendix A

## ESTIMATION OF THERMODYNAMIC PROPERTIES OF COAL AND CHAR

### A. Coal at room temperature

No accurate or even approximate measurements of the thermodynamic properties of coal are available in the literature. Some approximations have been suggested [Krikosian 1972] and used by IGT (1978-1979).

In the theoretical approximation some assumption about the coal structure have to be made. For a coal of a structure $CH_nO_mN_pS_q$, $T\Delta S^o_{298}$ is estimated by Krikosian (1972) as:

$$T\Delta S^o_{298} = -0.05689-3.6909n-6.109m-5.627p-1.079q \qquad (A-1)$$

where $T\Delta S^o_{298}$ is given in Kcal/gr-mole.

For a typical Eastern coal the structure of the dry coal is equivalent to $CH_{0.8}O_{0.1}N_{0.02}S_{0.023}$ [Datman 1976]. If N and S are neglected, a typical Eastern coal can be considered as $CH_{0.8}O_{0.1}$.

For this coal $T\Delta S^o_{298}$ is equal to -3.62 Kcal/gr-mole (equation (A-1)). The free energy of formation can be determined using the heat of combusion. For the above coal this value is 14,000 BTU/lb or 8.22 Kcal/gr, or 8.22x14.4=118.4 Kcal/gr-mole of coal.

$$CH_{0.8}O_{0.1} + 1.15O_2 \longrightarrow CO_2 + 0.4H_2O_{(1)} \qquad \text{(A-2)}$$

$$\Delta H^o_{coal} = \Delta H^o_{CO_2} + 0.4\Delta H^o_{H_2O_{(1)}} - \Delta H_{combustion}$$

$$= -94.054 + 0.4x(-68.3) + 118.4 = -3.0 \text{ Kcal/gr-mole}$$

The free energy of formation can be calculated using the relation:

$$\Delta G^o{}_{298} = \Delta H^o{}_{298} - T\Delta S^o{}_{298} = -3.0 - 3.62 = 0.62 \text{ Kcal/gr-mole}$$

## B. Effect of Temperature

The correction for temperature is done by using the data of $(H_T-H_{298})$ for the formation reaction:

$$C + \frac{n}{2}H_2 + \frac{m}{2}O_2 \longrightarrow CH_nO_m \qquad \text{(A-3)}$$

$$\Delta H^o_{coal,T} - \Delta H^o_{coal,298} = \frac{M_{coal} - 12}{12} \times (H_T - H_{298})_{graphite} - \frac{n}{2}(H_T - H_{298})_{H_2} - \frac{m}{2}(H_T - H_{298})_{O_2}$$

$$\Delta S^o_{coal,T} - \Delta S^o_{coal,298} = \frac{M_{coal} - 12}{12} \times (S_T - S_{298})_{graphite} - \frac{n}{2}(S_T - S_{298})_{H_2} - \frac{m}{2}(S_T - S_{298})_{O_2}$$

where M is the molecular weight of the coal ($M_{coal}$=12+n+16xm). The values of $S_T-S_{298}$ and $H_T-H_{298}$ are available from standard JANNAF tables. The free energy of formation is calculated by $\Delta G^o{}_T=\Delta H^o{}_T-T\Delta S^o{}_T$.

C. Char

The char in most cases is composed of very little amount of oxygen and has about 0.2-0.4 molar ratio of hydrogen to carbon. In this work a typical char is assumed to be $CH_{0.3}$.

The structure of the char is not known. Different experimental information shows that it can be assumed to be aliphatic, cycloaliphatic or aromatic.

The calculations for the thermodynamic properties of the char are done by using formation reactions, assuming that the char has different structures. The three options are shown in reactions (A-4), (A-5) and (A-6).

$$0.874C + 0.021C_6H_{14} \dashrightarrow CH_{0.3} \qquad \text{(A-4)}$$

$$0.85C + 0.025C_6H_{12} \dashrightarrow CH_{0.3} \qquad \text{(A-5)}$$

$$0.70C + 0.05C_6H_6 \dashrightarrow CH_{0.3} \qquad \text{(A-6)}$$

Using reaction (A-4) the $\Delta G^{o}_{298}$, $\Delta H^{o}_{298}$ of the char are:

$$\Delta G^{o}_{298} = 0.021 x \Delta G^{o}_{n\text{-hexane}(1),298} = 0.021 x (-0.91) = $$
$$= -0.02 \text{ Kcal/gr-mole}$$

$$\Delta H^{o}_{298} = 0.021 x \Delta H^{o}_{n\text{-hexane}(1),298} = 0.021 x (-47.5) = $$
$$= -1.02 \text{ Kcal/gr-mole}$$

The results are summarized in the following table.

| Char Structure | Char Properties [Kcal/gr-mole] | | | Gasification (A-7) | |
|---|---|---|---|---|---|
| | $\Delta G^{o}_{298}$ | $\Delta H^{o}_{298}$ | $T\Delta S^{o}_{298}$ | $\Delta G^{o}_{298}$ | $\Delta H^{o}_{298}$ |
| graphite (ref.) | | | | 23.9 | 41.9 |
| n-hexane | -0.02 | -1.0 | -0.98 | 23.9 | 42.9 |
| cyclohexane | 0.16 | -0.73 | -1.09 | 23.7 | 42.8 |
| char I (benzene) | 1.55 | 1.0 | -0.55 | 22.3 | 40.9 |
| char II (m-xylene) | 0.77 | -0.18 | -0.95 | 23.1 | 42.0 |

Also are given the corresponding values for the gasification reaction:

$$CH_{0.3} + H_2O_{(1)} \longrightarrow CO + 1.15H_2 \qquad \text{(A-7)}$$

As expected, the thermodynamic values are almost identical for all cases.

# Appendix B

## CHEMICAL EQUILIBRIUM IN GAS-SOLID REACTIONS

There is a basic difference between multiphase and single phase systems. Theoretically, in a single phase system, there will be a finite equilibrium concentration of all initial species. No reaction can be completely irreversible in a single phase system. On the other hand, in a multiphase system, if the partial pressures of the compounds in the gas phase are below the equilibrium partial pressure over the solid (or liquid), one or more solid compounds can completely disappear from the solid phase. Therefore, the conditions at equilibrium have to be clearly defined. In the following case the conditions are such that the amount of steam or hydrogen added is not sufficient to cause total disappearance of the solid phase. The amount of steam and hydrogen converted will then be constrained by equilibrium conditions between the solid and gas phase.

If there are several solid components the question arises: how many solids remain at equilibrium and which of the solids determines the equilibrium. Consider the following simplified case. A carbon ($C_{(1)}$) with a positive free energy compared to graphite of 2 Kcal/gr-mole, is gasified with hydrogen. This carbon can decompose to a different type of carbon ($C_{(2)}$) with a free energy equal to zero. The second type of carbon can also be formed by decomposition of the methane formed. The individual reactions are written as:

$$C_{(1)} + 2H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_4 \qquad \text{(B-1a)}$$

$$C_{(2)} + 2H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CH_4 \qquad \text{(B-1b)}$$

$$C_{(1)} \xrightarrow{k_3} C_{(2)} \qquad \text{(B-1c)}$$

Reaction (B-1c) is assumed to be truly irreversible, which is a permissible assumption for solid-solid decomposition reactions. It is further assumed that the reaction is carried out at constant pressure (typical conditions of a gasifier). Figure B.1 shows a kinetic trajectory of the system in a batch reactor with initial feed ratio (mole $C_{(1)}$/mole $H_2$) of 1:1.

Two extreme cases are shown. In the first it is assumed that $k_1 >> k_2$ and that $k_1 >> k_3$. In this case $CH_4$ will reach a pseudo equilibrium concentration, which can be computed from the equilibrium constant of reaction (B-1a). In the second case it is assumed that $k_1 < k_2$ and that $k_3$ is larger than in the first case. The system behaves as if the only carbon exists is $C_{(2)}$.

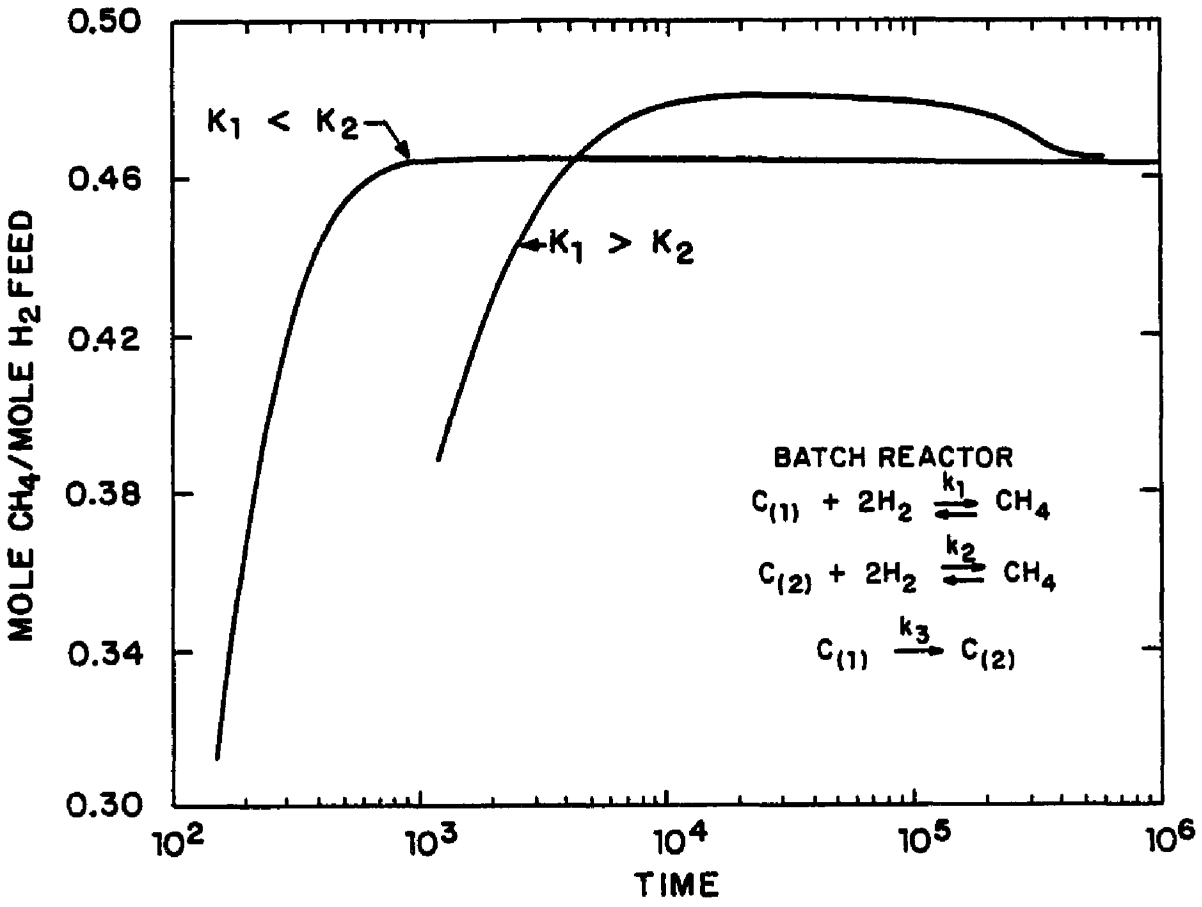


Figure B.1: Methane yield as a function of of time in a batch reactor for the reaction system B-1.

Consider now a stirred tank reactor in which part of the solid is removed unconverted. Both solid and gas residence time can then be independently varied. For a closer approximation of a real gasifier, the rate of the feed gas is varied, while the solid is added and removed at such a rate as to keep both solid holdup and solid conversion constant. For a fixed solid conversion only one free variable remains which is the feed rate of the hydrogen. In Figure B.2, the yield of $CH_4$ per mole $H_2$ feed is shown as a function of residence time for two char conversions. At high residence times, the increase of residence time has a negligible effect on both cases. The equilibrium yield is determined by the properties of $C_{(2)}$. The case of $k_1 >> k_2$, $k_3$ exhibits a pseudo equilibrium yield for low char conversions. For the case of $k_2 > k_1$ the system does not exhibit a pseudo equilibrium yield, and therefore, it is not plotted.

In a gas-solid reaction, countercurrent flow of solid and gas is possible and if the reaction system is similar to reactions (B-1), a countercurrent flow reactor has a significant advantage for the case of $k_1 >> k_2$, $k_3$. This advantage is shown in Figure B.3b where the yield from a two-stage reactor (Figure B.3a) is compared with the yield in Figure B.2. It is shown that if the reactor is operated with low conversion in the upper stage and high conversion in the lower stage, the yield of $CH_4$ can be increased

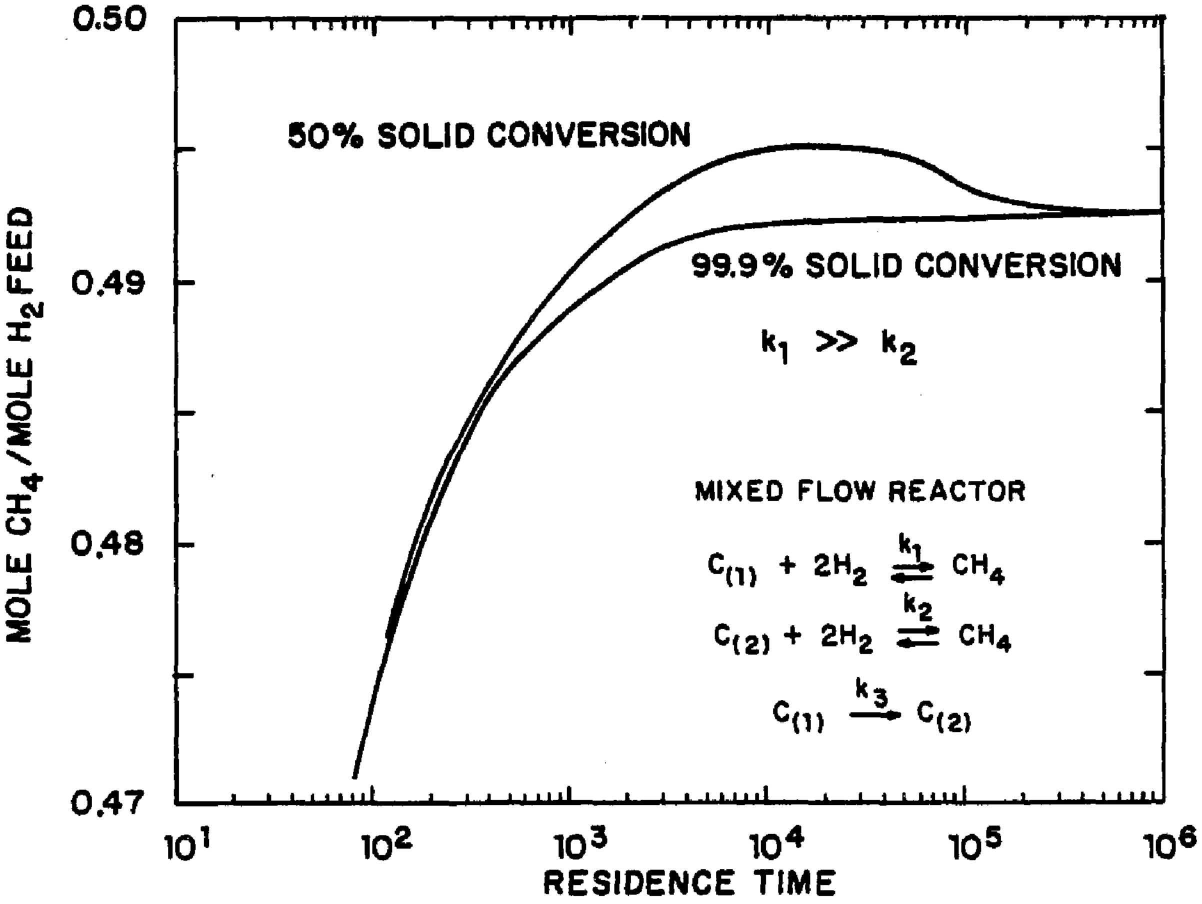


Figure B.2: Methane yield as a function of residence time in a mixed flow reactor for the reaction system B-1.

above that of the single mixed flow reactor with the same high char conversions. The optimum ratio of the two stages depends on the ratios of $k_1/k_2$ and the value of $k_3$.

The system of reactions (B-1) was explained for its simplicity. Real hydrogasification is more complex. One possible variation would be that $k_3$ is zero and the initial $C_{(2)}$ is formed by nucleation from the gas phase. The overall form of the solution is similar to Figures B.1 to B.3, although a system with nucleation has the potential for other complexities such as multiple steady states and limiting cycle instabilities [Caram and Scriven 1976; Othmer 1976].

Another possible interesting reaction in hydrogasification of char is of the type:

$$CH + XH_2 \longrightarrow YCH_4 + \ldots\ldots + CH \qquad \text{(B-2)}$$

As an example, the reaction scheme

$$CH_{0.3} + 0.485H_2 \xrightarrow{k_1} 0.3CH_4 + 0.7CH_{0.1} \qquad \text{(B-3a)}$$

$$\Delta H^{o}_{298} = -6.1 \text{ Kcal} \quad \Delta G^{o}_{298} = -13.3 \text{ Kcal}$$

$$CH_{0.1} + 1.95H_2 \underset{k_{-2}}{\overset{k_1}{\rightleftarrows}} CH_4 \qquad \text{(B-3b)}$$

$$\Delta H^{o}_{298} = -18.2 \text{ Kcal} \quad \Delta G^{o}_{298} = -12.6 \text{ Kcal}$$

is compared with the direct hydrogasification of $CH_{0.3}$

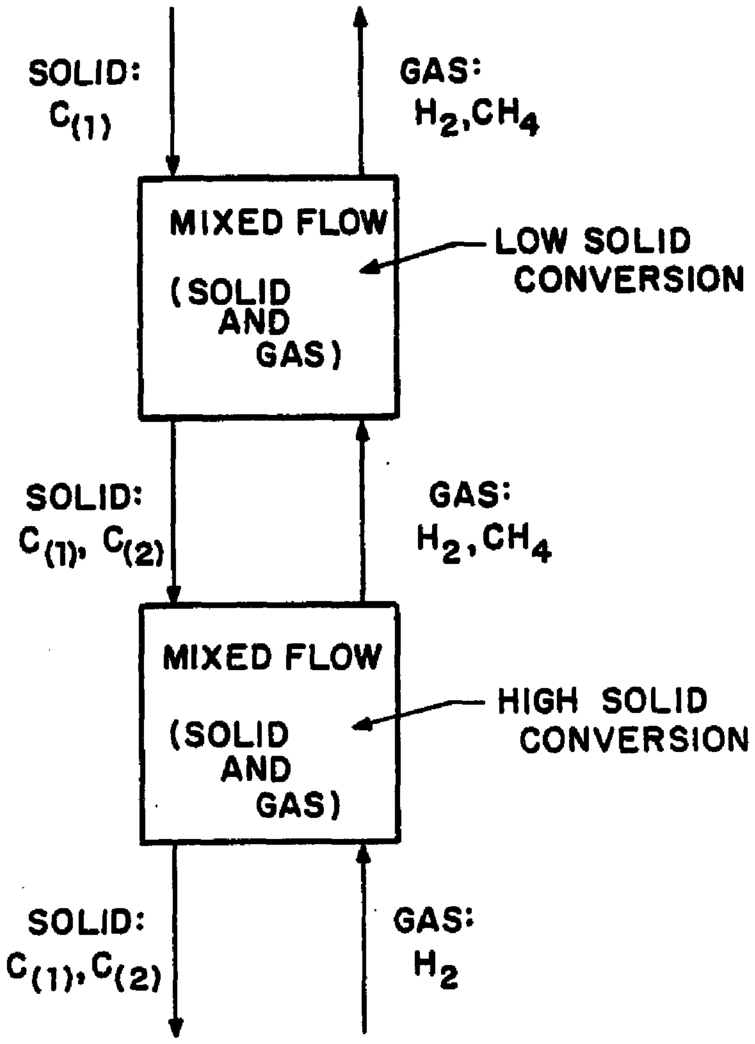


Figure B.3a: Schematic diagram of a countercurrent flow reactor for the reaction system B-1.

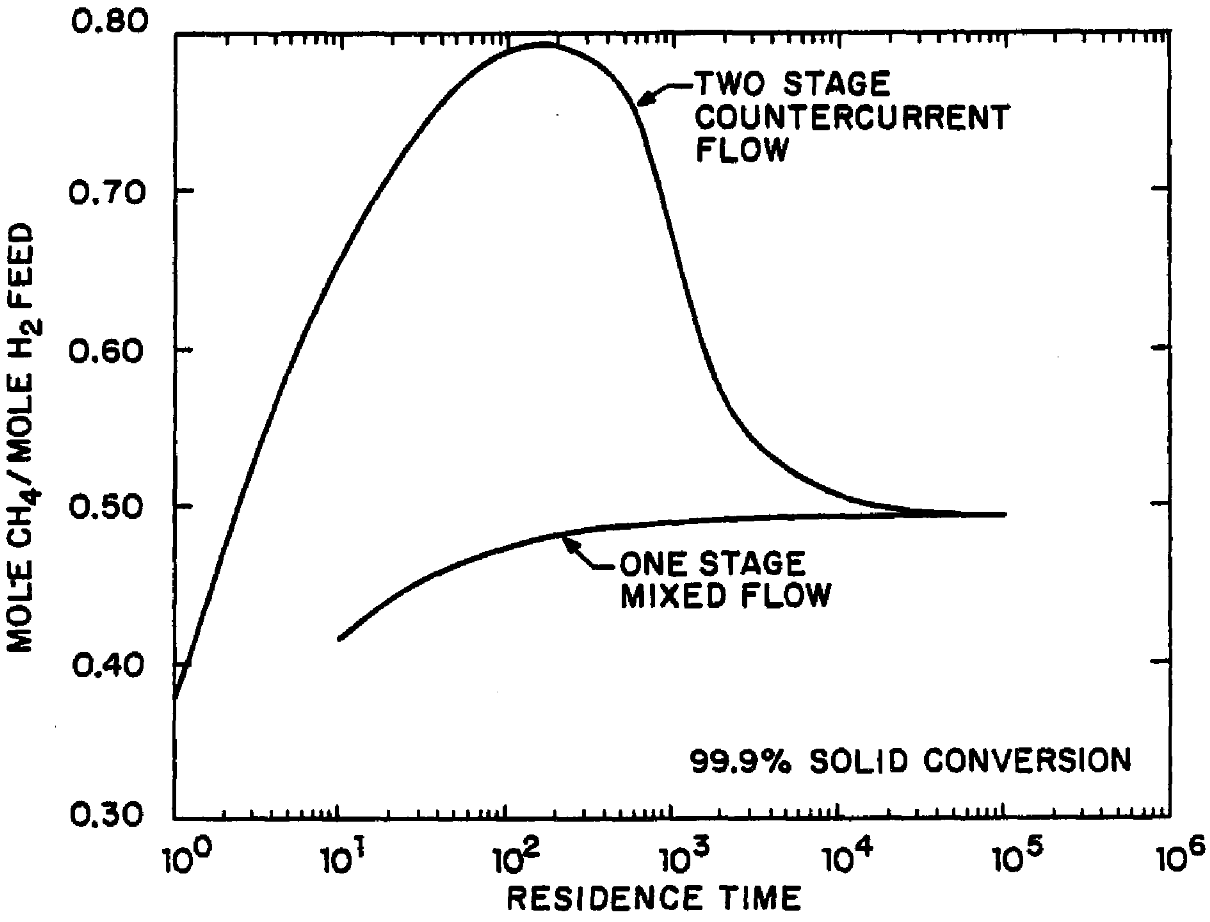


Figure B.3b: Methane yield as a function of residence time in a countercurrent flow reactor for the reaction system B-1.

$$CH_{0.3} + 1.85H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_4 \qquad \text{(B-4)}$$

$$\Delta H^\circ_{298} = -18.9 \text{ Kcal} \quad \Delta G^\circ_{298} = -13.7 \text{ Kcal}$$

(The values of $\Delta H^\circ_{298}$ and $\Delta G^\circ_{298}$ in reactions B-3,4 are approximate estimates).

If the equilibrium pressure of $CH_4$, in reaction (B-3a), is higher than the gasification pressure, then for all practical purposes reaction (B-3a) can be considered irreversible at practical pressures. The equilibrium yield of $CH_4$ in reaction (B-3a) is solely a function of initial $H_2/CH_{0.3}$ ratio. The maximum yield for reaction (B-3a) is, therefore, 0.3/0.485=0.618 and it is not temperature dependent.

Gasifying the char ($CH_{0.3}$) in a batch gasifier following the system in reaction (B-3), the methane will exhibit a pseudo equilibrium yield, which is higher than the yield achieved by the equilibrium of reaction (B-4) at the same conditions (see Figure B.4). If the system is left to react for a long time it will reach a lower equilibrium yield over $CH_{0.1}$.

A much higher yield can be achieved if the gasification reaction is conducted in a two-stage countercurrent gasifier (see Figure B.5a). The char ($CH_{0.3}$) which is introduced in the upper stage is reacted with $H_2$-$CH_4$ mixture from the

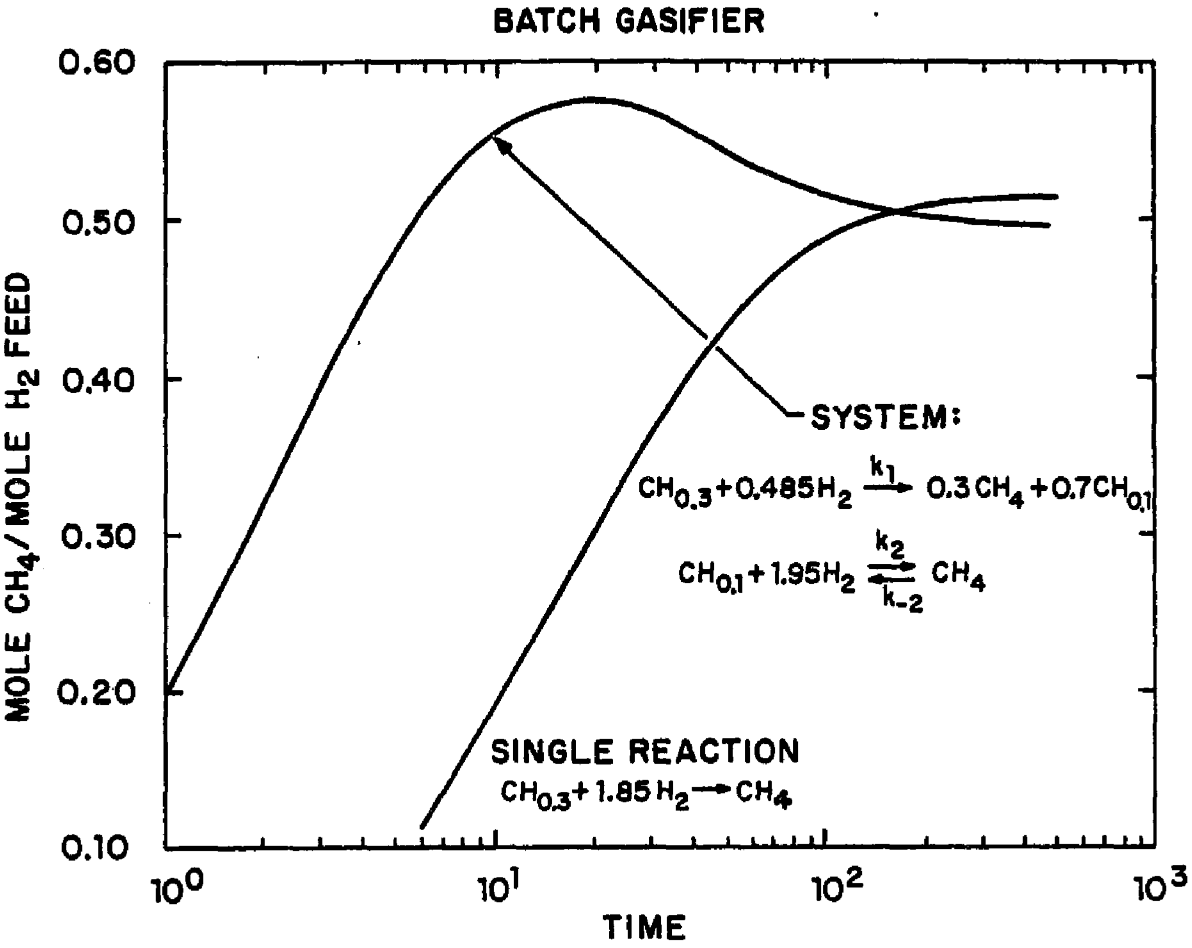


Figure B.4: Methane yield as a function of time in a batch reactor for the reaction system B-3.

lower stage and is completely converted to $CH_4$ and $CH_{0.1}$ according to reaction (B-3a). The unconverted char is then gasified with $H_2$ in the lower stage and the gas composition reaches equilibrium over $CH_{0.1}$. The yield of $CH_4$ as a function of residence time and conversion is shown in Figures B.5b and B.5c. The behavior is very similar to that of Figure B.3.

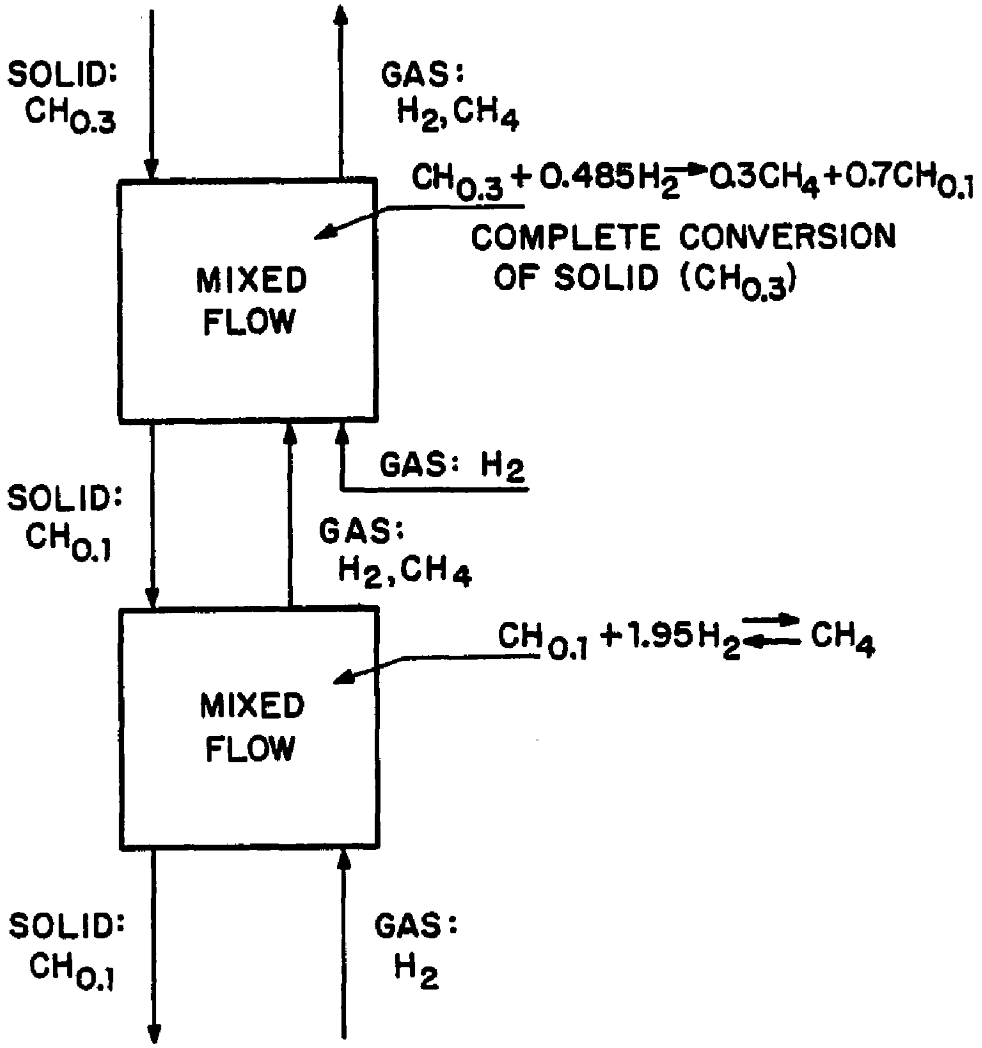


Figure B.5a: Schematic diagram of a countercurrent flow reactor for the reaction system B-3.

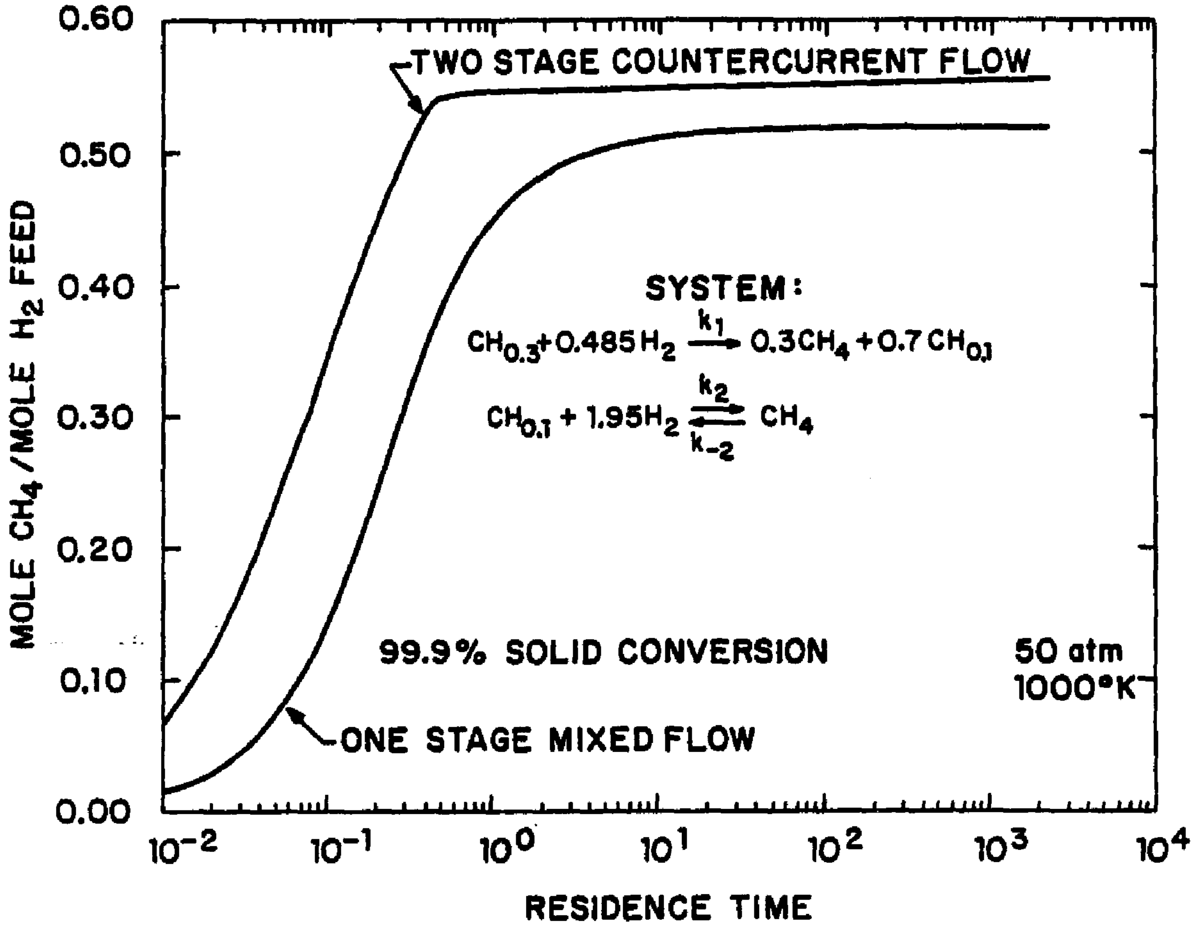


Figure B.5b: Methane yield as a function of residence time in a countercurrent flow reactor for the reaction system B-3 (99.9% solid conversion).

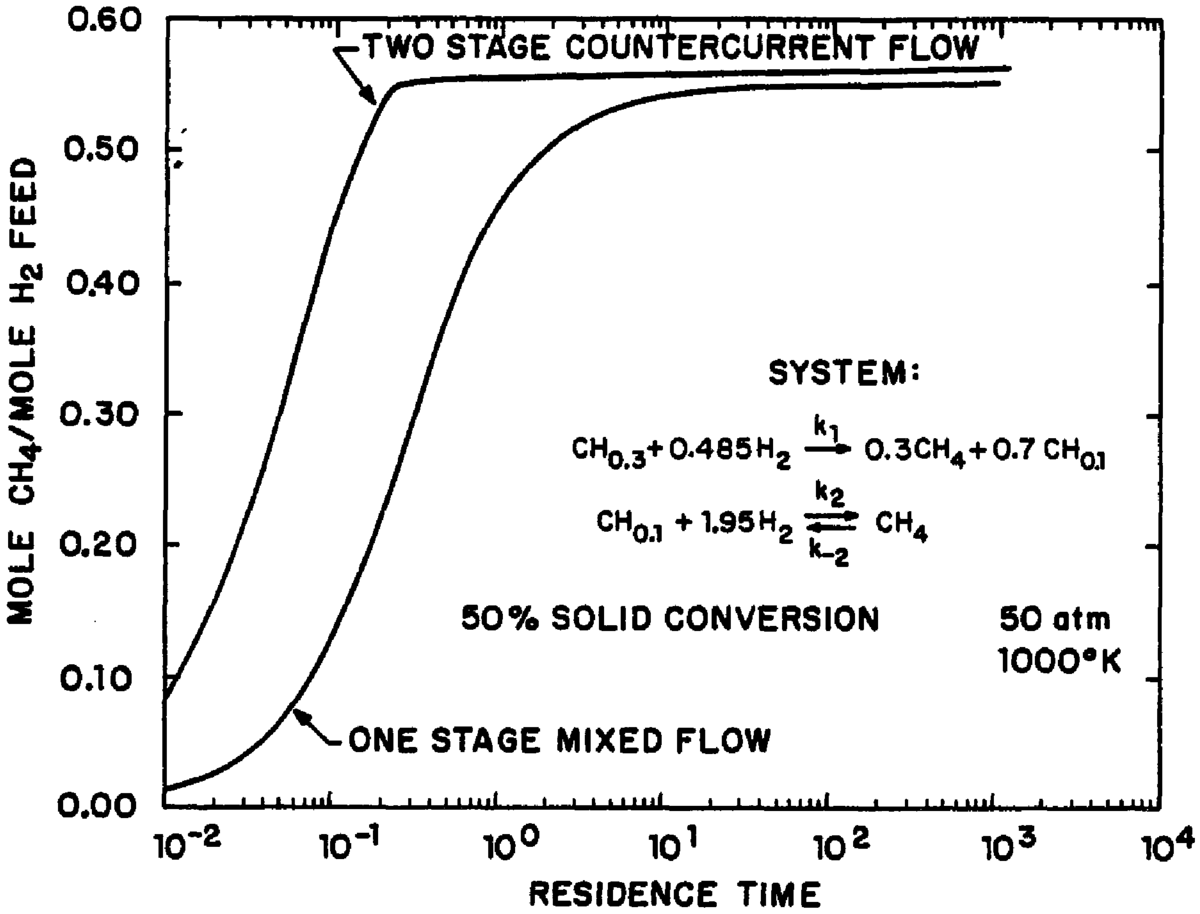


Figure B.5c: Methane yield as a function of residence time in a countercurrent flow reactor for the reaction system B-3 (50% solid conversion).

There is, however, a significant difference between reactions (B-1) and (B-3). In reaction (B-1), the pseudo equilibrium yield can be estimated from thermodynamic properties of the char. In the system described by reaction (B-3), a knowledge of the kinetic path is needed to calculate the equilibrium point. The knowledge of the thermodynamic properties of $CH_{0.3}$ and $CH_{0.1}$ is not enough since the reaction can be written in a different way, such as

$$CH_{0.3} + 0.875H_2 \longrightarrow 0.5CH_4 + 0.5CH_{0.1}$$

Once we understand the nature of the potential equilibrium relations and the effect of multiple solids, we can design experiments which give a more complete picture of the real gasification process. These data are not really necessary for the design of a gasifier. In the case given by the system in reaction (B-3), it is enough to understand that high char conversion is limited by the properties of $CH_{0.1}$ and that in order to utilize the higher free energy of $CH_{0.3}$, at high conversion, a countercurrent reactor has to be used.

The gasifier design will be dominated by the conversion of $CH_{0.1}$, and the limits of methane yield can be obtained by using thermodynamics. The gasification in the top stage, where $CH_{0.3}$ is converted to $CH_4$ and $CH_{0.1}$, is kinetically controlled, and if the reaction is fast it can be considered irreversible.

# BIBLIOGRAPHY

Air Products and Chemical Corp., Cryogenic Methane Separation-Catalytic Hydrogasification Process Analysis, Final Report, Allentown, Pennsylvania 1980.

Anthony, D.B., Howard, J.B., Coal Devolatilization and Hydrogasification, AIChE J., 1976, 22, 4.

Aris, R., Elementary Chemical Reactor Analysis, Prantice Hall, Englewood Cliffs, N.J. 1969.

Blackwood, J.D. and McGrory, F., The Carbon-Steam Reaction at High Pressure, Aust. J. Chem. 1957 11, 16-33.

Cabrera, A.L., Heinemann, H., Somoryai, G.A., Methane Production from Catalyzed Reaction of Graphite and Water Vapor at Low Temperatures (500-600K), LBL-12812, 1981.

Caram, H.S., Scriven, L.E., Non-Unique Reaction Equilibria in Non-Ideal Systems, Chem. Eng. Sci. 1976, 31, 163.

Corneil, H.G., et al., Production Economics for Hydrogen, Ammonia and Methanol during the 1980-2000 Period, Exxon Research and Engineering Co., BNL-50663, 1977.

Dent, J.F. et al., An Investigation into the Catalytic Synthesis of Methane by Town Gas Manufacture, 49th Report of the Joint Research Committee, University of Leeds, 1945.

Detman, R., Factored Estimates for Western Coal Commercial Concepts, FE-2240-5, 1976.

Exxon Research & Engineering Co., Exxon Catalytic Coal Gasification process, FE-2369-24, 1978.

Faith, E.L., Vermeulen, T., AIChE J. 1961, 13, 936.

Flower, J.R., Linnhoff, B., Thermodynamic Analysis in the Design of Process Networks, paper presented at conference C.A.C.E. '79, 214th event of EFCE, Montreux, Switzerland, 1979.

Funk, J.E., A Thermoeconomic Analysis of Large Scale Thermochemical Producction of Hydrogen, EPRI EM-287, 1976.

Gaensslen, H., Thermal Efficiency and Production Economics of Chemical Plants, Lurgi Kohle Und Minerraloltechnik GmbH, West Germany, 1978.

Gaggioli, R.A., Petit, P.J., Second Law Analysis, for Pinpointing the True Inefficiencies in Fuel Conversion Systems, ACS Reprints 1976, 21, 56.

Gruber, G., Advances in Chemistry Series 1975, 146, 31-46.

IGT, Coal Gasification Pilot Plant Support Studies, FE-2806-1,2,3,4, 1978-1979.

Johnson, J.L., Kinetics of Bituminous Coal Char Gasification with Gases Containing Steam and Hydrogen, Advan. Chem. Ser. 1974, 131, 145.

Johnson, P.J., Computer Simulation, Second Law Analysis and Economics of Coal Gasification, University of Kentucky, Ph.D thesis, 1980.

Keenan, J.H., A Steam Chart for Second Law Analysis, Mech. Engr., 1932, 54, 195.

Krambeck, F.J., The Mathematical Structure of Chemical Kinetics in Homogeneous Single-Phase Systems, ARMA, 1970, 38, 317.

Krikosian, O.M., Thermodynamic Properties of Wyoming Coals, Technical note 72-18, UCID-16587, Livermore, CA, Lawrence Livermore Laboratory, 1972.

Kugeler, K., Possibilities and State of Development of Nuclear Coal Gasification Processes, Chem. Eng. Science, 1980, 35, 2005.

Lin, C., Available Work Energy and Coal Conversion Processes, West Virginia University, Ph.D thesis, 1977.

May, W.G., Mueller, R.H., Sweetser, S.B., Carbon-Steam Reaction Kinetics from Pilot Plant Data, I&EC 1958, 50, 1289.

Nuttall, L.J., Conceptual Design of Large Scale Water Electrolysis Plant Using Solid Polymer Electrolytic Technology, Int. J. Hydrogen Energy, 1977, 2, 395.

Nuttall, L.J., Production and Application of Electrolytic Hydrogen Present and Future, ACS Symposium Series 116, 10, 1980.

Othmer, H.G., Nonuniqueness of Equilibria in Closed Reacting Systems Chem. Eng. Sci. 1976, 31, 993.

Riekert, L., *The Efficiency of Energy Utilization in Chemical Processes*, Chem. Eng. Sci., 1974, 29, 1613.

Rostrup-Nielsen, J.R., *Equilibria of Decomposition Reactions of Carbon Monoxide and Methane over Nickel Catalysts*, J. Catal. 1972, 27, 343.

Shinnar, R., Kuo, J.C.W., *Gasifier study for Mobil Coal to Gasoline Processes*, FE-2766-13, 1978.

Shinnar, R., *Gasoline from Coal*, ChemTech, 1978, 8, 686.

Shinnar, R., Shapira, D., Zakai, S., *Thermochemical and Hybrid Cycles for Hydrogen Production. A Differential Economic Comparison with Electrolysis*, I&EC PDD, 1981, 20, 581.

Shinnar, R., Fortuna, G., Shapira, D., *Thermodynamic and Kinetic Constraints of Catalytic SNG Processes*, to be published in I&EC PDD, 1982.

Shinnar, R., Feng, C., *Thermodynamic Constraints of Catalytic Processes*, 1982, to be published.

Solomon, P. R., Prepr. Div. Fuel Chem., Am. Chem. Soc., 1979, 24, 154.

Squires, A.M., *Steam-Oxygen Gasification of Fine Sizes of Coal in a Fluidised Bed at Elevated Pressure*, Trans. Inst. Chem. Engrs., 1961, 39, 3.

Stone and Webster Engr. Co., *Application Study of a Nuclear Coal Solution Gasification Process for Oklahoma Coal*, GA-A12068, 1972.

Stone and Webster Engr. Co., *Comparative Evaluation of High and Low Temperature Gas Cleaning for Coal Gasification-Combined Cycle Power Systems*, EPRI-AF-416, 1977.

Wei, J., Prater, C.D., *The Structure and Analysis of Complex Reaction Systems*, Advan. Catal. 1962, 13, 204.

Wen, C.Y., Huebler, J., *Kinetic Study of Coal Char Hydrogasification*, I&EC PDD, 1965, 4, 147.

Yoon, H., Wei, J., Denn, M.M., *Modeling and Analysis of Moving Bed Coal Gasifiers*, Final Report, EPRI AF-590, 1977.

Zaharadnik, R.L., Grace, R.J., *Chemistry and Physics of Entrained Coal Gasification*, Advan. Chem. Ser. 1974, 131, 127.