

CHAPTER I  
INTRODUCTION

- A. The Gasification Processes.
- B. The Reactions Mechanisms.
- C. The Present Work.

## A. THE GASIFICATION PROCESSES

Water gas is produced from coal as well as from hydrocarbon gas or oil.

I.1 Coal Gasification Processes - Steam-coal reactions are carried out in fixed beds as well as in fluidized beds.

(a) Fixed Bed Processes - The various processes differ from each other, according to the supply of heat of reaction and the adoptability of coal.

In the conventional water gas generator, the air and steam are blown through the fuel bed alternately. Thus the reaction heat is generated and stored in the fuel bed during air blow period and utilized in the steam run. The fuel is restricted to coke or anthracite because of their non-caking characteristics.

Other process having the fixed fuel bed is the Leuna slagging generator (4). Oxygen along with superheated steam is introduced into the reactor in such a proportion that the heat produced by coal-oxygen reaction keeps the ash in molten condition for its easy removal. The combustion of coal also supplies the heat for steam-carbon reaction. Some times fluxing material like limestone is added to remove the ash in molten condition.

Thyssen Galocsy slagging generator (4) is similar to Leuna type. Here heat is supplied from two sources. (a) The gas

from the process or any other source is burned in a mixture of oxygen and steam, and admitted into the fuel bed at a temperature high enough for the steam-carbon reaction. (b) Additional heat is supplied by combustion within the fuel bed, supported by secondary oxygen admitted directly into the bed. The temperature in the generator is of the order of  $1600^{\circ}\text{C}$ . Non caking coal is essential for smooth running in these processes.

The above processes work at atmospheric pressure. When methane is required in the gas produced, the gasification is done under pressure which also increases the capacity of the plant. In Lurgi type of pressure gasification process, oxygen and steam mixture is admitted into the reactor at about 20 atmospheres pressure. Non caking coals are essential for satisfactory operation.

(b) Fluidized Gasification Processes - Jolly, Poll and Stanton (17) of Fuel Research Station, Greenwich, have studied the gasification of non-caking and weakly caking bituminous coals in a fluidized bed reactor. The reactor was made out of cast iron and was surrounded by a combustion chamber. The coal and steam mixture was admitted at the base of the reactor and the heat of reaction was supplied by burning water gas or coal powder with oxygen outside the reactor in the combustion chamber. It was observed that the coefficient of heat transfer between the fluidized solids and the metal wall of the gasification chamber was sufficiently high to enable the heat of reaction to be supplied by conduction through the wall from a surrounding combustion zone. The possibility of

applying the principle of indirect heating depends on the availability of suitable material of construction.

In Winkler type processes (4), the coal is fluidized by steam-oxygen mixture. The function of oxygen again is to burn part of the fuel and supply heat of reaction. Caking coals are unsuitable for fluidization processes due to their agglomerating property. The economy of the process depends upon the cost of coal and prevention of dust carry over.

May et al. (21) and Squires (24) have studied the fluidized gasification process upto a pressure of 245 psig.

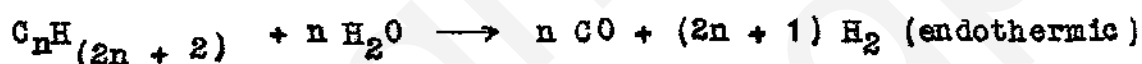
(c) Other Processes - Elliot<sup>(2)</sup> and coworkers<sup>^</sup> have suggested the vortex reactor for gasification of bituminous coal. The unit was operated under slagging condition. Oxygen was fed along with steam for the combustion of coal for supply of heat of reaction.

The Koppers (4) pulverized fuel gasification process can be used, for any type of coal, caking or non-caking. Pulverized fuel is picked up by a stream of oxygen and admitted through nozzles at each end of a horizontal cylindrical generator. Superheated steam enters through an annulus surrounding each nozzle and is apparently directed into the burning mixture of oxygen and coal. The opposing jets promote considerable turbulence in the space between them and the reaction is thus complete. Agglomerations of ash particles that are too heavy to remain suspended in the gases fall into the dust legs provided for this purpose.

I.2 Water Gas from Hydrocarbons - The processes developed for producing water gas from hydrocarbon gas or oil can be grouped in the following three categories.

- a) Steam reforming
- b) Partial oxidation
- c) Combination of steam reforming and partial oxidation.

(a) Steam Reforming - Steam reforming of hydrocarbons is carried out with an excess amount of steam over nickel catalyst. The basic reactions for this process are:



The overall reaction is endothermic and the necessary heat is supplied either by regenerative heating by burning part of the charge stock (30) or by external heating (26). The operating conditions are 5 to 25 atmosphere pressure and 650 to 1050 °C temperature. The conversion is about 70%.

(b) Partial oxidation - Hydrocarbon and oxygen are separately heated and burnt in a specially designed burner situated at the top of the refractory lined reactor (28). This oxidation converts part of the hydrocarbon feed into carbondioxide and steam. The heat generated by this reaction, then causes the unoxidized hydrocarbon fraction to react with carbondioxide and steam to form carbon monoxide and hydrogen. In the homogeneous reaction, it is

necessary to recirculate large amounts of the product gases to keep the hydrocarbon content sufficiently low to prevent carbon deposition. The catalyst is not used, but the pressure of 220 to 340 psig is essential.

(c) Combination of steam reforming and partial oxidation - Various processes (19, 27, 32) are developed for the manufacture of carbon monoxide and hydrogen by reactions of hydrocarbons with oxygen and steam.

The reaction is carried out first in the homogeneous phase by burning methane in a mixture of oxygen and steam at the top of a refractory lined chamber whereby the temperature is raised to about 1200 °C. The second phase of the reaction uses a nickel based catalyst at about 1000 °C. Almost complete conversion of the hydrocarbon is achieved.

## B. THE REACTIONS MECHANISMS

Different minimum possible reactions taking place simultaneously in the present series of experiments are :

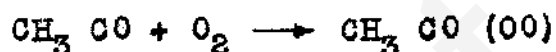
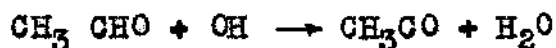
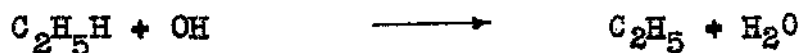
1. Hydrocarbon - Oxygen reaction
2. Steam - Coal reaction
3. Carbon monoxide - Steam reaction
4. Carbondioxide - Coal reaction

I.3 Hydrocarbon - Oxygen Reaction - At the temperature of combustion, hydrocarbons rapidly dissociate into free hydrocarbon radicals (8, 12, 23). The hydrocarbon radicals are very active and have affinity for oxygen. Hence, they combine with oxygen to form oxygenated compounds or radicals which have only transitory lives. These oxygenated compounds form aldehydes.

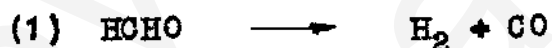
Depending on the amount of oxygen present, the aldehydes may break down thermally to form carbon monoxide and hydrogen or it may burn to either carbon monoxide and water or to carbon-dioxide and water. This process of hydroxylation is very rapid. In the mixture of hydrocarbons, the higher ones will react first and then lower hydrocarbons will react. Similarly in the mixture of hydrocarbon and hydrogen or hydrocarbon and carbon monoxide, the hydrocarbon burns first and then hydrogen or carbon monoxide.

Hydrocarbons, especially the higher ones, also may decompose into carbon (soot) and hydrogen. If the conditions such as

preheating hydrocarbon and air or premixing favour hydroxylation, there will be no soot formation. Thus generalized mechanism can be as follows for a simple case of ethylene:



Depending on the amount of oxygen present, the formaldehyde thus formed may either react as follows -



#### I.4 Steam - Carbon Reaction -



Long and coworkers (20) have studied the reaction extensively. The reaction rate at a given temperature is represented by

$$\text{rate} = \frac{k_1 p_{\text{H}_2\text{O}}}{1 + k_2 p_{\text{H}_2} + k_3 p_{\text{H}_2\text{O}}}$$

where  $k_1$ ,  $k_2$  and  $k_3$  are constants and  $p_{H_2O}$  and  $p_{H_2}$  are the partial pressures of steam and hydrogen respectively. For the temperature range of 680 °C to 800 °C,  $k_1$ ,  $k_2$  and  $k_3$  are given by the relations:

$$k_1 = 10^{10.2} e^{(-62,300/RT)} \quad \text{lb mole / min. atm. lb.}$$

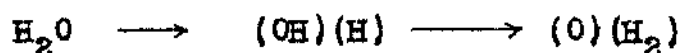
$$k_2 = 33 \quad \text{atm}^{-1}$$

$$k_3 = 10^{4.5} e^{(-20,000/RT)} \quad \text{atm}^{-1}$$

The constant  $k_1$  depends largely on the rate of adsorption of steam on carbon surface,  $k_2$  is the equilibrium constant for the adsorption and desorption equilibrium of hydrogen on the carbon surface and  $k_3$  depends primarily on the rate of reaction between adsorbed water molecules and carbon as well as on value of  $k_1$ .

May & coworkers (21) have shown that the value of  $k_1$  is less for fluid bed as compared to that for fixed bed. While, there is not much of a difference in the values of  $k_2$  and  $k_3$  for fluid and fixed beds.

The mechanism (20) of the reaction is the initial formation of an adsorbed hydrogen atom and an adsorbed hydroxyl radical, followed by the transfer of a hydrogen atom from the hydroxyl to the carbon; the first stage of the reaction is,



Hydrogen evaporates rapidly but a steady state at which a

considerable amount of hydrogen remains on the surface, is soon reached. Hydrogen progressively occupies the sites left vacant by the reaction of the adsorbed oxygen with carbon. Under these conditions (when hydrogen is present) carbon monoxide has little tendency to return to the surface, while the sites which normally take up carbon monoxide are now preferentially occupied by hydrogen. Hence carbon monoxide does not retard the steam reaction. The reaction is retarded only by hydrogen (not even by carbon dioxide).

May and coworkers (21) have shown that the reaction is of 0 order above 5 atm. pressures. At low pressures, the reaction order may appear as high as 1 : however the pressure required for this is substantially less than atmospheric. At 1 atm. pressure the reaction order may be about 0.5 depending on the temperature level.

(a) Effect of Depth of coal bed - As the reaction is of positive order to steam and retarded by hydrogen, the specific rate of gasification decreases according to the increase in the depth of coal bed.

(b) Effect of Particle Size - The rate is independent of particle size over the range 0.0083" to 0.25". In this range, rate of diffusion of the gas throughout particle is much greater than the chemical reaction rate (15) i.e. the composition of the gas in the pores does not differ significantly from that in the voids

between the particles. Further subdivision of the particles (smaller than 0.0083") exposes fresh surface to reaction.

(c) Effect of Steam Rate - It is observed (15, 21) that the gasification rate increases as the steam rate is increased.

Gasification rate  $\propto$  (steam rate)<sup>0.8</sup> for zero burn-off

Gasification rate  $\propto$  (steam rate)<sup>0.7</sup> for 40% burn-off.

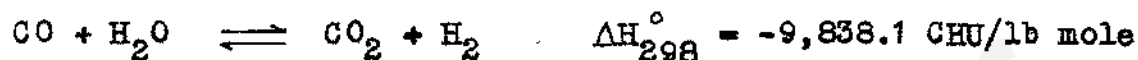
At temperatures below 1200 °C, the rate of gasification is controlled by chemical reaction, while at temperatures above 1200 °C, the rate of diffusion reaction controls the rate of gasification. At high relative velocity between reacting mixture and reacting particles, the stagnant gas film is minimum, the rate of diffusion process is very high and approaches the rate of chemical reaction. At low relative velocities of reacting mixture and reacting particles, the diffusion process decreases until viscous conditions are established and the rate of diffusion process is substantially constant. Thus at low relative velocities of reacting mixture and reacting particles, the reaction rate is minimum.

(d) Effect of Bed Conditions - Rates of gasification in fluidized beds are lower than in fixed beds due to following reasons:(15).

(1) The relative velocity of reacting gases and reacting solid is lower than in fixed bed as the solids also follow the gas path.

(ii) In the fluidized bed, a larger portion of the gas passes rapidly through the bed in the form of bubbles so that the effective residence time of the bubbles is less.

### 1.5 Water Gas Shift Reaction -

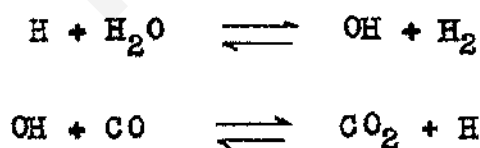


The carbondioxide formed in the steam-coal reaction is due to water gas shift reaction (13, 15, 21) and not by direct reaction of steam with carbon.

Increase in temperature increases the proportion of carbon monoxide in the equilibrium mixture while excess of steam tends to depress carbon monoxide formation.

The reaction is stated (1) to be almost instantaneous above 1492 °C but is relatively slow below 900 °C.

Ingles (13) has studied the mechanism over the temperature range of 750 - 850 °C. The mechanism of the reaction was explained by chain mechanism and not by surface reaction mechanism.



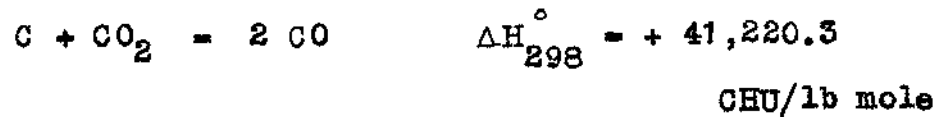
The role of the carbon is that of a chain initiator. The rate of reaction is stated to be of approximately first order with respect to carbon monoxide and of high fractional order with respect to hydrogen.

The rate of shift reaction was found to increase with the increase in the proportion of hydrogen in the initial feed mixture. It was found by Long and coworkers (20) that the hydrogen is adsorbed on the carbon surface, so the increase in hydrogen content should decrease the rate of shift reaction, if it followed a surface reaction mechanism. But as found by Ingles, the increase in hydrogen content, increases the shift reaction rate, hence the reaction does not follow the surface reaction mechanism.

Since the reaction  $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$  consists essentially of a transfer of oxygen atom from a steam molecule to a molecule of carbon monoxide, hydrogen assists such a transfer, is evident. The role of hydrogen is thus either (I) to help in releasing oxygen from steam molecule (II) or to help in combining oxygen with carbon monoxide or both. Since it is well known that gas phase combination of oxygen atom and carbon monoxide is extremely rapid, the effect of hydrogen on the water gas shift reaction must be attributed to the facilitating of oxygen release from steam by gas phase reaction.

The two reactions involved (steam - carbon reaction and water gas shift reaction) have very different activation energies - about 70 K. cal for steam-carbon reaction and roughly 25 K. cal for shift reaction (21). Consequently their relative reaction rates change drastically with temperature. At low temperature, the shift reaction appears to be fast as compared to steam carbon reaction while at high temperatures the reverse is true.

### 1.6 Carbondioxide Carbon Reaction -



Equilibrium conditions show that as the temperature is increased, there is decrease in the carbondioxide content.

Gadsby and coworkers (5) have studied the mechanism extensively. The reaction rate at a given temperature is represented by

$$\text{rate} = \frac{k_4 p_{\text{CO}_2}}{1 + k_5 p_{\text{CO}} + k_6 p_{\text{CO}_2}}$$

where  $k_4$ ,  $k_5$  and  $k_6$  are constants and  $p_{\text{CO}_2}$  and  $p_{\text{CO}}$  are the partial pressures of carbondioxide and carbon monoxide respectively. For the temperature range, 700 °C to 830 °C,  $k_4$ ,  $k_5$  and  $k_6$  are found to vary exponentially as follows:

$$k_4 = 10^{8.8} \cdot e^{(-58,800/RT)} \quad \text{lb mole/min} \cdot \text{atm} \cdot \text{lb.}$$

$$k_5 = 10^{-7.9} \cdot e^{(-45,500/RT)} \quad \text{atm}^{-1}$$

$$k_6 = 10^{6.5} \cdot e^{(-30,100/RT)} \quad \text{atm}^{-1}$$

where T is temperature °K and R is gas constant = 1.987.  $k_4$  and  $k_6$  increase while  $k_5$  decreases with increase of temperature. Their

values at 727 °C and at 838 °C are given below.

	727 °C	838 °C
$k_4$ lb mole/min atm lb	.000089	.0016
$k_5$ atm <sup>-1</sup>	115	11.2
$k_6$ atm <sup>-1</sup>	1.0	4.0

The reaction between carbondioxide and carbon occurs in two stages. In the first stage, the carbondioxide molecule decomposes into an atom of oxygen which is adsorbed by the carbon and a molecule of carbon monoxide which passes into the gas phase. The second state is the 'evaporation' of the adsorbed oxygen atom together with an atom of carbon from the solid to form carbon monoxide.

The retardation of reaction rate by carbon monoxide is due to the adsorption of the gas on the reaction sites. It can be seen from the above table that at higher temperatures, the reduction in the value of  $k_5$  is predominant indicating that at higher temperatures the retardation effect reduces.

It has been shown by Long et al.(20) that the carbondioxide - carbon reaction can not occur in the presence of steam. Hence in the present investigation, the possibility of the above reaction can be neglected.

### C. THE PRESENT WORK

In the present investigation, charcoal has been gasified by steam in presence of oxy-acetylene flame which supplied the heat for steam-carbon reaction as well as helped in maintaining the high enough temperatures in the reactor.

Extremely high direct heat transfer rates were realized within the reactor as denoted by the vertical temperature profile.

The complex reactions involved have been studied for various feed rates of acetylene, oxygen, steam and charcoal.

The equilibrium yields are predicted by the method of free energy minimization. Adiabatic equilibrium temperatures were also calculated by trial and error procedure.

With the background of the knowledge of equilibrium and limited kinetic data as a function of temperature and activities of components available in the literature, for each individual reaction involved, the plausible mechanism of the process has been discussed.

An approximate period of residence of the gas and bed densities were predicted by extension of the cold model of continuous gas solid fluidization system developed in this laboratory.

The effect of change of feed rates on the gasification were explained in the pattern commensurate with the above mechanisms.

LITERATURE CITED

1. Beherenes, H ; Mechanism of Kinetics of the Water Gas Reaction in Cooling Combustion Gases. Z. Physik Chem. 195, 24 (1950).
2. Elliot, M. A ; Perry, H ; Jonakin, J ; Corey, R. C ; Khullar, M. L, Gasification of Pulverized Coal with Oxygen and Steam in a Vortex Reactor. Ind. Eng. Chem. 44, 1074 (1952)
3. Fielder, A. C., "Gasification and Liquification of Coal." The American Institute of Mining and Metallurgical Engineers, New York, 1953
4. Foster, J. F ; Lund, R. J; "Economics of Fuel Gas From Coal". McGraw-Hill, New York, 1950
5. Gadsby, J, Long, F. J, Sleightholm, P, Sykes, K. W, Mechanism of the Carbondioxide - Carbon Reaction Proc. Roy. Soc. (London) A 193, 357 (1948)
6. Goring, G. E., Curran G. P., Tarbox, R. P., Gorin, E., Kinetics of Carbon Gasification by Steam. Ind. Eng. Chem. 44, 1051 (1952)
7. Goring, G. E., Curran, G. P., Tarbox, R. P., Gorin, E., Kinetics of Carbon Gasification by Steam. *ibid*, 44, 1057 (1952)

8. Griswold, J, "Fuels Combustion and Furnaces", McGraw-Hill, New York, 1946.
9. Gulbransen, E. A., Andrew, K. F., Reactions of Carbondioxide with pure Artificial Graphite at Temperatures of 500 ° to 900 °C. Ind. Eng. Chem., 44, 1048 (1952)
10. Gumz, W, Gasification of Solid Fuels at Elevated Pressures. *ibid*; 44, 1071 (1952).
11. Haslam, R. T., Hitchcock, F. L., Rudow, E. W., The Water Gas Reactions. *ibid*, 15, 115 (1923).
12. Haslam, R. T., Russel, R. P., "Fuels and their Combustion." McGraw-Hill, New York, 1926.
13. Ingles, O. G., Water Gas Shift Reaction in Fuel Systems. Trans. Fard. Soc. 48, 706 (1952)
14. Johnstone, H. F., Chen, C. Y., Scott, D. S., Kinetics of the Steam Carbon Reaction in Porous Graphite Tubes. Ind. Eng. Chem. 44, 1564 (1952)
15. Jolley, L. J., Poll, A., Effects of Reactivity and Some other Variables on Gasification of Coke with Steam. Jour. Inst. Fuel, July, 1953
16. Jolley, L. J., Stanten, J. E., Reactivity to Steam and Air of Coke made from Coals of different caking properties and Rank. Reproduced from Conference on Science in the use of Coal, Institute of Fuel.

17. Jolley, L. J., Poll, A., Stantan, J. E., Fluidized Gasification of Non-caking Coals with Steam in a Small Pilot Plant. Reporduced from "Gasification and Liquification of Coal." American Institute of Mining and Metallurgical Engineers, 1953.
18. Jolley, L. J., Poll, A., Noaks, C. C., Stantan, J. E., Production of Water Gas in Fluidized Beds. Reproduced from, International Conference on Complete Gasification of Mined Coal. Liege 1954
19. Linden, H. R., Reid, J. M., Hydrogen from Natural Gas. Petroleum Refiner, Vol 35, No. 6, pp 194, (June, 1956).
20. Long, F. J., Sykes, K. W., Mechanism of the Steam Carbon Reaction. Proc. Roy. Soc., 193, 377 (1948)
21. May, W. G., Mueller, R. H., Sweester, S. B., Carbon-Steam Reaction Kinetics from Pilot Plant Data. Ind. Eng. Chem. 50, 1289 (1958)
22. Scott, G. B., Mechanism of the Steam-carbon Reaction *ibid*, 33, 1279 (1941)
23. Smith, M. L., Stinson, K. W., "Fuels and Combustion." McGraw Hill, New York, 1952.
24. Squires, A. M., Steam-Oxygen Gasification of Fine Sizes of Coal in a Fluidized Bed at Elevated Pressure. Trans. Instn. Chem. Engrs. 39, 3-27 (1961)