PRODUCTION OF CALCIUM CARBIDE IN A PLASMA-JET FLUID BED REACTOR

M. H. EL-NAAS, R. J. MUNZ and F. AJERSCH*

CRTP, Department of Chemical Engineering
McGill University, Montreal
*Department of Metallurgical Engineering
Ecole Polytechnique, Montreal

ABSTRACT

A new plasma-jet fluid bed process for the production of calcium carbide has been studied. Unlike in the present electric arc furnace, reaction in the new process takes place in the solid phase at about 2150 K. A thermodynamic analysis showed that the plasma process could lower the energy consumption by up to 40%. A laboratory-scale fluid bed reactor with a DC plasma torch was used for the study. Calcium oxide powder with a mean particle size of 170 µm was reacted with graphite powder. Results show that the reaction takes place mainly in the jet zone and that conversion to calcium carbide increases linearly with reaction time. Microscopic analysis of the product indicates that the reaction between graphite and lime takes place through gaseous intermediates and that the overall reaction rate is controlled by chemical kinetics.

1.0 INTRODUCTION

The synthesis of calcium carbide from calcium zinc alloy and coal was first discovered by Wohler in 1862. Industrial production of the material in electrical furnaces started twenty years later [1]. Presently calcium carbide is being produced by reacting carbon in the form of coke or coal and calcium oxide in the form of lime in large electric arc furnaces at about 2400 K. The energy consumption for a typical electric arc furnace is of the order of 4 kWh/kg CaC_2. The molten product, which contains about 80% CaC_2, is cast, crushed and ground to the size required by the industry. Industrial applications of calcium carbide include the desulphurization of steel and cast iron, the production of acetylene and the production of cynamide.

Several patents have been granted for the production of calcium carbide using different furnace designs and different heating mechanisms. Baba and Shohata [2] and Eriksson [3] patented processes using high frequency plasma for the production of calcium carbide. In both processes the energy consumption is much higher than that of the present electric arc furnace.

Plasma fluidized and spouted beds have been studied extensively in the past thirty years [4-8]. Plasma fluidized beds combine the high energy of plasma and the good mixing of fluidized beds making them ideal for highly endothermic gas-solid and solid-solid reactions. In the present work, the production of calcium carbide in a plasma fluidized bed has been investigated.

2.0 EXPERIMENTAL APPARATUS

The experimental set-up consisted of a power supply, a DC plasma torch, a fluid bed, a CO analyzer and a temperature measuring system. A schematic diagram of the set-up is shown in Figure 1. The plasma torch has a conical thoriated tungsten cathode and an annular copper anode. The design power of the torch is of the order of 20 kW. Power to the torch is controlled by varying the current. Argon was used to initiate the arc and hydrogen was then added to increase the arc voltage and hence raise the power and plasma enthalpy.

The fluid bed consisted of two parts: the reactor section and the disengaging section. The inner part of the reactor is a graphite cylinder (8 cm ID and 35 cm in height) surrounded by a graphite felt 2 cm in thickness; the cylinder and the felt are located inside a stainless steel cylinder (13 cm ID) which is insulated from the outside to minimize heat loss. The lower part of the reactor housed the distributor and the plasma torch. The disengaging section is a stainless steel cylinder 25 cm ID and 25 cm in height. The large diameter lowers the gas velocity and minimizes elutriation of particles.

The reactants were calcium oxide powder and graphite powder with mean particle sizes of 170 µm and 150 µm respectively. They were charged into the batch reactor at a stoichiometric ratio of (3C to 1CaO) with a total mass of 1 kg. Argon was used to fluidize the bed at 1.1 times the minimum fluidization velocity.

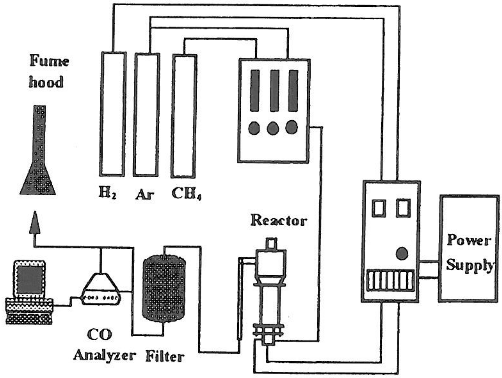

Fig. 1 : Schematic Diagram of the Apparatus

3.0 RESULTS AND DISCUSSION

3.1 Thermodynamic Analysis

A thermodynamic analysis of the reaction of calcium oxide and carbon was carried out using FACT (Facility for Analysis of Chemical Thermodynamics)[9] to determine the equilibrium chemical composition of the reaction at different temperatures and initial compositions and to estimate the energy requirements for the plasma process. The subprogram EQUILIB was used for equilibrium calculations. It was assumed that only pure reactants (graphite and calcium oxide) were present to react in a closed system. Other substances assumed to be present at equilibrium included: CaC_2, CO, Ca, Ar and H_2; no solutions were considered for the calculations. The temperature was varied from 1800 to 2200 K.

The equilibrium composition is plotted against temperature in Figure 2. The reaction between calcium oxide and carbon takes place at about 1700 K and reaches completion at 2150 K. In the absence of argon and hydrogen, however, the reaction does not proceed below 2150 K. The decline of CaC_2 after reaching a maximum at 2100 K and the rise of carbon after reaching a minimum could be an indication of the decomposition of CaC_2 at high temperature; this could also be due to the presence of acetylene at the range where it would be stable (2000-2500 K).

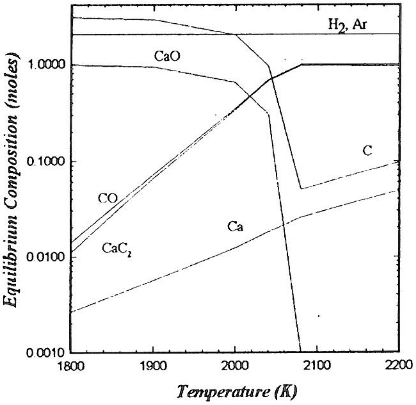

Fig. 2: Equilibrium Composition vs Temperature

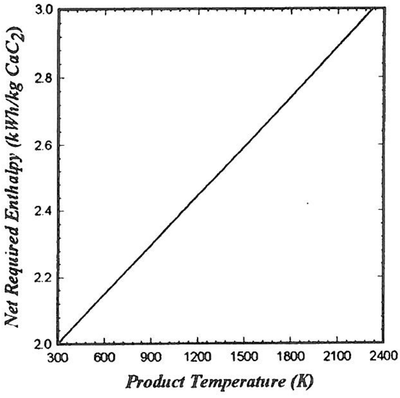

Fig. 3: Net Enthalpy vs Product Temperature

A heat balance for the plasma process was calculated using the subprogram REACTION. The theoretical required enthalpy for the process is the sum of the enthalpy required to heat the reactants from room temperature (300 K) to the reaction temperature (chosen as 2150 K) and the enthalpy of the reaction (at 2150 K) minus the enthalpy that could be gained by cooling the products to a temperature T_p. This net required enthalpy is plotted against product temperature T_p in Figure 3. It is shown that if the products are withdrawn at 2150 K, the theoretical net enthalpy for the process is 2.9 kWh/kg CaC_2. If the products are cooled to 300 K, the enthalpy requirements will be 2.0 kWh/kg CaC_2. Assuming torch efficiency of 80%, the energy requirements will be 3.6 and 2.5 kWh/kg CaC_2 for 2150 K and 300 K respectively. This indicates that the plasma process could achieve up to 40% saving even without including the enthalpy of combustion of carbon monoxide.

3.2 Effect of plasma gas composition

Argon at a flow rate of 40 l/min was used as the plasma gas. The plasma power achieved with argon, however, was too low (6 kW) for the reaction to reach appreciable conversion. Thus, hydrogen was added to argon at three concentrations: 33% , 45% and 67% (vol%) to increase power and improve the plasma enthalpy. Experiments were conducted with the three concentrations while keeping the plasma gas flow rate at 40 l/min and current at 240 A. The static bed height was 20 cm, and the plasma jet was about 8 cm in height. The exhaust gas was continuously analyzed for carbon monoxide to determine the overall conversion of CaO.

A plot of CaO conversion versus run time for different plasma gas compositions is shown in Figure 4. The conversion of calcium oxide increased linearly with the reaction time and increased exponentially with increasing hydrogen concentration in the plasma gas. The hydrogen effect is only due to increasing the plasma power and hence the plasma gas temperature and not due to involvement of hydrogen in the reaction. This fact was confirmed by comparing two runs with different hydrogen concentrations but same power as shown in Figure 5. The sensitivity of conversion to power (or temperature) was evident when power was varied during experiments by varying the current. The fact that the rate of conversion is constant with time and sensitive to plasma temperature suggests that the overall reaction rate is controlled by chemical kinetics. Microscopic analysis of the solid

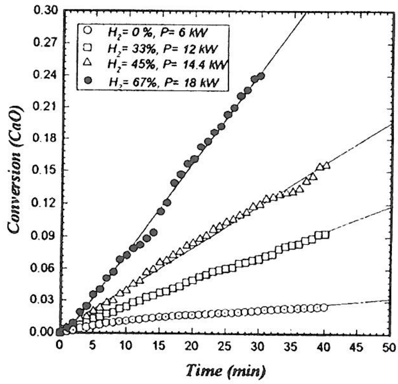

Fig 4 : CaO Conversion vs Reaction Time

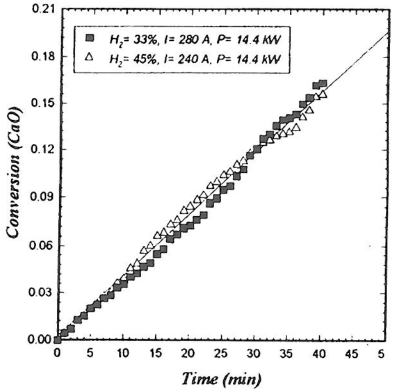

Fig. 5: CaO Conversion vs Reaction Time.

product indicated that the reaction between calcium oxide and carbon occurred through gaseous intermediates, namely calcium vapour and carbon monoxide.

3.3 Bed Stability

The reactor in this work can be divided into two zones: the jet zone at the bottom and the bed zone where most particles are present in the fluidized state. The jet zone is about 8 cm in height and 4 cm in diameter; temperature in this zone is much higher than that of the bed zone. Particles circulate from the bed into the jet zone and react as they pass through the jet, where the temperature is high enough for reaction. Melting and agglomeration of particles occurred at high temperatures (at 30 minutes for 67% hydrogen and at 70 minutes for 45%) leading to the destabilisation of the bed. This occurred before the bed reached the temperatures needed for reaction. A plot of CaO conversion against bed temperature is shown in Figure 6. It is clear that up to 30% conversion is achieved at a bed temperature much less than that needed for reaction This indicates that the reaction is taking place only in the jet zone.

3.4 Effect of Stoichiometry

Calcium carbide is formed through the following reaction:

$$CaO + 3C \rightarrow CaC_2 + CO \qquad (1)$$

Experiments were conducted with excess graphite and excess calcium oxide to determine the effect of stoichiometry on the reaction rate. The rate of conversion for three stoichiometries is plotted against reaction time in Figure 7. For the reaction with excess calcium oxide (1CaO : 1.5 C), less carbon is available for reaction, and hence the rate of conversion is lower than that of reaction (1). On the other hand, having excess carbon is

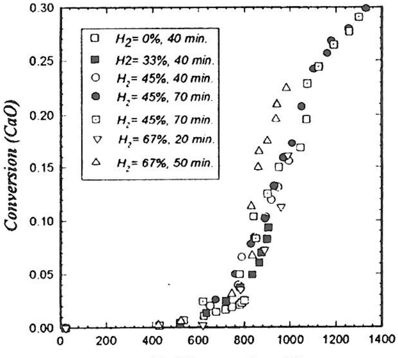

Fig. 6: CaO Conversion vs Reaction Time.

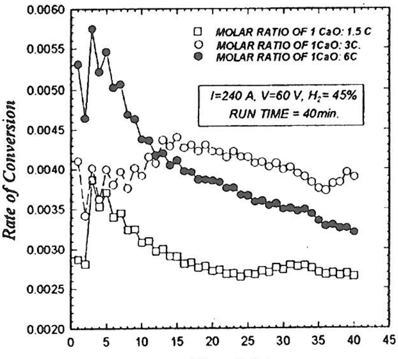

Fig. 7: Rate of Conversion vs Reaction Time.

expected to lead to a higher rate than in reaction (1). The observed rate, however, declined with reaction time. This decline is believed to be due to the fact that the bed heat capacity is highest with excess carbon; therefore more energy goes to heating the bed and less goes to the reaction.

4 .0 CONCLUSIONS

A plasma fluid bed process for the production of calcium carbide has been investigated. A thermodynamic analysis indicated that the solid phase reaction should be complete at 2150 K, and that the plasma process could lower energy consumption by up to 40%. Experimental results showed that the reaction between calcium oxide and carbon took place in the jet zone and that conversion increased linearly with reaction time. The rate of conversion is controlled by chemical reaction. Melting and agglomeration of particles led to destabilization of the bed at high temperature, making it impossible to reach high conversion. With optimized reactor design, high conversions can be achieved.

5.0 ACKNOWLEDGEMENTS

The financial support of the Secretariat of Scientific Research of Libya via a scholarship to M. H. El-Naas, NSERC, and FCAR, Quebec, are gratefully acknowledged.

6.0 REFERENCES

1- Kampmann, F-W., Portz W., Frorath F-K., Hoechst A. G., Knapsack W. and Koln K.,"Calcium Carbide", Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., VCH Verlagsgesellschaft, Weinheim (FRG), (1985).

2- Baba, K. and Shohata N., Manufacture of calcium carbide micropowders by high-frequency plasma method, Japanese patent 63112409, (1988).

3- Eriksson, S., Calcium carbide from powdered limestone or lime, Belgian patent 897179, (1983).

4- Goldberger, W. M. and Oxley J. H., Quenching the plasma reaction by means of the fluidized bed, A.I.Ch.E. Journal, vol. 9, (1963), PP. 778-782.

5- Jurewicz, J., Proulx P. and Boulos M. I., The plasma spouted bed reactor, ISPC-7, Eindhoven, July (1985).

6- Wierenga, C. R. and Morin T. J., Characterization of a plasma fluidized bed reactor, AIChE Journal, vol. 35, (1989), PP. 1555-1560.

7- Flamant, G., Hydrodynamics and heat transfer in a plasma spouted bed reactor, Plasma Chemistry and Plasma Processing, vol. 10, (1990), PP. 71-85.

8- Munz, R. J. and Mersereau O. S., A plasma spout-fluid bed for the recovery of vanadium from vanadium ore, Chem. Eng. Sci., vol. 45, (1990), PP. 2489-95.

9- Bale, C. W., Pelton A. D. and Thompson, W. T., “Facility for Analysis of Chemical Thermodynamics, User’s Guide”, 1st edition, McGill University and Ecole Polytechnique (1979).