

## Carbon Dioxide Acceptor Gasification Process

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-----Introduction

Production of both hydrogen rich and high BTU gas from coal has been under study in the Research Division of Consolidation Coal Company for several years. There are a number of partially or fully developed processes which are available for this purpose. These are all too expensive to be competitive with natural gas for the foreseeable future.

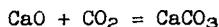
It is a feature of most of the available processes that oxygen is used to provide the endothermic heat of the gasification process. The high cost of oxygen is one of the more significant items which makes the conventional processes uneconomic.

It has thus become clear that elimination of oxygen is one of the prerequisites for the development of an improved process. The CO<sub>2</sub> acceptor process is one which satisfies this general objective. This paper describes some steps which have been taken in the development of the process. The emphasis is on a discussion of the properties of the acceptor as determined by the needs.

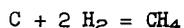
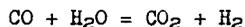
Process Description

The general principle of the CO<sub>2</sub> acceptor process is the use of a circulating lime-bearing acceptor.

The acceptor generates the heat required in the gasification step of the process by the reaction,



The absorption of carbon dioxide serves also to enrich the gas in hydrogen. More heat is thus evolved by intensification of the two exothermic reactions,



It thus becomes possible to supply all the heat requirements of the gasification process by use of a suitable acceptor.

The acceptor is regenerated by calcining in a separate step the calcium carbonate at a higher temperature. The heat required is supplied by burning the residual char from the gasifier with air.

A number of variations in the acceptor process have been described in a series of U. S. patents<sup>(1)</sup>. A typical flowsheet of the process is illustrated in Figure 1. The char feed is passed sequentially through the series of process steps shown from the devolatilizer to the regenerator.

The elements of the process flowsheet have been studied individually. The product yields obtained in the devolatilization of low temperature chars produced from Pittsburgh Seam coals have been determined in a continuous 10 lb/hr<sup>(2)</sup> fluidized bed unit. Gasification of char with steam and oxygen has been studied in a 200 lb/hr fluidized pilot scale unit<sup>(3)</sup>. A detailed study has also been made of basic kinetics of the gasification reactions of char with pure hydrogen<sup>(3)</sup> and hydrogen-steam mixtures<sup>(4,5,6)</sup>.

No operating data are available for the integrated process as shown in Figure 1. A detailed heat and material balance around the process is, however, given in Table I. These data represent reasonable projections of the operating conditions of the process based on available data on the kinetics and thermodynamics of the individual reactions involved.

The process conditions in the gasifier were determined from the kinetics data which show that the following approaches to equilibrium in the different reactions are reasonable.

	<u>Percent Approach to Equilibrium</u>
$C(\text{graphite}) + 2 H_2 = CH_4$	80
$CO + H_2O = CO_2 + H_2$	100
$C(\text{graphite}) + H_2O = CO + H_2$	24.5

In Table I the  $CO_2$  present in the gasifier is equivalent to the equilibrium  $CO_2$  pressure for the acceptor reaction. Although our data show this reaction to be rapid, a small partial pressure driving force actually would be required.

The flowsheet and material balance serves largely as a framework for the discussion of required acceptor properties. Since the acceptor is the heart of the process, selection of a suitable material is the required first step in the process development.

The acceptor must be physically rugged, such that it resists excessive attrition and thus is separable in the regenerator from the finely-divided char ash. It must be resistant to chemical deactivation caused by repeated cycling through the conditions imposed in the process as well as by interaction with char ash. Finally, the conditions within the gasifier and

regenerator must be consistent with the thermodynamic properties of the acceptor.

One feature of the acceptor which will be discussed in more detail later is its tendency to melt at certain conditions. For the conditions listed in Table I, this property necessitates that the partial pressure of steam does not exceed about 13 atmospheres. In Figure 1, this is accomplished, as shown, by recycling about 45 percent of the gasifier effluent and mixing with the incoming steam.

#### Experimental Method

The initial exploratory studies were carried out in the 1-1/2" I.D. high pressure Uniloy reactor system used in the earlier kinetics studies of the  $H_2$ - $H_2O$ -char system<sup>(4)</sup>.

The studies on the properties of the acceptor were carried out in the equipment shown schematically in Figure 2. The acceptor solids, usually prescreened to a size of 24 x 28 mesh were treated in a 1" I.D. x 8" long fluidized bed reactor. The thin-walled, stainless steel reactor was contained along with its electrically heated furnace in a one-liter high pressure autoclave.

For atmospheric pressure work, a quartz reactor was used to replace the high pressure reactor. The process gas in both reactors is introduced axially down through a dip tube, reverses direction and fluidizes the acceptor. The quartz tube reactor was heated by immersion in a fluidized sand bed furnace.

The reactor was supplied either with metered dry gas ( $CO_2$ ,  $N_2$ , and any desired premixed blend containing  $CO_2$ ,  $N_2$ ,  $SO_2$ ,  $H_2S$ , and  $H_2$ ) or with dry gas-steam mixtures. In the latter instance, the metered dry gas was passed through the steam generator. Steam partial pressure was determined by the water temperature in the generator which was controlled to  $\pm 0.1^\circ F$ .

The composition of the dry effluent gas was monitored continuously by a thermal conductivity cell. Dry feed gas was supplied continuously to the reference side of the cell.

Measurements of the equilibrium constants in several reactions of interest were made in the above equipment. A detailed description of the methods used and the results of this work will be published separately.

For study of deactivation at process conditions, the acceptor was put through a series of carbonation and calcination cycles which simulated the process conditions illustrated in Figure 1 and Table I. The charge to the reactor was 6 grams of 24 x 28 mesh acceptor and 60 grams of 100 x 150 mesh granular fused periclase which was used as an inert diluent. The diluent was used to minimize reaction heat effects and consequently to provide better temperature control in the carbonation and calcining steps. The total pressure

was adjusted to 8.87 atmospheres and the bed fluidized with a  $\text{CO}_2\text{-N}_2$  mixture. The partial pressure of  $\text{CO}_2$  was 5-8 atm. depending on the desired calcining temperature. The superficial gas velocity was held between 0.3-0.4 ft/sec at all times.

The bed was then heated rapidly to the calcining temperature which was held for different runs at 1900°F, 1950°F and 2000°F. The effluent gas analyzer monitored the course of the calcining. Upon completion of calcining, the inlet gas composition was adjusted to give 1.5 atm.  $\text{CO}_2$  partial pressure and the bed was cooled rapidly to 1700°F when 7.0 atm. steam partial pressure was substituted for most of the nitrogen. The bed temperature was then decreased to 1650°F where it was held until recarbonation was essentially complete as shown by the effluent gas analyzer. Nitrogen was substituted at this point for steam and the cycle repeated for the desired number of times. The time required for a complete cycle was 20-25 minutes.

At the end of the prescribed number of cycles the acceptor was fluidized at 1650°F with an  $\text{N}_2\text{-CO}_2$  gas mixture containing 1.5 atm. partial pressure of  $\text{CO}_2$  and held under these conditions for 15 minutes. The acceptor was then cooled rapidly and tested for activity.

A Chevenard thermobalance modified by using a linear transducer to detect beam position and sample weight was used to arrive at a standard activity measurement.

The acceptor sample (about 200 milligrams) was placed in a monolayer between two stainless steel screens held by a ring which rested on the support rod. Gas flow downward through the particles maintained differential conditions with respect to the  $\text{CO}_2$  partial pressure exterior to the particles.

The thermobalance was operated isothermally at 1525°F and at atmospheric pressure. Calcining and recarbonation were accomplished by changing the composition of the gas flowing through the sample holder. The gas inlet system provided practically instantaneous change from  $\text{N}_2$  used for calcining to  $\text{CO}_2$  used for recarbonation. The flow rates of each of the gases were chosen so that the combined effects of buoyancy and velocity head were the same.

The sample first was calcined and the weight loss recorded. It was then recarbonated for a standard time period of 7 minutes.

The standard activity value used in the discussion which follows is an average carbonation ratio, R, from the two above operations defined as follows:

$$R = \frac{(\text{Wt. Loss } \text{CO}_2 \text{ in gms} + \text{Wt. gain } \text{CO}_2 \text{ in gms})}{2 (\text{gms Theoretical } \text{CO}_2 \text{ Content})} = \frac{\text{Average } \text{CaCO}_3}{\text{CaCO}_3 + \text{CaO}}$$

The study of potential activity loss due to repeated sulfiding of the acceptor and regeneration of the  $\text{CaS}$  formed was made in the quartz tube reactor. The acceptor was sulfided in an  $\text{H}_2\text{S-H}_2$  mixture at 1650°F and was regenerated by fluidizing in air at 1950°F until  $\text{SO}_2$  evolution ceased.

An accelerated test for potential deactivation due to interaction with ash was used. Acceptor sized to 20 x 24 mesh in either the carbonate or oxide form was briquetted using a Celvacene grease binder with -100 mesh ash in a weight ratio of 53 parts acceptor in oxide form to 30 parts of ash. The ash was derived by air combustion of char from Pittsburgh Seam coal in a fluidized bed. Ash was used in both oxidized and reduced forms. The briquets were calcined at 1500°F and crushed. The +8 mesh fragments were treated for 16 hours in a fixed bed at various temperatures and with several different types of atmospheres. In some cases after the initial treatment, the acceptor-ash fragments were subjected to the standard cycling between carbonation and calcination. A final activity test was then run in the thermobalance as described above after the acceptor had been cleaned of adhering ash.

## Results and Discussion

### a. Fixed Bed Experiments

The initial experiments using a fixed bed of char and lime demonstrated the basic feasibility of the process from the chemical point of view. Comparative results from a pair of fixed bed runs with and without lime present are shown in Table II. The char used here is the same devolatilized "Disco" char earlier employed in the kinetics studies. Sand was used in the blank experiment to give the same volumetric ratio of char to inorganic material.

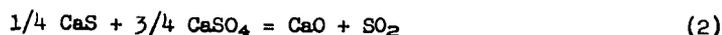
The data of Table II are without a great deal of quantitative significance due to uncontrolled temperature gradients in the bed and variation of carbon burnoff with time. They do illustrate, however, the principle of the CO<sub>2</sub> acceptor method in providing for removal of carbon dioxide from the gas with simultaneous enrichment of the product gas in hydrogen and methane.

### b. Study of Melt Formation

In the fixed bed run, the acceptor melted at the conditions used. Subsequent investigations showed that neither melting or agglomeration occurs in a fluidized bed of acceptor at 1650°F and 11 atm. steam partial pressure, over the entire range of carbonation ratios. A detailed investigation of melt formation is now underway. Results so far show that the steam partial pressure may be as high as 13 atm. at 1650°F without forming the melt, and that the melt is a ternary liquid composed of Ca(OH)<sub>2</sub>, CaCO<sub>3</sub>, and CaO. Phase equilibria behavior of this interesting system will be published when the work is completed.

### c. Thermodynamic Limitations

Equilibria in the reactions given below are the most pertinent to the process:



The experimentally determined values for reaction (1) are given in Table III. No reliable values for this equilibrium have been available in the literature previously.

The experimentally determined values for reaction (2) are shown in Figure 6. The values check well with those previously determined by Zawadski<sup>(7)</sup>.

The data in reaction (3) are shown in Figure 5. Some of the literature data imply that the equilibrium  $\text{CO}_2$  pressure depends on the origin of the calcium carbonate. Our measurements on stones ranging in composition from pure limestone to impure dolomite, and having widely different geologic origins, have shown that the equilibrium  $\text{CO}_2$  pressure is independent of all conditions except temperature. Figure 5 shows that our data agree very well with those of Smyth and Adams<sup>(3)</sup>, who used pure calcite as the source of  $\text{CaCO}_3$ . These data must now be accepted as providing the correct values.

Experimentally, all three reactions have been shown to be rapid and equilibrium should be closely approached in actual operation of the process. The high values for the equilibrium constants in reaction (1) mean that substantially all the sulfur released from the char in the gasifier will be absorbed by the acceptor as  $\text{CaS}$ . This sulfur must be rejected as  $\text{SO}_2$  in the regenerator. The regenerator must be operated with a slight deficiency of oxygen such that there is no oxygen breakthrough. Under these conditions the equilibrium for reaction (2) is controlling.

Reaction (3) determines the minimum temperature for operation of the regenerator to provide a driving force for calcination of the acceptor. The required temperature is higher, of course, the higher the operating pressure of the system. The operating pressure is thus set by steam pressure limitation in the gasifier, i.e., less than 13 atmospheres and by the limitation set on regeneration temperature by the equilibrium in reaction (3). It is on this basis that the operating pressure of 300 psia used in the illustrative example in Figure 1 and Table I was arrived at. Further calculations show that the driving force for the calcining reaction goes to zero at  $1935^\circ\text{F}$  and a pressure of 300 psia.

The sulfur rejection reaction (2) is not controlling since as the data in Table IV show the relative driving force is much greater than for the calcining reaction. The sulfur rejection problem would become limiting only for coals whose sulfur content is well beyond that of most steam coals.

#### d. Acceptor Selection

The choice of acceptor solids is determined by the factors of physical strength, high reactivity in carbonation and calcination reactions and resistance to deactivation upon exposure to process conditions.

A number of limestones and dolomites satisfactorily met the first two conditions. The reactivity for calcining and recarbonation reactions are also suitably high. Examples of the reactivity of a typical dolomite both in fresh and thermally treated conditions are given in Figures 3 and 4.

The data in Figures 3 and 4 show the rate of the calcining and recarbonation reactions as measured on the thermobalance at 1525°F in a nitrogen and CO<sub>2</sub> atmosphere, respectively. It is noted that in either case the reaction is nearly complete after 2 minutes exposure time. A more detailed kinetic study is now in progress.

None of the limestones or impure dolomites, however, showed sufficient resistance to deactivation under process conditions to be useful in the process. A dolomite from Western Ohio (Greenfield formation) had excellent resistance to deactivation and was selected for further detailed study.

The reserves of the Greenfield dolomite are sufficiently large so that it would be a logical choice for a future gasification plant located in either Illinois or the Ohio River Valley.

Analysis of the Greenfield stone is given below:

	<u>Wt. %</u>
CaCO <sub>3</sub>	52.28
MgCO <sub>3</sub>	44.61
Al <sub>2</sub> O <sub>3</sub> + SiO <sub>2</sub> + Fe <sub>2</sub> O <sub>3</sub>	2.24
FeCO <sub>3</sub>	0.20
Unaccounted for	0.67

At process conditions and at all experimental conditions used in this work, the MgCO<sub>3</sub> component of dolomite is unstable and decomposes to form MgO which is completely inert at these conditions.

#### e. Deactivation Under Process Conditions

The effect of cycling the 24 x 28 mesh Greenfield dolomite through simulated process conditions is shown in Table V. In no case did the activity decrease significantly below 0.80 Standard Carbonation ratio. Since some fresh acceptor make up inevitably will be required because of incomplete separation of the acceptor and spent char in the regenerator, the equilibrium activity of the recirculating acceptor will be at a level somewhat above 0.80.

The physical strength of the stone is remarkably high. At least 98 percent and usually at least 99 percent of the original acceptor was recovered as +48 mesh material after each one of the above tests.

The makeup requirements for the process in Table I were based on 94 percent recovery of the regenerated acceptor from the spent char in the regenerator which is adequately conservative.

A similar series of runs were carried out in which the Greenfield dolomite was converted to CaS followed by regeneration of the CaO by oxidative decomposition of the CaS at 1950°F. No deactivation of the stone due to the sulfur cycle was noted.

The stone is also highly resistant to deactivation by interaction with char ash as the results in Table VI show. The activity of the acceptor on exposure to ash does not depend upon the oxidation states of the ash that can exist at process conditions, nor on the extent of carbonation of the lime.

BIBLIOGRAPHY

- (1) Consol CO<sub>2</sub> Acceptor Patents
- |                                 |                |                |
|---------------------------------|----------------|----------------|
| E. Gorin                        | U.S. 2,654,661 | Oct. 6, 1953   |
| E. Gorin                        | U.S. 2,654,662 | Oct. 6, 1953   |
| E. Gorin                        | U.S. 2,654,663 | Oct. 6, 1953   |
| E. Gorin                        | U.S. 2,682,455 | June 29, 1954  |
| E. Gorin                        | U.S. 2,682,456 | June 29, 1954  |
| E. Gorin                        | U.S. 2,682,457 | June 29, 1954  |
| E. Gorin                        | U.S. 2,705,672 | April 5, 1955  |
| R. P. Tarbox                    | U.S. 2,807,529 | Sept. 24, 1957 |
| E. Gorin and<br>W. B. Retallick | U.S. 3,108,857 | Oct. 29, 1963  |
| E. Gorin and<br>C. H. Rice      | U.S. 3,115,394 | Dec. 24, 1963  |
- (2) Batchelor, J. D., Gorin, Everett, and Zielke, C. W., Ind. Eng. Chem., 52, 161 (1960).
- (3) Smyth, F. H. and Adams, L. H., JACS, 45, 1167 (1923).
- (4) Goring, G. E., Curran, G. P., Tarbox, R. P., and Gorin, Everett, Ind. Eng. Chem., 44, 1057 (1952).
- (5) Goring, G. E., Curran, G. P., Zielke, C. W., and Gorin, Everett, *ibid*, 45, 2586 (1953).
- (6) Unpublished Data, Consolidation Coal Company.
- (7) Zawadski, J., Z. Anorg. Chem., 205, 180 (1932).
- (8) Zielke, C. W. and Gorin, Everett, Ind. Eng. Chem., 47, 820 (1955).
- (9) Zielke, C. W. and Gorin, Everett, *ibid* 49, 396 (1957).

TABLE I

Material Balance in CO<sub>2</sub> Acceptor Process  
 Basis: 100 lbs MAF Char Feed, Pressure - 300 psia

Unit Operation	Devolatilizer		Gasifier		Regenerator	
	Input Temp., °F	Output Temp., °F	Input Temp., °F	Output Temp., °F	Input Temp., °F	Output Temp., °F
MAF Char (lbs)	800	1470	1470	1650	1650	1650
Char Ash (lbs)	800	1470	1470	1650	1650	1650
MgO·CaO	--	--	1950	2.338	0.442	2.338
MgO·CaCO <sub>3</sub>	800	1470	--	--	1.872	--
MgO·CaS	--	--	--	--	0.024	--
H <sub>2</sub>	1650	1390	--	1650	4.855	0.001
CH <sub>4</sub>	--	--	--	--	0.789	--
CO	4.835	1.481	--	--	1.466	0.075
CO <sub>2</sub>	0.789	1.396	--	--	0.481	3.448
H <sub>2</sub> O (g)	1.466	0.740	--	--	2.106	0.113
N <sub>2</sub>	0.481	1.926	1450	8.214	0.025	5.834
H <sub>2</sub> S	2.106	0.057	--	--	0.004	--
SO <sub>2</sub>	0.025	0.045	--	--	--	0.031
Air	0.004	--	--	--	--	--
Reject Stream	--	--	--	--	320	7.361
Char MAF (lbs)						1950
Ash (lbs)						13.15
CaO: MgO (mols)						0.158

Ash (lbs/100 lbs MAF Char)

Total 13.29  
 Inorganic Sulfur 0.48

Feed Char - Pgh. Seam, LTC Char (900°F)

H 3.72 87.25 1.84 5.24 1.94  
 N 0  
 C 0  
 Org. S 1.94

Ultimate Analysis (MAF)  
 Heating Value, Btu/MAF lb 14,480

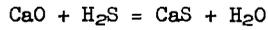
TABLE II

Comparative Fixed Bed Runs in the  
Presence and Absence of Lime

Steam Feed Rate,  $8.8 \times 10^{-3}$  mols/hr. Total Pressure, 30 atm.

<u>Run</u>	<u>Wt. Solids Charged</u> lbs	<u>Average Dry Make Gas Composition</u>				<u>Steam Conversion</u> %	<u>Median Bed Temp.</u> °F
		<u>CO<sub>2</sub></u>	<u>H<sub>2</sub></u>	<u>CH<sub>4</sub></u>	<u>CO</u>		
Blank	( Char - 0.5 ( Sand - 1.87	23	48	9	20	*	1620
Lime	( Char - 0.5 ( Lime - 0.87	0.5	79.5	17	3	70	1640

\* Not determined.

TABLE IIIEquilibrium Data in Reaction

<u>°F</u>	<u>K = H<sub>2</sub>O/H<sub>2</sub>S</u>
1310	2030
1420	1320
1550	837
1660	587

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TABLE IV

Thermodynamic Driving Force in  
Regenerator at 1950°F and 300 psia

P <sub>CO<sub>2</sub></sub> Driving Force Atm.	0.55
P <sub>CO<sub>2</sub></sub> /Equil. P <sub>CO<sub>2</sub></sub>	0.93
P <sub>CO<sub>2</sub></sub> /Equil. P <sub>CO<sub>2</sub></sub>	0.37
<u>Regenerator Effluent Gas, Mol %</u>	
H <sub>2</sub>	0.01
CO <sub>2</sub>	36.29
N <sub>2</sub>	61.39
H <sub>2</sub> O	1.19
CO	0.79
SO <sub>2</sub>	0.33

TABLE V

Effect of Cycling Greenfield Dolomite (24 x 28M)  
Thru Simulated Process Conditions

Recarbonation Conditions - 1650°F - 1.5 atm. CO<sub>2</sub> - 7.0 atm. H<sub>2</sub>O

Calciner Temp.	Total Time at Process Conditions, hrs.	No. of Cycles	Std. Carb. Ratio
1900°F	2.9	2	0.87
↓	2.2	5	0.77
↓	7.4	5	0.80
↓	8.0	20	0.80
1950°F	2.3	5	0.81
↓	5.5	12	0.81
↓	8.5	20	0.76
2000°F	2.5	5	0.81
↓	6.0	12	0.77

TABLE VI

Effect of Ash

The acceptor was briquetted with ash and held for 16 hours at the conditions listed.

Run	Acceptor	Form of Ash	°F	No. of Cycles	Ambient Gas	Std. Carb. Ratio
Q22	oxide	oxidized	1650	1	air	.81
Q19	↓	reduced <sup>(1)</sup>	1650	1	H <sub>2</sub>	.90
Q20	↓	reduced	1900	1	H <sub>2</sub>	.76
Q24	↓	oxidized	1900	1	(2)	.76
H76	carbonate	↓	1900	0	(2)	.80
Q33	oxide	↓	1950	5	(2)	.76

(1) Ash in form of 70% burnoff char.

(2) Inlet gas was 90% CO<sub>2</sub>-10% H<sub>2</sub> which was converted by the water gas shift reaction at run conditions to the following composition:  
CO<sub>2</sub> 80.5 mol %, H<sub>2</sub> 0.5%, H<sub>2</sub>O 9.5%, CO 9.5%.

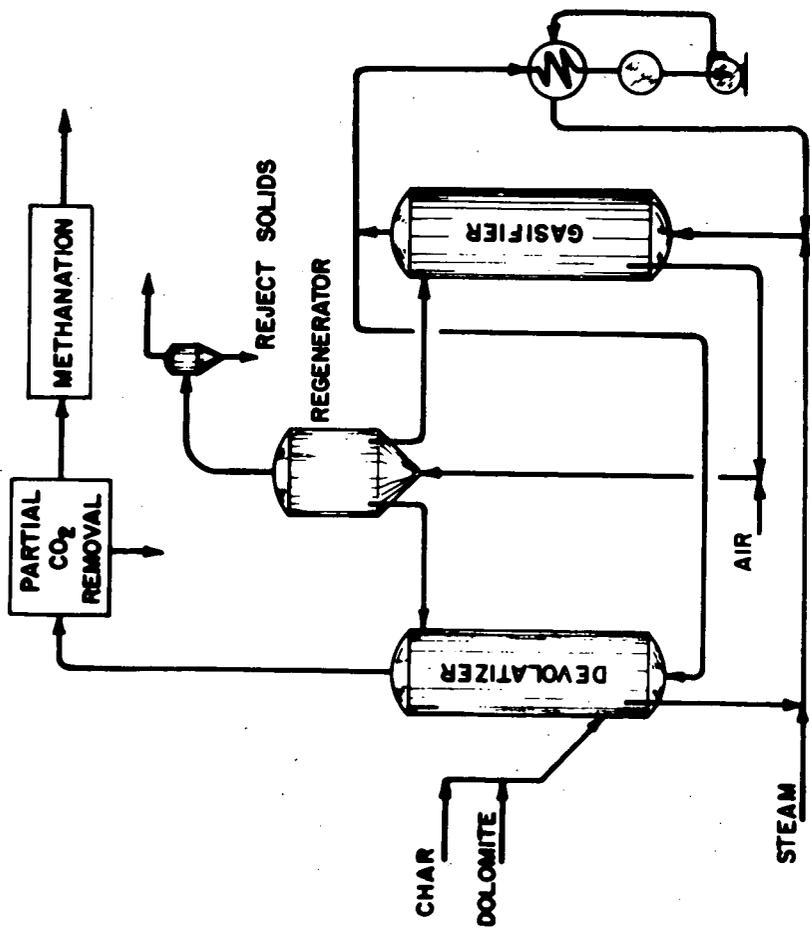


FIGURE 1

**FLOW DIAGRAM**  
**CO<sub>2</sub> ACCEPTOR PROCESS**

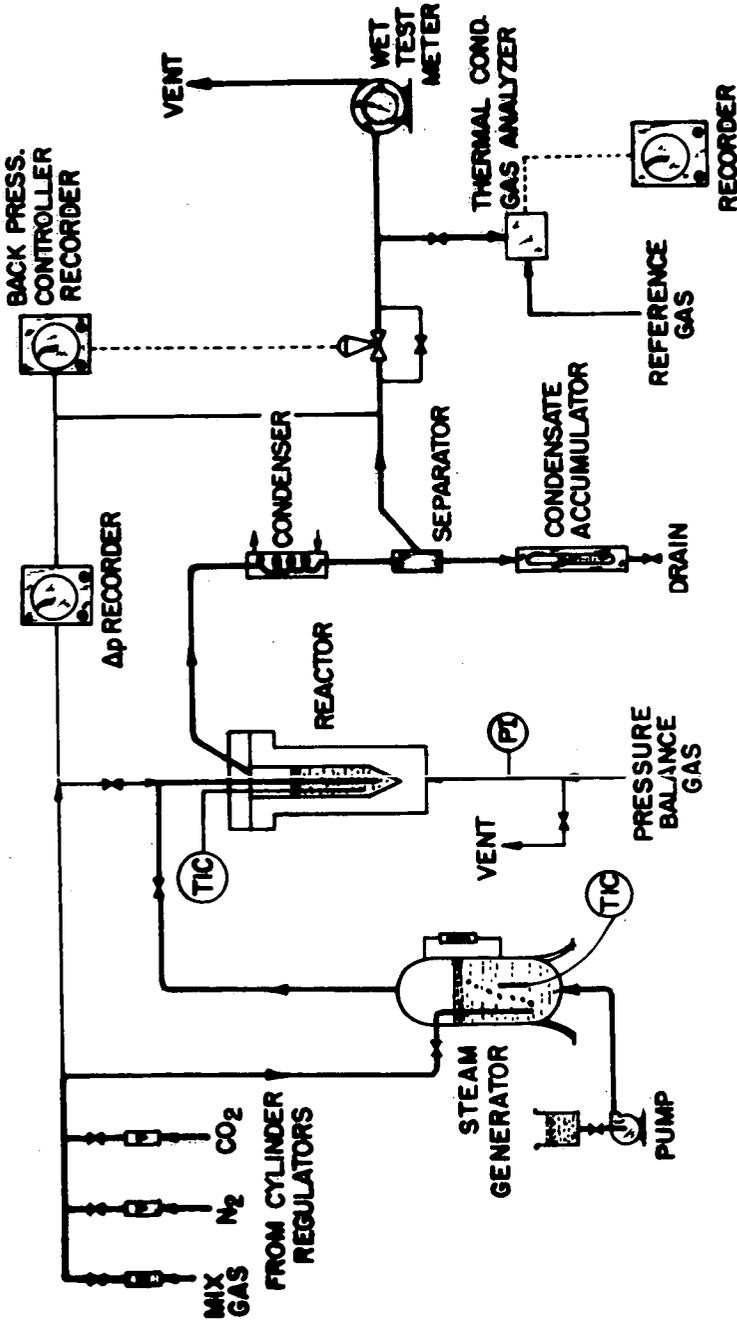


FIGURE 2

# FLOW DIAGRAM GASIFICATION BENCH UNIT

**CALCINING OF DOLOMITE**  
AT 1525°F 20 x 24 MESH  
AT ZERO ATM. CO<sub>2</sub>

**THERMAL HISTORY**  
x FRESH  
▲ 1900°F - 1/10 Hr.  
▲ 1900°F - 16 Hrs.

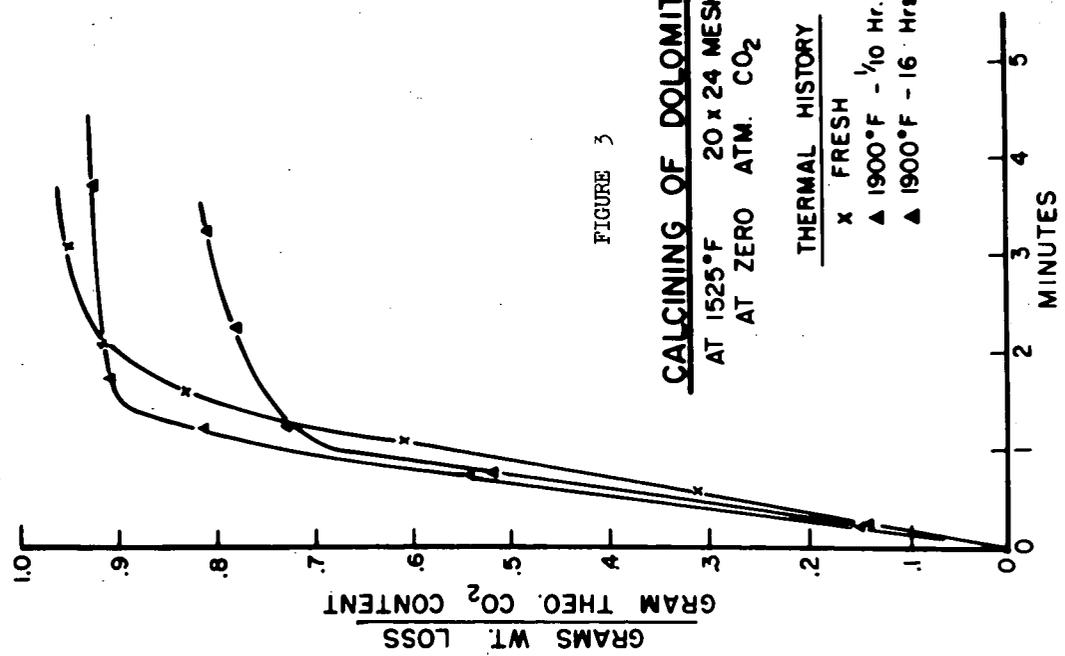


FIGURE 3

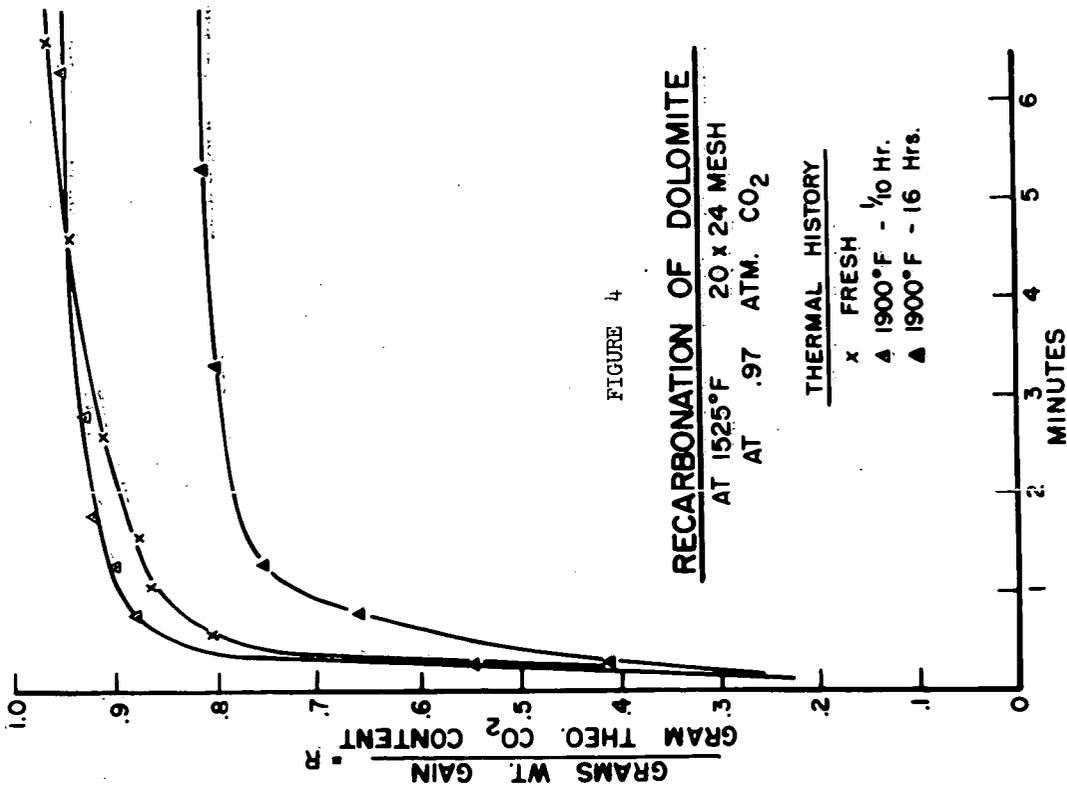


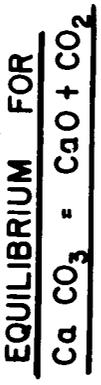
FIGURE 4

**RECARBONATION OF DOLOMITE**  
AT 1525°F 20 x 24 MESH  
AT .97 ATM. CO<sub>2</sub>

**THERMAL HISTORY**

- x FRESH
- Δ 1900°F - 1/10 Hr.
- ▲ 1900°F - 16 Hrs.

FIGURE 5



○ THIS WORK  
• SMYTH & ADAMS

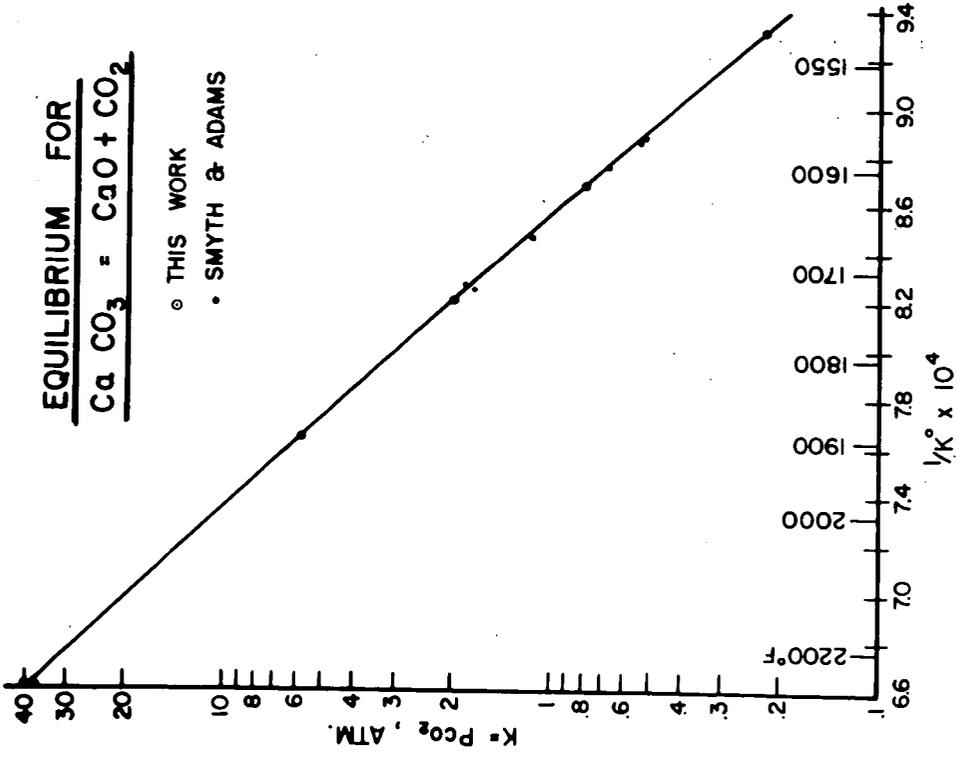


FIGURE 6

EQUILIBRIUM FOR

