

Effect of Sodium Carbonate upon Gasification of Carbon and Production of Producer Gas¹

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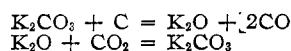
THE publication, in 1926, of the report of the research fellowship of the Institution of Gas Engineers (6) reopened a very promising field of investigation for those interested in the gasification of solid carbon fuels. This report showed that small additions of sodium carbonate to coke greatly increased its reactivity to both steam and carbon dioxide. Among other substances that produced the same effect, but to a smaller degree, were oxides of iron and calcium. The following year the work was extended and in 1927 three papers were presented under one general title, by Sutcliffe and Cobb (10), Branson and Cobb (3), and Dent and Cobb (5), which contained excellent work on the reactions at temperatures 600° to 1000° C. Further reports from the Institution of Gas Engineers appearing in 1928 and 1929 (7, 8) contained much detailed information on the influence of the methods of preparation and on the reactivity of treated cokes. The authors were content to explain the effects obtained as being catalytic without any statement of the mechanism of the reactions.

A paper by Dent and Cobb (4) on the equilibrium between carbon dioxide and carbon, which appeared in 1929 and may be considered as presenting the conclusions drawn from the reports of their earlier work, contains the following statements:

Heating a carbon containing unsaturated carbon atoms with a high energy content gradually transforms these into more stable atoms, corresponding with a higher percentage of carbon dioxide at equilibrium. Some types of carbon undergo this change more readily than others, and it is minimized by impregnation with sodium carbonate.

We have taken the view that the presence of the sodium carbonate is without effect upon the equilibrium between carbon monoxide and carbon dioxide over carbon, except in so far as it influences the nature of the carbon surface exposed to the gases, and that at a given temperature and pressure the equilibrium depends solely upon the energy content of the carbon atoms on the surface.

In 1921 Taylor and Neville (11), studying the effect of catalysts on the reaction of carbon with steam at 490°, 525°, and 570° C., concluded that the acceleration of the reaction $C + CO_2 = 2CO$ was not due to the alternate reduction and reformation of the alkali carbonates which might occur as follows:



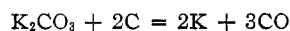
but was caused by increased adsorption of carbon dioxide by the carbon surface in the presence of active catalytic agents.

This paper presents a study of the effect of sodium carbonate upon the gasification of carbon. Sodium carbonate reacts in appreciable measure with carbon at temperatures above 800° C. and the rate becomes rapid above 900° C. The reaction products are carbon monoxide and sodium, which vaporizes and reacts with carbon dioxide and steam in the vapor state. The use of coke impregnated with sodium carbonate in the gas producer will cause a more rapid approach to equilibrium and will also cause a change in the gas composition due to the presence of sodium vapor, giving gases higher in carbon monoxide and hydrogen than would otherwise be obtained. No great advantage is indicated in the use of sodium carbonate in a water-gas machine operated according to the usual procedure. The increased reactivity of the fuel bed would be disadvantageous during the blasting period and would offset the gains to be expected during the period of steaming.

Reduced nickel exhibited an anomalous behavior: Its activity in the carbon dioxide-carbon reaction was greater than that of the other catalysts, but its effect upon the adsorption capacity of the carbon was less and, further, its effect upon the steam-carbon reaction diminished with increasing time of gasification. The temperature range at which Taylor and Neville worked is much below that of 800–1100° C. usually met or exceeded in gasification of carbon, and their conclusions should not be extended to higher temperatures without a careful

redetermination of the experimental data.

The literature thus reviewed shows that sodium carbonate has been recognized as a powerful factor in increasing the reactivity of coke at temperatures up to 1000° C., without any definite explanation of the mechanism of the reaction. No mention has been made of the possibility that metallic sodium may be an agent in the reaction, although it is well known that sodium may be formed through the interaction of carbon and sodium carbonate. Roscoe and Schorlemmer (9) in 1883 described the commercial production of potassium and sodium by the reduction of alkali carbonates with carbon. No equation for the reaction between sodium carbonate and carbon was given, but an equation was given for the reduction of potassium carbonate with carbon:



Temperatures were not stated, but the fact that the reduction could be carried out in cast-iron vessels gives some idea of the temperature.

Determination of Products of Reaction

The first step in the experimental work was to determine the products of the reaction between sodium carbonate and carbon, with special emphasis on the conditions prevailing between 800° and 1100° C. It was known that this reaction gave metallic sodium as one of its products, but no quantitative study had been made.

The first apparatus consisted of a hollow graphite rod containing the charge, placed within a glass sleeve which could be evacuated. The temperature was controlled by the quantity of current passing through the graphite rod, and the gaseous products were pumped off as desired. This failed to give quantitative data because of condensation products forming on the walls of the glass sleeve, but it did indicate that substantially pure graphite and sodium carbonate reacted as expected and gave a gaseous product which after cooling consisted almost entirely of carbon monoxide. The substitution of an electrically heated nickel boat for the graphite tube gave similar results and indicated that

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nickel was not acting in any important way as a catalyst at 850–1050° C.

A more successful apparatus is shown in Figure 1. It had become evident from the earlier work that vapors of sodium and also sodium oxide condensed almost instantly on a cool surface, and advantage was taken of that fact in the new apparatus. A nickel capsule was supported in a small electric muffle. A tube 7 mm. in diameter passed through the bottom of the capsule, extending upward from the bottom of the capsule a distance of 3 cm. and downward a distance of 7 cm. This tube was rigidly attached to the capsule by means of lock nuts. The annular space in the bottom of the capsule was then charged with a mixture of carbon and sodium carbonate and the capsule closed. A tube of nickel 2 mm. in diameter was placed inside of the capsule tube and concentric with it. This tube was then placed with its upper end level with the upper end of the capsule tube, and its lower end was sealed to a glass tube which passed through a rubber stopper. The rubber stopper was placed in flask *A* which contained potassium hydroxide solution, in such a manner that the glass tube dipped below the surface of the potassium hydroxide solution. A tube was then run from the top of flask *A* to a water aspirator.

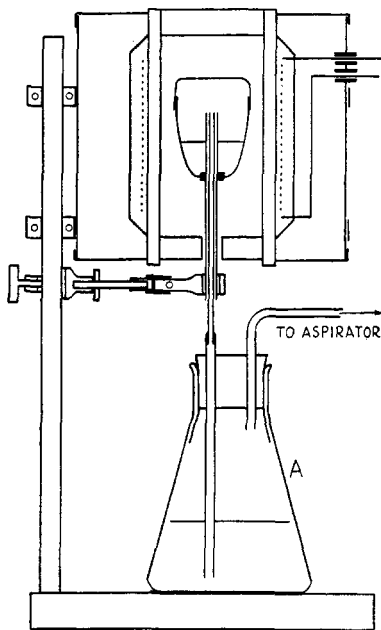


Figure 1—Apparatus for Determining Products of Reaction between Sodium Carbonate and Carbon

To operate the device a charge of potassium hydroxide solution of known carbonate content was placed in flask *A*. The aspirator was started and the temperature of the capsule raised to 1000° C. The temperature was held constant for 10 minutes and the aspirator was adjusted to draw about 20 cc. of gas per minute through the potassium hydroxide solution. This method of operation caused a stream of preheated air to meet the reaction products inside of the capsule and at the same time drew the resulting mixture into the outlet tube. The carbon monoxide evolved was oxidized to carbon dioxide by the incoming air and the carbon dioxide was then drawn into the caustic solution and absorbed. The sodium was oxidized also and deposited out quantitatively in the first cool part of the 2-mm. nickel tube, as sodium oxide and carbonate.

The measurements consisted in a titration of the carbonate formed in the potassium hydroxide solution. This was done with standard sulfuric acid, using methyl orange and phenolphthalein indicators. The glass tube supporting

the nickel tube was then cut with a file, just above the rubber stopper, and the 2-mm. nickel tube with the attached portion of glass tube placed under distilled water. The tube and the water were agitated, and after an hour the solution was titrated for alkali with part of the same acid used to determine the carbonate. Phenolphthalein and methyl orange indicators were used in order also to obtain a measure of the quantity of carbonate deposited out in the tube. The sum of the two carbonate determinations was then calculated back to mols of carbon monoxide and the alkali determination calculated back to atoms of sodium. The experimental data are given in Table I.

Table I—Experimental Data Showing Reaction Products of Sodium Carbonate and Carbon at 1000° C.

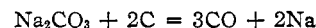
(1) Difference between phenolphthalein and methyl orange end points in potash solution.
(2) Same as (1) in rinsings from small nickel tube.
(3) Total acid for methyl orange end point in rinsings from small nickel tube.
(4) Ratio of sum of titrations (1) and (2) to titration (3), giving ratio of CO to Na.

(1)	(2)	(3)	(4)
Cc.	Cc.	Cc.	
15.9	3.9	12.9	1.532
3.6	7.6	7.2	Omit
21.6	5.8	18.5	1.484
25.9	5.3	20.8	1.498
17.8	4.1	14.3	1.534
			Av. 1.512

The experimental data show the ratio

$$\frac{\text{Mols CO}}{\text{Atoms Na}} = \frac{3.03}{2.00}$$

and from that at 1000° C. the equation



is seen to hold quite quantitatively. A small amount of thermal dissociation of sodium carbonate into carbon dioxide and non-volatile sodium peroxide would account for the slightly larger quantity of carbon monoxide than the theoretical amount. This equation has been the one usually assumed for this reaction, but it has not previously been demonstrated.

Pressure-Temperature Relation for Reaction

The next step was to determine the relation between the temperature of the reacting mixture and the pressure at which the products of the reaction were evolved. The two requirements were that the entire reaction vessel should be maintained at the same temperature as the reacting mixture, and that the connection with the manometer should be small in diameter. In this way there could be no reversal of the reaction in the reaction vessel and the amount of reversal in the small tube to the manometer would be insignificant. This latter effect could be even further reduced if the tube to the manometer could be cooled at a point near the reaction vessel causing the sodium to condense out without recombining with the carbon monoxide.

The device constructed to meet these requirements is illustrated in Figure 2. A heavy-walled nickel reaction chamber was constructed of 1-inch (2.5-cm.) standard nickel pipe. A section of pipe 9 cm. long was closed on both ends by welding to each end plates of sheet nickel 4 mm. thick. The welding was done with extreme caution, with an oxyacetylene torch. After repeated failures an effective technic was developed which produced a container that was gas-tight up to 1150° C. The main factors in producing an effective weld were: first, the manipulation of the torch with sufficient facility to produce a workman-like appearing weld in a minimum of time; and second, the employment of a flame that

was neutral or very slightly reducing (1). The use of a borax flux was found to be without effect owing to the high melting temperature of the nickel.

The reaction vessel having been formed, a hole 6 mm. in diameter was drilled through the center of one of the end plates. A charge of graphite and sodium carbonate was then placed inside of the chamber A. A nickel tube 7 cm. long with a bore of 2 mm. and an outside diameter of 6 mm. was driven into the hole in the top of the reaction chamber and welded in place. A copper tube 35 cm. long was then joined to the top of the nickel tube with silver solder as shown at B.

The complete reaction chamber was then assembled within an electric furnace with a platinum-platinum-rhodium thermocouple, C, and with means for cooling the outlet tube. The outlet tube was cooled with four turns of a copper coil, D, made of tubing with 3-mm. bore, which passed around the silver-solder joint between the nickel and the copper sections of the outlet tube. The leads to the copper coil passed upward to the outside of the furnace and were here connected to inlet and outlet lines through which cooling water was passed. Directly below the cooling coil a disk of Sil-O-Cel insulating material was slipped over and attached securely to the nickel outlet tube with alundum cement. The disk was 2 cm. thick and had a diameter 2 mm. less than the inside diameter of the furnace tube. Supported upon this Sil-O-Cel disk was a sheet asbestos sleeve of the same outside diameter as the disk and of sufficient length to extend upward to the outside of the furnace. The hot junction of the thermocouple was placed between the reaction-vessel wall and a small nickel flange clamped to the tube wall as shown at C, in order to avoid erroneous indications of temperature due to radiation from the somewhat hotter surfaces of the furnace. Experiments with and without the flange indicated that this precaution was not essential, for the temperature of the furnace rose so slowly that the difference in temperature between the furnace surfaces and the reaction vessel was scarcely measurable. The thermocouple and potentiometer were calibrated as a unit before and after the tests against a couple standardized at the Bureau of Standards.

The copper outlet tube was connected by a heavy-walled rubber tube to a branched glass tube which connected with a manometer and a vacuum pump. The manometer was of the closed type with a range from 0 to 900 mm. of mercury. It was boiled out for several hours to insure readings accurate within the accuracy of the millimeter scale used for measurement.

Measurements were taken with this apparatus in the following manner: The temperature of the furnace was raised to 500° C., and held at this temperature for 1 hour while the vacuum pump was running. In this way the pressure was reduced to less than 1 mm. of mercury. The system was closed and the vacuum pump stopped. The temperature of the furnace was then raised slowly until a rise in the pressure was noted. The current passing through the furnace was regulated to maintain this temperature constant and the pressure was read after it had been constant for 5 minutes. The temperature of the furnace was raised, with interruptions at convenient temperature intervals, while the pressure was read.

Data were obtained in this manner from a mixture of sodium carbonate and graphite and from a mixture of sodium carbonate and foundry coke. The pressure at which the gaseous product was evolved showed a definite relation to the temperature, as shown in Figure 3. The composition of the gas evolved at atmospheric pressure (735 mm. of mercury and about 1000° C.) was determined by Orsat analysis and found to be:

	SAMPLE A	SAMPLE B
	%	%
CO ₂	0.5	0.4
O ₂	0.5	0.0
CO	99.0	98.2
N ₂	0.0	1.4

Figure 3 shows that at 800° C. the pressure is about 10 mm., and does not change rapidly with increase in temperature. As the temperature rises above the melting point of sodium carbonate 852° C., however, the slope increases and the pressure at which the products are evolved changes rapidly with the temperature. At approximately 1000° C. the

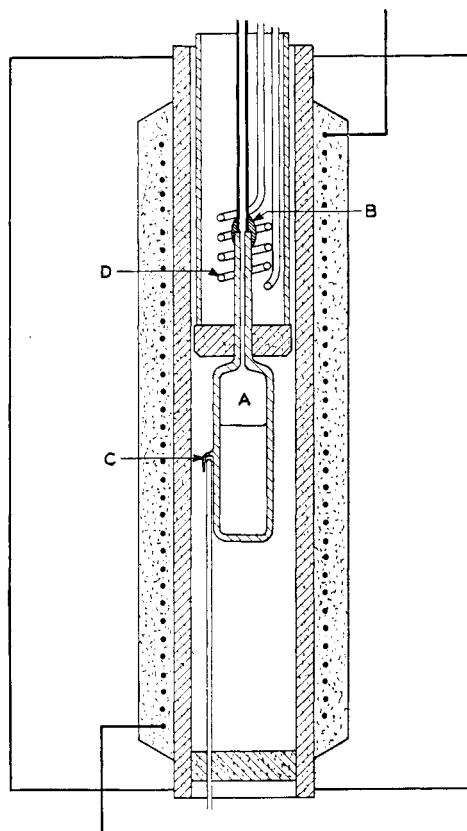


Figure 2—Apparatus for Determining Pressure-Temperature Relation

pressure has risen sufficiently so that the reaction proceeds continuously at atmospheric pressure. The points on the curve marked "after evolution of gas" were obtained by permitting gas to pass off freely at atmospheric pressure for 20 minutes and then closing the system and holding it until the pressure again became constant. The purpose of this procedure was to show that an alteration in the percentage composition of the material in the reaction vessel did not alter the pressure-temperature relationship.

Continuous Gasification Experiments

A series of gasification experiments was next performed to show the probable mechanism of the action of sodium carbonate in increasing the reactivity of carbon in a gas producer. This was done by reproducing the reducing section of a gas generator on a laboratory scale and treating in this laboratory generator fuels treated with sodium carbonate and fuels not so treated.

The equipment consisted in the main of a sheet-nickel tube 3 to 5 cm. in diameter, 48 cm. long and 0.29 mm. thick, formed from two semi-cylindrical halves having longitudinal flanges 8 mm. wide (Figure 4). With the tube assembled the flanges formed two exterior webs 8 mm. wide, which

extended the full length of the tube on each side. The flanges were formed to be as nearly true and flat as possible, so that when a U-strip was placed over the full length of each web the tube was substantially leakproof against small differences of pressure. As a precaution against leaks, the tube was assembled with a lute of kaolin and water. The tube proved to be without leaks under all the conditions which it was required to fulfil. It was constructed to be separable longitudinally so that it could be opened to expose the contents completely without disturbing them.

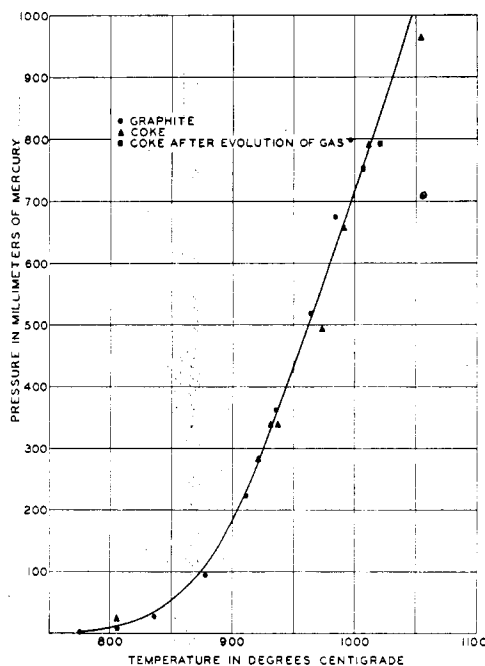


Figure 3—Pressure-Temperature Relation in Reaction of Sodium Carbonate and Carbon

This nickel tube, which formed the inclosure for the miniature producer bed, was placed within the two separable sections of an electrically heated furnace designed for the ultimate analysis of organic compounds. These sections were placed on a stand in a vertical position and connected through rheostats to the line. An inlet tube joined the bottom of the nickel tube at a point where a nickel grid was inserted to act as a grate. The inlet tube had two connections, one of which was in communication, through a flowmeter, with a source of carbon dioxide or air and the other in direct communication with a source of superheated steam. In the top of the nickel tube there was inserted a glass collecting head with a side outlet for gas and a top opening for a thermocouple. This glass head was luted in place with wet kaolin and the gas outlet connected with a laboratory spiral condenser. The outlet of the condenser connected through a T-tube with a drip receiver and with the gas-analyzing system.

The producer was first operated at rates of gas flow which gave a time of contact comparable with commercial operation. However, this rate did not bring about a significant spread in the data and therefore a gas rate giving a time of contact about one-tenth of that prevailing in commercial practice was used throughout the experiments.

Results with Air and Graphite Fuel

The nickel producer tube was filled with granules of Acheson graphite and the temperature of the lower section was raised to about 900° C. A stream of air was admitted at a rate of 1.2 liters per minute and the external heating discontinued when the combustion became self-sustaining. The upper section of the tube was then also electrically

heated to assist in forming a longer reduction zone. The resulting analyses under these conditions were:

CONSTITUENT	LOWER SECTION ONLY HEATED		ENTIRE TUBE HEATED	
	Sample A	Sample B	Sample A	Sample B
	%	%	%	%
CO ₂	20.6	20.5	20.6	20.6
O ₂	0.0	0.2	0.0	0.0
CO	0.0	0.0	0.5	0.2
N ₂	79.4	79.3	78.9	79.2

It will be noted that almost all the oxygen of the air remained in the form of carbon dioxide, the maximum amount of carbon monoxide found being 0.5 per cent.

The next step was to replace the charge of untreated graphite with a charge of granules that had been treated with sodium carbonate. The particles were soaked in a saturated solution of sodium carbonate and then dried. The treated fuel contained about 5 per cent of sodium carbonate and some water of crystallization, which soon disappeared upon heating. Both sections of the furnace were heated and air was again passed through the charge at 1.2 liters per minute. The resulting gas had the following composition:

CONSTITUENT	GRAPHITE TREATED WITH SODIUM CARBONATE	
	Sample A	Sample B
	%	%
CO ₂	1.0	4.9
O ₂	0.0	0.0
CO	32.7	29.7
N ₂	66.3	65.4

The acceleration in the rate of reaction is shown by the great decrease of carbon dioxide and increase of carbon monoxide. There is no indication of marked dissociation of the sodium carbonate, for the ratio of total oxygen to nitrogen is the same in the product gas as in the entering air.

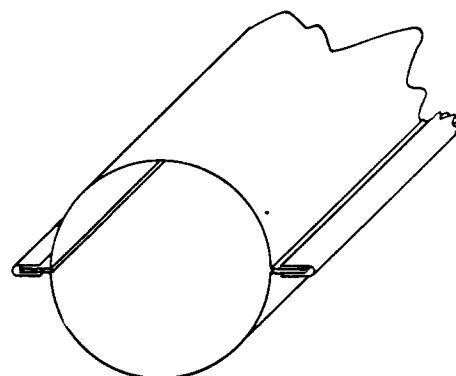


Figure 4—Detail of Furnace for Determining Migration of Sodium Carbonate

At the end of this experiment the tube was removed from the furnace, placed in a horizontal position, and opened longitudinally by removing the clamps. The distribution of the sodium carbonate in the fuel was checked by laying a strip of muslin moistened with phenolphthalein solution over the exposed granules. The picture thus obtained indicated qualitatively that all or the main part of the sodium had remained in the fuel bed. A slight migration away from the combustion zone, which was about 3 cm. in length, was noted.

This experiment was preliminary in nature, but it showed that the addition of sodium carbonate markedly increased the reactivity of the graphite. It also showed that if the temperature was to be controlled and measurable with a constant gas rate, experiments with air or oxygen would have to be replaced with experiments with carbon dioxide and steam.

Rate of Reaction of CO₂ with Graphite and Sugar Char, and with These Materials Treated with Na₂CO₃

The method of operation was then modified as follows: The nickel tube was charged to a depth of 10 cm. with small pieces of unglazed porcelain and on top of this was charged a layer of fuel 25 cm. deep. A gas rate of 6.25 liters per minute was decided upon when operating with carbon dioxide and of 5 grams per minute when operating with steam. The time of contact under these conditions was roughly 1/7 second.

The following series of experiments was then performed:

- (1) Carbon dioxide with untreated graphite
- (2) Carbon dioxide with graphite plus sodium carbonate
- (3) Steam with untreated graphite
- (4) Steam with graphite plus sodium carbonate
- (5) Carbon dioxide with untreated sugar char
- (6) Carbon dioxide with sugar char plus sodium carbonate

Tests of the action of carbon dioxide were made both with graphite and sugar char. The graphite was obtained from the Acheson Graphite Company, and was in the form of their standard No. 9 resistance granules. The granules varied in size from 2 to 5 mm. in diameter and, when lightly packed, left 48.8 per cent of free space in the volume occupied. The graphite contained about 1 per cent ash, the main part of which was silica and iron oxide with small amounts of calcium and magnesium oxides. The sugar char was made in silica from pure sucrose, and was light and friable but sufficiently strong to remain in granules. The ash content of the sugar char was negligible. The graphite was chosen mainly because of its uniformity and convenient physical shape, but the material offered the further advantage of being highly non-reactive and consequently well fitted to give strongly contrasting results. The sugar char was used as a check material to show whether contaminating material in the graphite was having a marked effect on the behavior of the graphite, and whether the allotropic form of the carbon caused any marked difference in the reaction. The materials after impregnation with sodium carbonate contained about 5 per cent Na₂CO₃.

Table II—Rate of Reaction of CO₂ with Graphite and Sugar Char, and with These Materials after Treatment with Na₂CO₃

TEMP.	VOLUME FLOW	APPROX. TIME OF CONTACT	COMPOSITION OF OUTLET GAS		
			CO ₂	CO	N ₂
° C.	Liters/min.	Sec.	%	%	%
UNTREATED GRAPHITE AND CO ₂					
780	6.2	0.15	98.0	0.2	1.8
850	6.2	0.15	96.5	0.4	3.1
900	6.2	0.14	95.8	2.0	2.2
950	6.2	0.14	88.6	9.8	1.6
970	6.2	0.13	83.8	14.8	1.4
TREATED GRAPHITE AND CO ₂					
750	6.2	0.15	99.5	0.2	0.3
800	6.2	0.15	95.0	4.7	0.3
850	6.2	0.14	77.3	23.0	0.3
900	6.2	0.14	63.6	36.2	0.2
950	6.2	0.13	3.2	89.0	7.8
UNTREATED SUGAR CHAR AND CO ₂					
800	6.5	0.19	98.5	0.5	1.0
850	6.5	0.19	97.6	1.0	1.4
900	6.5	0.18	97.0	1.8	1.2
965	6.5	0.17	89.5	8.1	2.4
TREATED SUGAR CHAR AND CO ₂					
800	6.5	0.19	96.8	2.2	1.0
850	6.5	0.19	89.5	9.7	0.8
890	6.5	0.18	59.4	39.1	1.5
950	6.5	0.17	4.0	88.0	8.0

The results of the four series of tests are given in Table II and Figure 5. The surprising thing about the results is, not that sodium carbonate increases the rate of reaction many fold (twenty fold at 900° and tenfold at 950° C.), but that

there is substantially no difference in the results between the graphite and sugar char.

The differences between the untreated graphite and sugar char are so small that a single curve represents both series. In the same way a single curve represents the results with the treated graphite and sugar char. The difference in the allotropic form of the carbon has apparently made no perceptible difference in the reactivity of the product.

Rate of Reaction of Steam with Graphite, and with Graphite Treated with Na₂CO₃

The technic of the tests with steam was similar to that described for carbon dioxide. The results are given in Table III and Figure 6. The rate of reaction of steam with untreated graphite is so slow that even at the highest temperature of the tests (940° C.) the exit gases still contained 97.8 per cent of undecomposed steam. The results with graphite containing 5 per cent sodium carbonate are very different, the exit gases under similar conditions carrying only 5.0 per cent of steam, but 6.5 per cent carbon dioxide, with 38.8 per cent carbon monoxide, and 49.7 per cent hydrogen.

Table III—Rate of Reaction of Steam with Graphite, and Graphite Treated with Na₂CO₃

TEMP.	WEIGHT OF WATER	APPROX. TIME OF CONTACT	COMPOSITION OF OUTLET GAS						
			H ₂ O	CO ₂	O ₂	CO	H ₂	CH ₄	N ₂
° C.	G./min.	Sec.	%	%	%	%	%	%	%
UNTREATED GRAPHITE AND STEAM									
748	5	0.13	99.2	0.0	0.3	0.0	0.0	0.0	0.5
856	5	0.12	98.7	0.2	0.0	0.1	0.2	0.0	0.8
940	5	0.11	97.8	0.4	0.0	0.4	1.0	0.0	0.4
TREATED GRAPHITE AND STEAM									
750	5	0.13	98.4	0.4	0.0	0.2	0.5	0.0	0.5
830	5	0.13	92.2	2.4	0.0	0.3	4.7	0.0	0.4
940	5	0.11	5.0	6.5	0.2	38.8	49.7	0.0	0.0

Migration of Sodium Carbonate within Fuel Bed

The laboratory generator illustrated in Figure 4 served to show the migration of the sodium carbonate within the fuel bed during continuous operation. A fuel bed of treated graphite granules which had been reducing a flow of carbon dioxide of 6.25 liters per minute for 6 hours, at 900° C., was removed with the tube from the furnace. The tube was carefully opened and samples of the contents were removed from sections 2.5 cm. apart. The samples were weighed and placed in distilled water. The solutions were titrated after 1 hour with sulfuric acid, using methyl orange as an indicator, and the relative amounts of alkali per gram of fuel at the various levels were thus determined.

There was a decided increase in the alkali content in the lower part of the fuel bed, a very slight decrease in the portion just above, and again a small increase in the top portion of the bed which was not heated. The initial fuel contained 5.0 per cent of sodium carbonate. At the end of the experiment the sections of the fuel bed contained the amounts shown in Table IV. It is evident that as the graphite was converted to carbon monoxide by the carbon dioxide the sodium migrated upward and became concentrated just above the most active zone. There was a small loss of sodium carbonate in the inactive heated zone toward the top of the furnace, but at least a part of the volatilized soda was recovered in the last few centimeters of the graphite which extended above the heated zone of the furnace. The experiment indicates that in actual producer operation there would be relatively little loss of soda if the top of the fuel bed were kept cool.

Table IV—Sodium Carbonate in Graphite after Continuous Operation

HEIGHT ABOVE GRATE LEVEL	Na ₂ CO ₃ IN GRAPHITE	HEIGHT ABOVE GRATE LEVEL	Na ₂ CO ₃ IN GRAPHITE
Cm.	%	Cm.	%
0.0	5.8	12.5	4.4
2.5	7.7	15.0	4.9
5.0	7.6	17.5	4.8
7.5	5.9	20.0	5.0
10.0	6.0	22.5	5.5

Effect of Hydrogen Chloride

In order to show the comparative effect of sodium carbonate and a less easily dissociable sodium compound upon the reactivity of carbon, without changing any of the factors except the substance with which the carbon was treated, the following experiment was devised: The nickel tube was charged with sugar char treated with sodium carbonate and operated by heating to 960° C. and passing in a stream of carbon dioxide into which a small stream of air was bled.

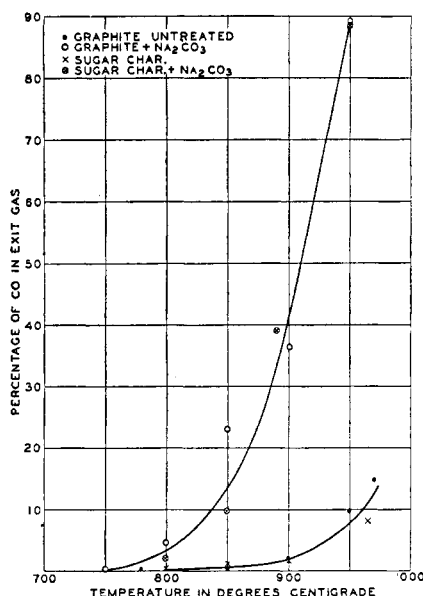


Figure 5—Percentage of Carbon Monoxide in Exit Gases When Using Treated Graphite or Sugar Char as Shown in Upper Curve, and When Using Untreated Graphite or Sugar Char as Shown in Lower Curve

The product was then analyzed. With other conditions held constant the small stream of air was next saturated with hydrogen chloride vapor. An effect was noted after about 2 seconds. The gaseous product, which had been freely burning in the open air, ceased to burn and could not be reignited. After 10 minutes of treatment with hydrogen chloride vapor the original inlet gas composition was restored and the producer operated for 10 minutes, as before, without hydrogen chloride vapor. At 960° C. a sample of the product was again taken and analyzed. The results of the experiment follow:

CONSTITUENT	BEFORE ADDITION OF HCl	AFTER ADDITION OF HCl
	%	%
CO ₂	35	72
O ₂	0	0
CO	53	18
N ₂	12	10

Mechanism of Reaction

The accepted conception of the mechanism of simple combustion, in which solid carbon is oxidized to carbon

dioxide in a stream of air, involves the principles of diffusion and fluid flow. The transport of carbon in the form of carbon dioxide out into the gas stream and the transport of oxygen from the gas stream to the surface of the solid carbon take place according to the laws of diffusion through a relatively stationary layer of gas whose effective thickness is determinable with the help of the principles of fluid flow. Rates of simple combustion of solid carbon are consequently predictable, and the agreement between calculated and actual rates for simple cases indicates that the accepted conception of the mechanism is largely correct.

No acceptable mechanism has been proposed for the reduction of a stream of carbon dioxide by heated solid carbon which permits calculations similar to the above. Attempts to apply diffusion or fluid-flow calculations to this case are rendered difficult by the fact that the volume of carbon monoxide flowing from the interface is double the volume of the carbon dioxide approaching the interface. This condition imposes upon the relatively stationary surface layer of gas in contact with the carbon a general drift away from the carbon surface. This drifting of the layer makes difficult the calculation of the transport of material through it by diffusion and equally difficult the calculation of the thickness of the layer.

It is possible that the adverse drift of this layer against the penetration of carbon dioxide sets up an abnormally high diffusional resistance and is the mechanism mainly responsible for decreasing the rate of the reaction between carbon dioxide and carbon. The rate is notably low as compared with the rate of simple combustion, where no such drift within the layer takes place.

Another view of the mechanism of the reaction is that a highly condensed molecular layer of abnormally high latent heat forms on the surface of the carbon, the molecules of the layer being so oriented that a boundary relatively passive to carbon dioxide is exposed to the surrounding gas. According to this view it is the rate of evaporation of this layer of high latent heat that controls the rate of the reaction.

The two mechanisms which have been pictured can only be effective in slowing down a heterogeneous reaction of this character when the solid substance involved has a very low vapor pressure. This is true in the present case, for the calculated vapor pressure of carbon at 1000° C., according to International Critical Tables, is 4.7×10^{-16} atmospheres. If the solid in question should have a considerable vapor pressure (10 to 100 mm.), an attached film could not exist to a great extent, for the evaporation of the atoms of the solid would continually rupture the film and expose new surface upon which the reaction could take place. Likewise the diffusion against adverse flow would be of less importance, for atoms of the solid would diffuse as vapor out of the stagnant layer and the process would go forward with the characteristic speed of a homogeneous reaction in the gas phase.

Effect of Sodium Carbonate

The presence of sodium carbonate acts to destroy both the retarding effect due to diffusion against adverse flow and the adherence of a film of carbon monoxide. The sodium carbonate, at temperatures above its melting point of 852° C., spreads upon the surface of the carbon, at the same time reacting with the carbon. The products of this reaction, as the experimental work has shown, are evolved at a considerable pressure (200 to 700 mm.) between 900° and 1000° C., and at a rather rapid rate. This precludes the possibility of a highly condensed film forming between the gas and the carbon. The products of the reaction, sodium and carbon monoxide in the molecular ratio 2Na to 3CO, pass out into the surrounding gas. The sodium reacts with the carbon

dioxide in the gas phase, forming sodium oxide and carbon monoxide (2). The sodium oxide further reacts with carbon dioxide, forming sodium carbonate. The sodium carbonate is drawn back to the surface, as the experiments have shown, and again enters the reaction. The net effect is in some respects similar to that which would obtain if the vapor pressure of the carbon should be increased to 10^{15} times its actual value. Sodium atoms are driven out into the surrounding gas, rupturing the condensed film and at the same time reducing the importance of diffusion against adverse flow by transporting the reaction out into the gas phase.

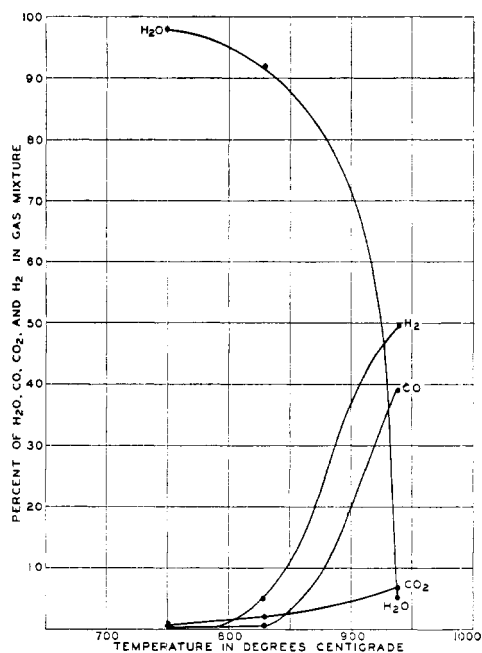


Figure 6—Decomposition of Steam by Graphite Containing 5 Per Cent Sodium Carbonate at Various Temperatures; Time of Contact above 0.13 Second

The gasification of carbon by water vapor presents an entirely parallel case. Diffusion against adverse flow and the formation of an attached film are here also probable causes for the low rate of the reaction $\text{H}_2\text{O} + \text{C} = \text{H}_2 + \text{CO}$. Sodium carbonate would be expected to perform a similar function in accelerating this reaction. This has been found to be the case, as the experimental work already cited shows.

The contention of Dent and Cobb (4) that the presence of sodium carbonate is without effect upon the equilibrium, for $\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$, except in so far as the sodium carbonate influences the allotropic modification of carbon that is exposed to the gases, is not in accord with the present work, or necessarily with their own experimental results. Their system comprised the elements carbon, oxygen, and sodium. The manner in which these elements arranged themselves in compounds determined the composition of the gases in the system. Carbon was present in excess of the amount required to form compounds with all the other elements present. In one of their experiments coke was impregnated with 7 per cent by weight of sodium carbonate and the impregnated coke was placed in a tube in a furnace. Carbon dioxide was circulated over the coke maintained at 800°C . in a closed system until a constant pressure was reached. The temperature of the furnace was then raised to 900°C ., and the coke was heated under a vacuum at this temperature for 30 hours. The temperature was again lowered to 800°C . and carbon dioxide circulated as before. This cycle of processes was repeated until the percentages of carbon dioxide

and monoxide at 800°C . did not show any further change. The data of their Table I are reproduced here as Table V. It is quite possible that the graphitization of the coke may be a factor in causing the changing percentages of carbon monoxide and dioxide in their results, as they hold, but in the light of the present experiments it is also possible to interpret the lower percentage of carbon dioxide during the first heatings as caused by vapors of sodium altering the gas composition. On successive heatings in vacuum to 900°C . more and more of the sodium would volatilize out of the system, and changing results might be expected until substantially all of the sodium had been removed. The presence of vapors of sodium must be considered in all studies where sodium carbonate and carbon are present at temperatures above 700°C .

Table V—Cobb and Dent's Data on Composition of Gas in Equilibrium with Coke Containing Initially 7 Per Cent Na_2CO_3

TOTAL TIME OF HEATING AT 900°C .	TIME TO ATTAIN EQUILIBRIUM	COMPOSITION OF EQUILIBRIUM MIXTURE AT 800°C .	
		CO_2	CO
Hours	Hours	%	%
50	12	7.0	93.0
80	7	8.8	91.2
110	15	10.9	89.1
155	32	13.5	86.5
190	34	13.7	86.3
250	55	13.8	86.2

Applications to Gas Manufacture

It has been shown that sodium carbonate greatly accelerates the action of carbon dioxide and steam on carbon at temperatures of 850° to 1000°C ., and that the influence of this material is much more potent than the differences which exist between porous sugar char and graphite. The vapors of sodium not only accelerate the reactions but must also change the gas composition to produce less carbon dioxide and more carbon monoxide.

The use of coke impregnated with sodium carbonate should give good results in the operation of gas producers. The capacity of the producer should be increased because of the shorter time of contact required, and the gas produced at a moderate temperature should contain less undecomposed steam and carbon dioxide, and more carbon monoxide and hydrogen. The changes in composition of the exit gas would be due mainly to a more rapid approach to equilibrium, but would also be due in part to an actual shifting in the gas composition caused by the presence of sodium vapors, which would become marked at temperatures above 900°C . The gas would have a higher heating value, the temperature of the exit gases would be lower and, in the case of gas that is scrubbed and used cold, the sensible heat loss would be lower. The thermal economy of the producer would thus be increased because of less sensible heat loss and higher potential heat recovery, both of these gains being made without any new sacrifices.

The cost of the sodium carbonate would have to be determined by actual operation. The retention of the sodium in the fuel bed, in the light of the experiments described herein, should be good, but this cannot be considered as proved for commercial practice. It is probable that the additional cost due to soda would not exceed 30 cents per ton of fuel consumed. Basic refractories might have to be used in the lining, but in the case of a producer this could probably be done quite easily.

The use of sodium carbonate does not offer much advantage in a water-gas machine of the present type. The reaction with steam would be accelerated and the presence of sodium carbonate would be advantageous during the gas-

making period. During the blasting period the reduction of carbon dioxide to monoxide would also be accelerated, and this would be disadvantageous because the purpose of the blast is to heat the fuel bed and this can best be accomplished if the gases pass out of the fuel bed with a maximum percentage of carbon dioxide. Some preliminary experiments on a full-sized scale have indicated the correctness of this reasoning. The increased reactivity of the fuel bed causes more losses during the blasting period than can be offset by gains during the steaming period.

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Purified Wood Fiber

The Paper-Making Characteristics of Wood Fiber High in Alpha-Cellulose¹

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CELLULOSE that is intended for paper-making purposes must possess certain properties which are not usually evident in the original state, but which can be developed by beating or hydrating the fiber in a hollander. When macerated in the presence of water, it is necessary that the fiber undergo some swelling and that there is formed a surrounding film of colloidal cellulose gel, which serves as a bond with which individual fiber units are firmly held together.

Various types of cellulose behave very differently when hydrated. In some cases the swelling and gel formation take place fairly rapidly; other fibers require considerable periods of wet rub to develop the desired cellulose mucilage. The properties of the hydrate are dependent upon the composition of the unbeaten fiber. The physical characteristics, both of gel and of fiber, determine the physical strength of the paper which can be produced from the beaten mass of fiber.

In order to make a comparison of the different types of pulps and half-stocks which can be used in the manufacture of paper, it is very important that one determine the rate of change which takes place as the beating action is continued. It is not sufficient to attempt an evaluation of the original pulps by a comparison of the beaten stocks or the paper made therefrom at a single stage of "slowness"² or for a given beating time. The need of this precaution will become apparent when one reviews the experimental data and curves given in this paper.

In the actual production of machine-made paper the hydration of the long fiber is rarely made in the absence of other materials, such as rosin size, alum, dyestuffs, and starch, although there are special products in which the presence

The strength of paper is dependent upon the inter-felting of fibers and upon the cellulose mucilage which bonds the fiber into a homogeneous sheet. The chemical composition of the cellulose determines largely the properties of the hydrate gel which is formed when the fiber is beaten in water. Wood fiber which contains high percentages of alpha-cellulose hydrates more slowly than ordinary sulfite pulp and forms a paper which is characterized by increased tearing resistance and folding endurance.

Hydration curves are included to illustrate differences in the paper-making behavior of ordinary wood pulps and of various purified-wood-fiber products. Papers made from the hydrated wood fiber that is high in alpha-cellulose simulate papers that can be produced from the better grades of rag stock.

Many commercial papers have been identified by the usual physical tests and have been grouped according to their fiber furnish. Purified-wood-fiber and rag papers are both superior in physical strength and toughness. The presence of purified wood pulp imparts physical weakness, particularly in respect to tearing resistance and fold endurance.

of extraneous matter is objectionable, as witnessed by the papers that are to be used for electrical purposes. The presence of rosin or coloring matter does not appear to affect the beating behavior markedly, and for simplicity most of the laboratory beating tests are made with water alone. When other than hydration data are required, the laboratory work is supplemented by special tests in which size, color, and alum are used. Occasionally the work must be extended to study the step of surface- or glue-sizing.

Beating in Ball Mills

In the study of paper-making fibers the laboratory investigation may involve the use of miniature hollanders or, as is more often the case, the beating tests are made in porcelain ball mills, which are charged with the determined mixture of fiber, water, and pebbles and then rotated under very carefully standardized conditions. The beaten stocks are diluted to a suitable concentration and are then converted into handmade sheets which are dried and subjected to the various paper tests at a controlled relative humidity of 45 per cent (Figures 1 and 2). The ease with which the water may be drained from the beaten fiber is determined and recorded in terms of "slowness." This slowness figure is expressed in minutes of time which are required for a given volume of water to drain from the stock suspension through a standard area of wire-mesh screen.

BALL-MILL PROCEDURE—The ball-mill beating procedure is with some modifications and refinements, that described in the T. A. P. I. report given in *Paper*, **19**, No. 9 (Nov. 8, 1916). The porcelain ball mills measure 10 inches in internal diameter and 13⁵/₁₆ inches in internal height (Figure 3). Flat porcelain covers are clamped into place against gaskets of soft rubber. A normal charge consists of 121 flint pebbles nearly uniform in size and weighing 10 pounds, the equivalent of 90 grams of bone-dry pulp added in the form of moist shreds, and a total of 2 liters of water. The mills are rotated on their long axis

¹ Received January 26, 1931.

² "Slowness" is explained in the previous paper of this series, *IND. ENG. CHEM.*, **23**, 131 (1931).