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Production of Carbon Disulfide

A process based on the system carbon monoxide plus sulfur at 500° C.

THE traditional method of manufacturing carbon disulfide involves reaction between charcoal and sulfur at about 850° C.; charcoal is used because the reaction of sulfur with coke is prohibitively slow at all reasonable temperatures. In England both raw materials have to be imported. Efforts to produce carbon disulfide by other means may be conveniently divided into two groups:

> Chemical reactions other than the straightforward $C + S_2 = CS_2$, involving sulfur dioxide or hydrogen sulfide instead of elemental sulfur and carbon monoxide or methane instead of elemental carbon.
>
> Replacing natural beech chars by artificially prepared carbonized briquets prepared from cheap low grade indigenous coals, and using the chemical reaction $C + S_2 = CS_2$.

By far the most widely used method is the reaction between charcoal and sulfur, which gives high equilibrium conversions around 850° C. (Table I). All the other reactions have been tried as possible alternatives, but none has found appreciable application in industry in Great Britain. The catalytic reaction of natural gas and sulfur (reaction V) is used in the United States, where ample supplies of cheap natural gas are available. This reaction has been studied in considerable detail by Folkins, Miller, and Hennig (*2*) and it is estimated that the process is responsible for around 40% of U. S. carbon disulfide.

In the case of reactions II and III, temperatures well above 1000° C. would have to be attained to obtain favorable equilibrium conversion to carbon disulfide. This would be a disadvantage from the standpoint of materials of construction; however, operations at these temperatures are practical with modern refractories (Carbofrax), as shown by laboratory and pilot scale experiments (*10*).

If in any alternative process, the operating temperature must be less than and preferably very much less than 850°C., the temperature of industrial practice, only reaction IV is left for further investigation.

Recent years have seen concentrated efforts to prepare carbonized briquets from low grade coals which are highly reactive to sulfur and are promising substitutes for natural beech chars in carbon disulfide manufacture. As there are very few published data on the kinetics of the charcoal-sulfur reaction, it was decided to study the behavior of these chars under various conditions.

Reaction between Carbon Monoxide and Sulfur

This reaction has been studied intensively by Stock (*11*, *12*) and others (*8*, *13*) and shown to occur in two consecutive steps:

$$2CO + S_2 = 2COS \qquad (1)$$

$$2COS = CO_2 + CS_2 \qquad (2)$$

The published values of Stock for the equilibrium constants for Reaction 2 in the temperature range 300° to 550° C. (which is of interest in the present investigation) were found to agree within limits of experimental accuracy. The rate of decomposition of carbonyl sulfide to carbon monoxide and sulfur is very much faster than its rate of conversion to carbon disulfide and carbon dioxide, thus limiting the over-all yield of carbon disulfide that can be produced.

Gaseous sulfur is known to exist (*3*, *9*) as a mixture of three species: S_2, S_6, and S_8; at low temperatures (in the range 300° to 600° C.) S_6 and S_8 predominate, whereas at high temperatures (above 700° C.) S_2 predominates. Therefore, strictly speaking Equation 1 should be written as:

$$2CO + \frac{2}{E}S_E = 2COS \qquad (3)$$

where S_E represents an equilibrium mixture of S_2, S_6, and S_8. Rewriting Equations 3 and 2 as:

$$2COS = 2CO + \frac{2}{E}S_E \text{ (CO reaction)} \qquad (3')$$

$$\text{and } 2COS = CO_2 + CS_2 \text{ (CO}_2\text{ reaction)} \qquad (2)$$

it is seen that carbonyl sulfide decomposes to carbon monoxide and sulfur on the one hand and to carbon dioxide and carbon disulfide on the other. Reaction 2 is endothermic and in the absence of 3′ an increase in temperature should therefore progressively increase carbon disulfide and carbon dioxide concentrations; but above 550° C. carbonyl sulfide begins to decompose according to Reaction 3′ and this reduces the amount of carbonyl sulfide and hence carbon disulfide and carbon dioxide which can be formed. Therefore yield of carbon disulfide is optimum in the neighborhood of 550° C., as illustrated by the following values of equilibrium gas compositions.

Temp., ° C.	Equilibrium Gas Composition, %				
	CO	S_E	COS	CO_2	CS_2
400	0.3	0.26	61.0	19.2	19.2
600	3.2	1.6	54.4	20.4	20.4
700	14.8	7.4	39.8	19.0	19.0

Before the war attempts were made in Germany (*1*) to manufacture carbon disulfide by interaction of carbon monoxide with sulfur on a pilot plant scale, but the tests were given up in 1942 because of shortage of manpower. No results have been reported.

It was thought that if the carbon monoxide–sulfur reaction were to be made the basis of a carbon disulfide manufacturing process in preference to the charcoal-sulfur process, a catalyst must be found to give a very fast reaction at low temperatures, to offset the disadvantage of low equilibrium conversion to carbon disulfide.

Kinetic Studies

Experimental Procedure. A mixture of carbon monoxide and sulfur vapors (in varying proportions) was passed over the catalyst mass contained in a 1-inch glass tube of 25-cc. capacity maintained at the required temperature, between 300° and 600° C. In a second set of tests carbon monoxide plus sulfur was replaced by pure carbonyl sulfide gas.

After excess sulfur had been condensed

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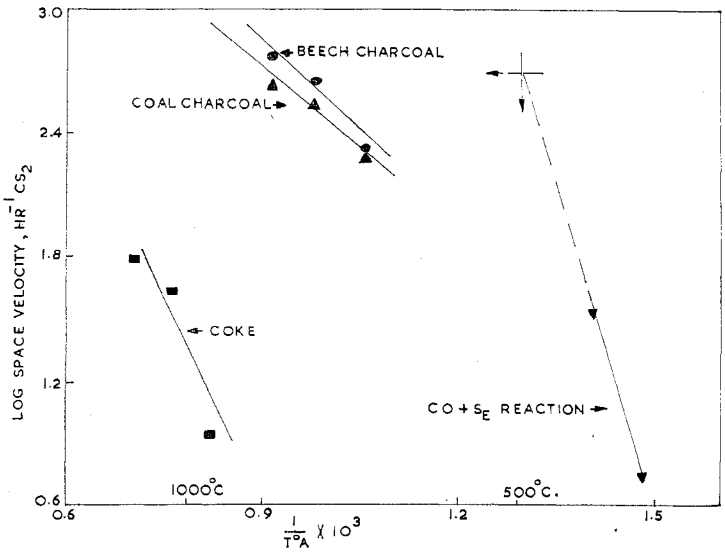


Figure 1. Arrhenius equation plots show low values of 12,000 to 14,000 cal. for beech and coal charcoals

out, carbon monoxide, carbon disulfide, carbon dioxide, and carbonyl sulfide were determined. Carbon monoxide, the only noncondensable gas, can be removed by the use of liquid air; carbon disulfide can be separated by distillation, using a bath of solidified ethyl alcohol at −114° C. However, it is not easy to separate carbonyl sulfide from carbon dioxide by a similar method because of the proximity of their boiling points; therefore advantage was taken of the thermal instability of carbonyl sulfide gas at high temperature (*11*), whereby it is decomposed into carbon monoxide and sulfur; the carbon monoxide can then be removed from carbon dioxide by the use of liquid air. Carbonyl sulfide was decomposed over a glowing platinum filament fused in a glass bulb; the filament was maintained at about 1000° C. The carbonyl sulfide could be quantitatively converted to carbon monoxide and sulfur within a minute.

Discussion. Previous workers had used silica and glass wool to catalyze the carbon dioxide reaction. As all such studies were principally concerned with the determination of the equilibrium constant for the reaction, no efforts were made to investigate the reaction rates systematically. As Reaction 1 is very fast, more or less independent of the nature of the surface, an extensive search was undertaken to find a catalyst surface to speed up the slower Reaction 2.

Metallic Surfaces. The choice of catalyst was guided by reference to those used in a similar reaction between methane and sulfur to produce carbon disulfide (*14*). These included silver sulfide, molybdenum sulfide, vanadium trioxide, zinc sulfide, copper promoted with chromium oxide, nickel promoted with alumina, and alumina promoted with manganese sulfide. The catalyst masses were prepared by precipitation in place of pumice or alumina. All attempts proved unsuccessful; in some cases they appeared to act as poisons, retarding the approach to equilibrium.

Silica and Glass Wool. In the original work of Stock on equilibrium determinations, silica and glass wool were extensively used as catalyst surfaces. These were re-examined. A mixture of carbon monoxide and sulfur vapors was passed over these surfaces for 1 to 6 minutes; conversions to carbon disulfide were very poor. These are referred to as gas phase tests (to differentiate them from liquid phase tests).

Interesting results were obtained when fine silica powder was suspended in liquid sulfur and carbon monoxide bubbled through it. The liquid sulfur reaction was maintained at 440° C.—just below the boiling point of sulfur (445° C.). These tests are designated as liquid phase tests.

The results obtained are expressed in Table II as a space velocity, which may be defined as the gaseous volume of carbon disulfide (measured at N.T.P.) formed per hour per unit volume of the reactor. The only available value for the carbon disulfide production rate in industrial practice has also been included, expressed as a space velocity. Under laboratory investigations, optimum values of the space velocities are given. An average value is given at each temperature.

From the liquid phase tests a value for the activation energy, E, of the reaction $2COS = CO_2 + CS_2$ may be obtained from the Arrhenius equation $d \ln K/dT = E/RT^2$, where K is the specific reaction rate at temperature T and E the activation energy expressed in calories. K could be replaced by the carbon monoxide flow rates for equal (below equilibrium) values of carbon disulfide concentrations. A value of E equal to about 50,000 cal. was obtained. Its magnitude indicated that a small increase in the operating temperature should substantially increase the space velocity. Thus on plotting the logarithm of space velocity *vs.* the reciprocal of absolute temperature at 400° and 440° C. and extrapolating to a slightly higher temperature (say 500° C.) a space velocity of 500 hr.$^{-1}$ is obtained (see Figure 1)—i.e., a 50° C. rise should increase the reaction rate about fifteen-

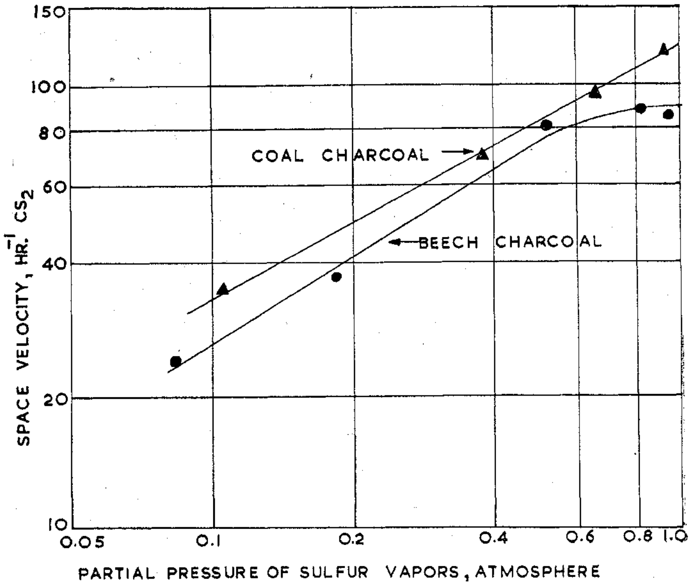
Table I. Carbon Disulfide May Be Made in Several Ways

Reaction	Basic Chemical Equation	Equilibrium, Mole %	Lit. Ref.	Type	Size, Inch	Temp., ° C.	CS_2 Production Rate, Lb./Hr./Cu. Ft. of Reactor
I	$C + S_2 = CS_2$	$S_2 = 9.4$; $CS_2 = 90.6$	(*1*)	Charcoal	Lumps	850	1.5
		$S_2 = 10.6$; $CS_2 = 89.4$	(*4*)	Coal charcoal	0.07	650	18
		$S_2 = 10.6$; $CS_2 = 89.4$	(*4*)	Beechwood charcoal	0.07	650	13
II	$C + 2H_2S = CS_2 + 2H_2$	$H_2S = 39.5$; $H_2 = 40.3$ $CS_2 = 17.8$; $S_2 = 2.4$	(*5, 6*)	Charcoal	Small particles	1125	Not detd.
III	$5C + 2SO_2 = CS_2 + 4CO$	$SO_2 = 0$; $S_2 = 2.2$ $CS_2 = 16.5$; $COS = 3.3$; $CO = 78$	(*10*)	Anthracite	0.05 (approx.)	1250	1.27
IV	$2CO + S_6 = 2COS = CO_2 + CS_2$	$CO = 0.4$; $CO_2 = 19.5$ $S_6 = 0.3$; $CS_2 = 19.5$; $COS = 60.3$	(*11, 12*)	Bubbling CO through liquid sulfur containing suspension of silica dust		440	7^a
V	$CH_4 + 2S_2 = CS_2 + 2H_2S$	$CH_4 = 0$; $CS_2 = 33.3$ $S_2 = O$; $H_2S = 67.7$	(*14*)	...	...	700	57

[a] Present investigations.

fold. This would mean operation under pressure (boiling point of sulfur, 500° C. at 35 p.s.i.g.).

Space velocities of this high order might be required to offset the very large amounts of unconverted sulfur as carbonyl sulfide in the product gases. A practical method must be found for removing carbon dioxide from carbonyl sulfide and recycling the purified carbonyl sulfide. This is purely an economic consideration and may be solved only by large scale trials and comparing the costs of the two processes—i.e., carbon monoxide plus sulfur at 500° C. *vs.* carbon plus sulfur at 850° C.



▶ Figure 2. Kinetic studies show the reaction is of a fractional order

Reaction between Charcoals and Sulfur

In industrial practice 1- to 2-inch lumps of charcoal react with sulfur; however, for investigations on a laboratory scale smaller particles, about $^1/_8$ inch, had to be used. This meant that some of the results obtained in the laboratory may not be applicable to plant practice, because the size of the charcoal particles might have a considerable influence on the rate of formation of carbon disulfide.

The reaction rate of a solid-gas reaction like the one under consideration is governed by two factors:

Chemical resistance, determined by the function exp (E/RT), where E is the activation energy and T is the absolute temperature, is greatly affected by temperature; in the case of the combustion of carbon, a 15° rise in temperature approximately doubles the combustion rate but is independent of the size of the solid particles.

Diffusional resistance, only slightly affected by temperature but greatly affected by the diameter of the particle and the gas velocity. Diffusional resistance, in the case of a coal, is governed by the nature of the volatiles contained in it. This has to be remembered in comparing reaction rates of different varieties of charcoal.

Depending on the temperature, one or the other of the two resistances would predominate. For the combustion of carbon such a temperature is about 1050° K. (*7, 15*).

It is not possible to translate the reactivity results obtained on a laboratory scale to a full scale plant. However, they are useful for comparing different types of coal and showing trends.

Experimental Procedure

About 25 cc. of charcoal as $^1/_8$-inch pieces was contained in a $^3/_4$ inch silica tube which was inserted horizontally in a Gallenkamp laboratory furnace. Liquid sulfur was contained in a glass tube 2 inches in diameter carrying an external winding. Nitrogen was bubbled through the sulfur boiler and a mixture of nitrogen and sulfur vapors was passed over charcoal. At the exit end excess sulfur was condensed out in a bath maintained at 140° C. and the crude carbon disulfide was condensed in a solid carbon dioxide–methanol bath. The system was always operated under a pressure of 1 atm.

Charcoals Used in Tests. Tests were carried out on the following samples:

Natural beechwood charcoal supplied as 1-inch lumps. Analysis: Moisture = 6%, ash = 1.5%, and volatiles = 13%.

Coal charcoal prepared from low grade coals by briquetting and subsequent carbonization at 500° C. in the laboratory of the British Coal Utilization Research Association at Leatherhead. Analysis: Moisture = 4.3%, ash = 3.4%, and volatiles = 13.5%. The sample was supplied as cubes about $^1/_8$ inch in size.

Coke lumps from boiler house.

Variables Studied. The rates of reaction, expressed as carbon disulfide space velocities, were determined under the following conditions (Table III):

1. At varying temperatures but fixed partial pressure of sulfur vapor.
2. At varying partial pressures of sulfur vapor but fixed temperature.
3. At varying total flow rates but fixed partial pressure of sulfur vapor and fixed temperature.

TEMPERATURE VARIATION. Preliminary tests had brought out two characteristics of the charcoal-sulfur reaction: Below about 625° C. there was no perceptible formation of carbon disulfide; if the charcoals were heated appreciably above 550° C. in absence of sulfur vapors but in an inert atmosphere of nitrogen, the charcoal surface underwent partial deactivation. Thus a charcoal sample treated in this way gave a space velocity only about half to a third of that in an atmosphere of sulfur above 550° C. No explanations for this effect can be given. No such effect was noticed in the case of coke.

Experiments with coke showed that it was reactive only above 1000° C. and even at that temperature did not compare favorably with the charcoals. It would be interesting to obtain the reaction rates with pulverized coke; the reaction between coke and sulfur vapors might well be predominantly diffusion controlled and therefore very much dependent on the particle size. Limitations of the apparatus make such studies impossible.

In the tests given in Table III the charcoals were always kept in contact with sulfur above 550° C. The logarithms of the carbon disulfide space velocities are plotted in Figure 1 against the reciprocal of the absolute tempera-

Table II. Comparison of Space Velocities

Liquid phase tests gave high space velocities

		Laboratory Investigations				
			$^1/_{16}$-Inch Silica Beads			
	Industrial Practice (*1*)	Metallic surfaces, Cu, Ni, etc., on pumice	Gas Phase Tests		Silicic Acid (3:1), Liquid Phase Tests	
Temp., ° C.	850	500	450	550	400	440
Space velocity, hr.$^{-1}$ CS$_2$	7	2	3	3.3	5.6	34

Table III. Coal Charcoal Was as Reactive as Beech Charcoal, Coke Was Relatively Unreactive

	Set 1			Set 2			Set 3			
							Constant			
	Variable, $T°$, C.	Constant mean partial pressure sulfur, atm.	Space velocity, hr.$^{-1}$ CS_2	Constant, $T°$, C.	Variable mean partial pressure sulfur, atm.	Space velocity, hr.$^{-1}$ CS_2	$T°$, C.	Mean partial pressure sulfur, atm.	Variable total gas flow at outlet, cc./min.	Space velocity, hr.$^{-1}$ CS_2
Coal charcoal	675	0.813	200	625	0.107	35	675	0.882	1366	195
	750	0.770	341	625	0.212	85[a]	675	0.923	2110	178
	825	0.734	437	625	0.386	70	675	0.921	2738	198
				625	0.662	97				
				625	0.935	121				
Beech charcoal	675	0.743	211	625	0.084	24	675	0.877	1456	219
	750	0.622	444	625	0.187	37	675	0.925	2201	184
	825	0.590	592	625	0.541	81	675	0.944	2818	118
				625	0.831	89	675	0.945	2749	109
				625	0.954	85				
Coke	825	0.991	...	...	...	...	...	...	...	...
	950	0.986	9	...	...	...	...	...	...	...
	1050	0.966	44	...	...	...	...	...	...	...
	1150	0.956	62	...	...	...	...	...	...	...

[a] Stray result.

tures. The slopes of straight lines drawn as nearly as possible through these points correspond, according to the Arrhenius equation, to activation energies of 12,000 and 14,000 cal., respectively, for the beech and coal charcoals. It is necessary to consider whether the observed rates of reaction correspond to true surface reaction rates, or whether the over-all rates are partly determined by rates of diffusion. It seems unlikely that at the flow rates and reaction rates used in these experiments diffusion in the gas phase could affect the over-all rate. On the other hand the charcoals are highly porous, and diffusion in the pores may be partly controlling and may affect the over-all rate. As the diffusional retardation increases as the rate of reaction increases, such an effect would reduce the apparent activation energies; this may account for the rather specially low values of 12,000 to 14,000 cal. quoted above. If this is the case, the true activation energies may be much higher.

VARYING PARTIAL PRESSURES OF SULFUR. The rate of production of carbon disulfide increased with the partial pressure of sulfur vapor, as expected; reaction rate increased three- to fourfold for a tenfold increase in the partial pressure of sulfur. In the case of beech charcoal, but not coal charcoal, the reaction tended to become a zero-order reaction as the partial pressure of sulfur vapor approached unity. In industrial practice economic considerations would tend to limit the sulfur throughput, so that sulfur partial pressures approaching unity are seldom obtained and are more likely to be in the region 0.2 to 0.4 atm. (total pressure unity).

A plot of the logarithm of space velocity *vs.* logarithm of the partial pressure of sulfur gives a straight line with a slope of about 0.6 (Figure 2); the reaction is therefore of a fractional order.

VARYING FLOW RATES OF SULFUR. The reaction rate would not be expected to be affected by mass flow rates, if the partial pressure of sulfur was constant. This expectation was fulfilled for the coal charcoal but not for the beech charcoal; in the latter case there was a progressive falling off in the space velocity with increased flow rates, although the sulfur concentration was never less than 0.88 atm. Because of this rather unexpected result the experiments were repeated under identical conditions; results were reproducible to within 6%. No explanation has so far offered itself.

Conclusion

Various methods of manufacturing carbon disulfide have been reviewed and compared with the traditional method involving the use of beechwood charcoal. The reaction between carbon monoxide and sulfur was singled out for investigation. Rates of reaction were high when carbon monoxide was bubbled through liquid sulfur at its boiling point containing a suspension of fine silica powder. An approximate value for the activation energy, E, equal to 50,000 cal. was obtained. This suggests that an increase in operating temperature (pressure reaction) should substantially increase the reaction rate. This might perhaps offset the disadvantage, for industrial application, of low carbon disulfide equilibrium yield.

The behavior of wood charcoal, artificially prepared reactive charcoal, and coke with sulfur was studied under various experimental conditions. Coal charcoal was as reactive as a natural beech charcoal. Coke was relatively very unreactive, even at 1000° C. However, it might be possible to increase the reactivity of coke (or cheap low grade coals) by employing it in pulverized form.

The reaction $C + S_2 = CS_2$ was found to be of a fractional order and its energy of activation was determined as about 13,000 cal. A possible explanation for this rather low value is suggested.

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