STEAM-COKE REACTIONS

Experimental Procedure and Results

Experiments were conducted in fluidized state in the same apparatus used for carbon dioxide-coke studies. For steam studies, the reaction tube was connected at the bottom to a preheater vaporizer by a tapered Pyrex joint. The preheater vaporizer was made of a Pyrex tube, 2 cm. in diameter and 30 cm. long, fitted internally with a Nichrome coil and packed with porcelain chips. At the bottom, the tube was fitted with an arm for introducing inert gas or other gases. A small side arm 12 cm. below the top of the tube served for the introduction of water. Water was injected into the heater through a syringe needle (22 gage 15 cm. long) sealed in the side arm. A small piece of asbestos was placed at the top of the needle to prevent droplet formation. The needle was attached to a syringe held vertically in the injector assembly which is shown in figure 8. The rate of water injection was controlled by the rate of traverse of the plunger of the calibrated syringe. To prevent recondensation of the water vapor, a small cylindrical heater was placed around the preheater tube and the reaction tube below the furnace. An infrared lamp was placed at the top of the furnace to prevent condensation of the unreacted water which was collected in a trap containing 5 pct. HCl held at 0° C. Gas samples collected were analyzed for CO_2, CO, H_2, He, or N_2 and combustible gases in an Orsat apparatus. Inert gas served as a tracer for material balance as well as to sweep the water vaporized.

The results obtained are shown in table 3.

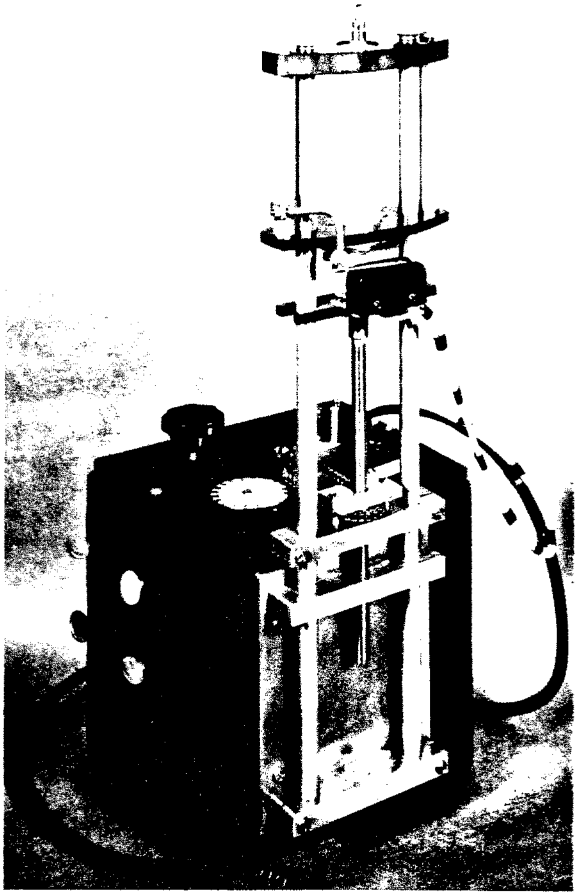

FIGURE 8.—Precision Water Injection System.

TABLE 3.—*Reaction of steam with a high-temperature metallurgical coke*

Run No.	Weight, grams	$N^{\circ}_{H_2O}$[1]	$N^{\circ}_{N_2}$[1]	Outlet gas composition, water-free basis, percent				f[2]	$N_C/N^{\circ}_{H_2O}$[3]	$\frac{(H_2)(CO_2)}{(H_2O)(CO)}$	u[4]	W/N_C[5]
				CO_2	CO	H_2	N_2					
Reaction Temperature 1,000° C.; Particle Size 60–80 Mesh (U.S. Standard)												
84	10	3.58	1.11	10.1	20.5	39.3	30.1	0.41	0.31	0.34	0.31	16.6
85	12	3.58	1.10	10.2	21.9	41.5	26.4	.49	.37	.45	.43	16.7
86	4	3.58	1.12	6.9	18.6	30.8	43.7	.22	.18	.11	.14	11.4
88	8	3.58	1.12	8.2	22.6	36.9	32.3	.36	.30	.20	.26	14.0
89	10	3.58	1.12	9.6	21.4	39.0	30.0	.41	.32	.31	.31	16.1
139	2	2.24	.62	8.4	16.1	30.3	45.2	.19	.15	.12	.12	11.2
140	3	2.24	.61	9.0	18.6	33.7	38.7	.24	.19	.15	.15	12.9
141	4	2.24	.62	9.3	19.4	36.1	35.2	.29	.23	.20	.19	14.7
142	6	2.24	.62	10.3	20.6	38.8	30.3	.36	.28	.29	.26	17.6
143	8	2.24	.62	10.9	21.4	40.6	27.1	.42	.33	.37	.33	20.2
144	10	2.24	.62	10.8	22.3	42.5	24.3	.49	.38	.47	.42	21.9
Reaction Temperature 1,000° C.; Particle Size 80–100 Mesh (U.S. Standard)												
145	8	1.40	0.62	9.6	21.2	38.3	30.9	0.55	0.44	0.55	0.52	24.2
146	10	1.40	.62	9.1	22.5	39.0	29.4	.59	.48	.58	.60	27.7
147	12	1.40	.61	3.2	35.8	40.7	20.3	.88	.87	.65	1.80	19.0
Reaction Temperature 1,000° C.; Particle Size 100–140 Mesh (U.S. Standard)												
148	9.8	0.876	0.437	7.8	26.6	37.9	27.7	0.69	0.62	0.65	0.84	33.7
149	11.7	.876	.439	6.1	29.5	38.7	25.7	.75	.69	.62	1.01	36.0
150	12.9	.876	.441	5.3	29.3	39.4	26.0	.76	.67	.57	1.06	41.0
151	9.8	.547	.437	5.3	27.0	32.6	35.2	.74	.73	.56	.98	45.6
152	12.2	.547	.437	2.9	29.9	34.2	33.0	.83	.80	.47	1.41	52.3
153	14.7	.547	.441	1.0	33.9	34.3	30.8	.90	.87	.61	2.01	52.3
Reaction Temperature 1,100° C.; Particle Size 40–50 Mesh (U.S. Standard)												
70	4.0	5.73	2.04	8.7	18.3	34.3	38.7	0.32	0.25	0.22	0.22	5.2
71	8.0	5.73	1.70	6.8	27.8	41.0	24.4	.50	.42	.25	.44	6.2
72	12.0	5.73	1.70	6.0	30.7	42.3	21.0	.60	.52	.29	.62	7.5
73	16.0	5.73	1.64	5.2	33.1	43.3	18.4	.67	.60	.32	.78	8.7
Reaction Temperature, 1,100° C.; Particle Size 20–30 Mesh (U.S. Standard)												
124	2.0	9.2	2.71	9.0	9.5	25.0	56.5	0.13	0.097	0.14	0.07	4.2
125	4.0	14.7	2.71	9.4	15.0	31.1	44.5	.13	.101	.09	.07	5.0
126	2.0	14.7	2.71	9.1	13.3	29.5	48.1	.11	.086	.08	.06	3.0
127	3.8	9.2	2.71	8.8	15.9	32.4	42.9	.22	.170	.16	.14	4.6
128	5.0	9.2	2.71	9.0	18.2	33.8	39.0	.26	.206	.17	.17	4.9
129	6.3	9.2	2.71	8.9	20.6	35.7	34.8	.30	.250	.19	.20	5.2
Reaction Temperature, 1,100° C.; Particle Size 50–60 Mesh (U.S. Standard)												
130	5.4	5.7	1.83	8.5	23.4	38.7	29.4	0.42	0.35	0.26	0.23	5.0
131	7.4	5.7	1.83	7.6	27.8	41.5	23.1	.57	.49	.36	.56	4.9
132	9.5	5.7	1.83	6.4	28.8	41.3	23.5	.561	.48	.28	.54	6.4
133	5.4	2.24	.91	7.7	25.5	38.6	28.2	.55	.48	.37	.52	9.4
134	7.2	2.24	.91	6.6	28.7	41.0	23.8	.70	.60	.59	.86	10.0
135	9.0	2.24	.91	5.3	30.6	42.0	22.1	.77	.66	.58	1.08	11.3
Reaction Temperature, 1,100° C.; Particle Size 80–100 Mesh (U.S. Standard)												
136	6.9	1.40	0.82	4.3	29.9	37.6	28.2	0.78	0.71	0.51	1.13	13.0
137	8.0	1.40	.82	4.1	30.8	36.9	28.2	.77	.72	.45	1.18	14.8
138	9.4	1.40	.82	3.9	32.5	37.2	26.4	.83	.81	.59	1.53	15.5

See footnotes at end of table.

TABLE 3.—*Reaction of steam with a high-temperature metallurgical coke*—Continued

Run No.	Weight, grams	$N^{\circ}_{H_2O}$ [1]	$N^{\circ}_{N_2}$ [1]	Outlet gas composition, water-free basis, percent				f [2]	$N_C/N^{\circ}_{H_2O}$ [3]	$\frac{(H_2)(CO_2)}{(H_2O)(CO)}$	u [4]	W/Nc [5]
				CO_2	CO	H_2	N_2					
Reaction Temperature, 1,200° C.; Particle Size 100–140 Mesh (U.S. Standard)												
58	1.2	1.43	0.340	6.7	35.1	41.7	16.5	0.70	0.60	0.39	0.85	2.6
59	1.7	1.43	.340	2.36	40.5	42.9	14.2	.83	.72	.27	1.37	3.1
60	2.6	1.43	.332	2.23	42.0	43.0	12.8	.88	.80	.39	1.72	4.2
61	3.6	1.43	.361	.59	43.3	43.7	12.4	.935	.89	.19	2.40	5.2
Reaction Temperature, 1,200° C.; Particle Size 80–140 Mesh (U.S. Standard)												
47	4.0	1.43	0.94	0.84	36.2	35.0	27.9	0.940	0.87	0.34	2.50	6.0
48	8.0	1.43	.97	.42	36.7	36.9	25.9	.996	.969	------	6.00	10.7
49	6.0	2.28	.64	1.04	42.2	43.5	13.3	.960	.905	.58	3.00	5.4
50	8.0	2.28	.47	.62	44.5	44.6	10.2	.990	.916	------	4.76	7.2
52	2.0	1.43	.89	3.85	30.0	33.8	32.4	.77	.65	.39	1.08	4.0
53	3.0	1.43	.89	1.00	35.8	35.7	27.5	.89	.83	.22	1.82	4.7
54	4.0	1.43	.79	1.19	36.7	38.0	24.1	.94	.87	.52	2.51	6.0
56	3.0	2.28	.44	1.22	44.4	44.5	9.9	.909	.89	.26	2.02	2.7
57	4.0	2.28	.35	1.04	45.3	44.8	8.9	.949	.80	.41	2.72	4.1
Reaction Temperature, 1,200° C.; Particle Size 40–50 Mesh (U.S. Standard)												
28	4.0	2.28	0.208	2.6	44.2	47.7	5.5	0.87	0.71	0.38	1.63	4.2
30	5.0	3.65	.264	2.1	45.2	47.9	4.8	.900	.71	.40	1.92	3.6
33	5.0	3.65	.340	2.4	44.1	48.0	5.5	.89	.79	.41	1.77	3.2
34	5.0	3.65	.441	4.2	41.0	46.6	8.2	.88	.67	.68	1.72	3.8
37	5.0	3.65	.766	3.7	39.2	44.6	12.5	.84	.72	.48	1.43	3.6
38	5.0	3.65	.228	3.4	30.5	35.3	30.8	.78	.69	.38	1.12	3.7
40	5.0	3.65	.128	.6	40.2	41.0	18.2	.80	.78	------	1.22	3.2
41	2.0	3.65	.262	6.4	20.7	30.8	42.1	.58	.46	.40	.57	2.2
42	4.0	3.65	.267	5.0	25.9	32.9	36.2	.75	.62	.53	1.01	3.2
43	6.0	3.65	.267	2.0	32.6	34.8	30.6	.87	.83	.40	1.63	3.7
44	8.0	3.65	.267	1.44	33.8	35.6	29.8	.928	.86	.53	2.33	4.7
45	10.0	3.65	.264	.77	35.2	36.0	28.0	.960	.93	.52	3.00	5.5
Reaction Temperature, 1,200° C.; Particle Size 20–30 Mesh (U.S. Standard)												
66	5.0	14.6	5.4	8.6	21.4	38.0	32.0	0.46	0.35	0.33	0.39	1.8
67	10.0	14.6	5.4	5.0	31.3	40.9	22.8	.68	.59	.34	.80	2.2
68	15.0	14.6	5.5	4.0	33.8	41.4	20.8	.76	.68	.38	1.05	2.8
69	20.0	14.6	5.4	2.4	37.6	41.8	18.2	.89	.78	.50	1.82	3.2
Reaction Temperature, 1,200° C.; Particle Size 16–20 Mesh (U.S. Standard)												
62	5.0	14.6	5.7	9.0	20.4	36.2	34.4	0.45	0.33	0.34	0.39	1.9
63	10.0	14.6	5.7	5.6	29.2	39.9	25.3	.63	.54	.32	.67	2.3
64	15.0	14.6	5.8	5.0	31.3	41.0	22.7	.73	.63	.42	.94	3.0
65	5.0	14.6	5.5	8.0	23.2	39.0	29.8	.50	.40	.34	.44	1.6
Reaction Temperature, 1,050° C.; Particle Size 50–60 Mesh (U.S. Standard)												
78	5.0	5.73	1.90	7.6	18.4	32.5	41.5	0.27	0.21	0.15	0.17	7.8
79	10.0	5.73	1.90	8.2	22.6	38.1	31.1	.42	.33	.26	.32	9.9
80	12.0	5.73	1.90	7.5	26.0	40.6	25.9	.53	.43	.33	.49	9.1
81	15.0	5.73	1.92	7.2	26.7	41.0	25.1	.56	.45	.34	.54	10.7
Reaction Temperature, 1,150° C.; Particle Size 30–40 Mesh (U.S. Standard)												
74	4.0	5.73	2.62	7.9	20.8	36.6	34.7	0.48	0.38	0.35	0.41	3.4
75	8.0	5.73	2.57	5.3	29.2	39.7	25.8	.69	.60	.40	.83	4.3
76	12.0	5.73	2.42	3.7	33.9	41.3	21.1	.83	.75	.53	1.40	5.2

[1] cm.³/sec. (STP).
[2] Fraction H_2O reacted (by hydrogen balance).
[3] Atom C/mole H_2O.
[4] Function defined by equation (37) (dimensionless).
[5] g. Coke/mg. C gasified/sec.

Theoretical Development

The reduction of water vapor to hydrogen by a reaction site on the surface of carbon and the reverse reaction may be expressed as

$$H_2O+C_f \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} H_2+C_o \tag{17}$$

where again C_f and C_o denote free and occupied sites. The actual gasification involves the occupied sites, that is, an occupied site leaves the solid phase to form carbon monoxide

$$C_o \xrightarrow{k_3} CO+nC_f \tag{18}$$

where, as in the case of carbon dioxide reaction, n is an integer having values of zero, one, or two. The significance of n has been discussed in connection with carbon dioxide reactions.

Carbon monoxide formed by the above reaction can, as does hydrogen, remove oxygen from occupied sites to form carbon dioxide which, in turn, can be reduced by a reaction site to carbon monoxide

$$CO+C_o \underset{k_1}{\overset{k_1'}{\rightleftharpoons}} CO_2+C_f. \tag{19}$$

For a differential section the instantaneous rate of gasification can be expressed as

$$dN_C=k_3(C_o)dW. \tag{20}$$

Under steady-state conditions the rate of formation of occupied sites would be equal to the rate of their disappearance

$$\begin{aligned} d(C_o)/dt=0=&[k_2(H_2O)+k_1(CO_2)](C_f)\\ &-[k_2'(H_2)+k_1'(CO)+k_3](C_o). \end{aligned} \tag{21}$$

Substituting $(C_t)=(C_o)+(C_f)$ into equation (21) and solving for (C_o)

$$(C_o)=\frac{[k_2(H_2O)+k_1(CO_2)](C_t)}{k_2(H_2O)+k_1(CO_2)+k_2'(H_2)+k_1'(CO)+k_3}. \tag{22}$$

As in the case of carbon dioxide reaction, k_3 in the denominator of equation (22) may be omitted for experiments not involving vacuum. Further, if it is assumed that oxygen exchange reactions are very fast and attain equilibrium

$$(C_f)/(C_o)=k_2'(H_2)/k_2(H_2O) \tag{23}$$

and

$$(C_f)/(C_o)=k_1'(CO)/k_1(CO_2) \tag{24}$$

it follows that

$$(H_2)/K_2(H_2O)=[k_2'(H_2)+k_1'(CO)]/[k_2(H_2O)+k_1(CO_2)] \tag{25}$$

where

$$K_2=k_2/k_2'. \tag{26}$$

According to the above assumptions water-gas shift equilibrium should be maintained in the gas phase, that is

$$(H_2)(CO_2)/(H_2O)(CO)=(k_2/k_2')/(k_1/k_1')=K_2/K_1=K. \tag{27}$$

These assumptions, however, when observed experimentally, have not always been valid. These assumptions will be discussed later in greater detail.

Substitution of equations (23) and (24) into (22) and omission of k_3 in the denominator leads to

$$(C_o)=\frac{(C_t)}{1+(H_2)/K_2(H_2O)}. \tag{28}$$

From equations (20) and (28) it follows that

$$[K_2+(H_2)/(H_2O)]dN_C=K_2k_3(C_t)dW. \tag{29}$$

Integrating the right side of equation (29) and rearranging

$$(1/N_C)\int_0^{N_C}(H_2)/(H_2O)dN_C=-K_2+K_2k_3(C_t)W/N_C. \tag{30}$$

As was the case in CO_2-C reactions, in performing this integration it is tacitly assumed that composition of the gas phase inside a particle is uniform and identical to that surrounding the particle. Let

$$Y=(H_2)/(H_2O), \tag{31}$$

then from a hydrogen balance

$$N_{H_2}=YN_{H_2O}^{\circ}/(1+Y), \tag{32}$$

from water-gas shift equilibrium

$$(CO_2)=K(CO)/Y, \tag{33}$$

from an oxygen balance

$$N_{H_2}=N_{CO}+2N_{CO_2}=(2K+Y)N_{CO}/Y, \tag{34}$$

and from a carbon balance

$$N_C=N_{CO}+N_{CO_2}=Y(K+Y)N_{H_2O}^{\circ}/(1+Y)(2K+Y). \tag{35}$$

Designating the left side of equation (30) by u

$$u=(1/N_C)\int_0^{N_C}YdN_C=-K_2+K_2k_3(C_t)W/N_C. \tag{36}$$

For negligible back mixing of gases, Y may be assumed to depend upon reaction rate only, that is, negligible longitudinal gas mixing. By partial integration equation (36) becomes

$$u=Y-(1/N_C)\int_0^{Y}N_CdY \tag{37}$$

or

$$u=Y-(N_{H_2O}^{\circ}/N_C)\int_0^{Y}(K+Y)Y/(2K+Y)(1+Y)dY. \tag{38}$$