On the Rate of Combustion of Coke Briquettes in the Fuel Bed

By

Ikutaro SAWAI, Masanaga KUNUGI and Hiroshi JINNO

Department of Industrial Chemistry

Introduction

Undoubtedly the combustion on the grate is one of the oldest and simplest ways of using solid fuel. The physical and chemical changes in this case, however, seem to be rather complicated and many problems worth studying still remain untouched.

Generally the combustion of solid fuel in the fuel bed is explained by the scheme represented in Fig. 1. Namely, the oxidation of coke to carbon dioxide by primary air, which comes from under the grate, takes place in a layer immediately above the ash bed. Oxygen is thus consumed and the concentration of carbon dioxide increases, which, however, is again converted into carbon monoxide in a layer, the so called reducing zone, just above the oxidizing zone. Although this general view of reactions was worked out in the first decade of this century, the quantitative formulation of these phenomena had not been touched until quite recently. Mayers[1] was the first who presented a formula which gave the temperature distribution in the fuel

Fig. 1. Composition of the Gases within the Fuel Bed of a Coal-fired Furnace.

bed. Having based himself on experimental data, he also succeeded in expressing the rate of oxidation μ_1 and reduction μ_2 in such commoner terms as porosity of coke or the void of the packed bed.[2]
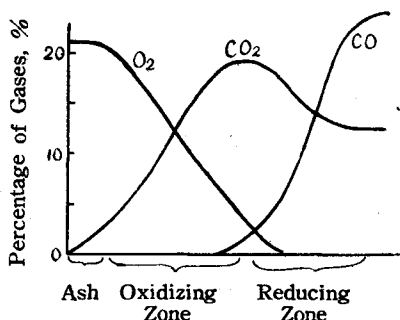
In the present paper, the oxidizing and reducing reaction in a packed fuel bed will be treated in minuter detail, and carefull considerations will be given to the effects of physical and chemical changes occuring at and near the carbon surface,

and, further, the results calculated with our theoretical formula will be compared with experimental data.

1. Theoretical Consideration

For the purpose of simplifying the problem, let us confine our attention to the investigation of the steady state, taking into consideration only the reaction of coke with air, and excluding other reactions such as of coke with water vapour or the distillation of coke.

As the first step let us consider somewhat in detail the reactions which will take place in the oxidizing zone.

Oxygen comes into contact with and reacts with the fresh carbon surface after passing through the boundary and ash layers by diffusion.

The chemical reactions can be formulated as

$$2C + O_2 \rightarrow 2CO, \qquad (1) \qquad\qquad C + O_2 \rightarrow CO_2, \qquad (2)$$

giving carbon mono-and dioxides as ultimate products.

However, the carbon dioxide thus produced may be reduced to carbon monoxide according to the reaction

$$CO_2 + C \rightarrow 2CO. \tag{3}$$

Now, in the present case, all three reactions (1), (2) and (3) may occur simultaneously on the carbon surface, and, in a temperature range of 900°–1400°C, the rates of reactions are so high that the equilibrium will be established instantaneously. Furthermore, as the eqilibrium constants for the above reactions are known to be larger than 10^2 at temperatures aforementioned, the concentration of carbon dioxide and oxygen at the carbon surface may be considered as practically zero.[3]

Carbon monoxide thus formed, however, may readily be oxidized to carbon dioxide by the reaction

$$2CO + O_2 \rightarrow 2CO_2, \tag{4}$$
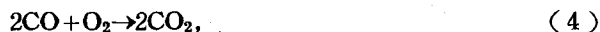
at a point very close to the surface, because the oxygen necessary for the reaction can be supplied by diffusion through the layer of ash, and consequently the main components which pass through the ash and boundary layers may be regarded as composed of oxygen and carbon dioxide.

Hence, it is possible to derive a theoretical formula representing the rate of the oxidizing reaction of carbon by taking into account only the interdiffusion of oxygen and carbon dioxide through both layers in the opposite direction.

Usually the rate of reaction K (mol/cm². sec) of coke with air is represented by the equation

$$K = kp_s, \tag{5}$$

where k (mol/cm². sec) is the reaction constant, and p_s the partial pressure of oxygen at the reaction surface.

On the other hand, the oxygen has to pass through, by interdiffusion, the boundary layer at the surface of coke and also the layer of ash before entering into the reaction. Hence, K becomes

$$K = \frac{D_1 (p - p_s)}{RT A_s \left[\dfrac{\alpha (r_0 - r)}{\sqrt{A_s \cdot A_t}} + \dfrac{F}{\sqrt{A_t \cdot A_0}} \right]}. \tag{6}$$

in which D_1 (cm²/sec) is the coefficient of interdiffusion of oxygen and carbon dioxide, A_s, A_t and A_0 (cm²) the area of reacting surface, the surface of coke, and the outer surface of boundary layer, respectively, R (cm³. atm/mol. °K) the gas constant, T (°K) the temperature of diffusing zone, α the factor for the coefficient of diffusional resistance in the ash layer, F (cm) the thickness of the boundary layer, p the partial pressure of oxygen at the outer surface of the boundary layer, r_0 (cm) the radius of the briquette, and r the radius of the part which still remains unaffected.

If we take "a" for the shape factor, we can substitute the terms A_s, A_t, and A_0 by $a\pi r^2$, $a\pi r_0^2$, and $a\pi (r_0 + F)^2$, respectively.

Putting the above relations in the equation (6), we have

$$K = \frac{D_1 (p - p_s)}{RT \left[\dfrac{\alpha r (r_0 - r)}{r_0} + \dfrac{F r^2}{r_0 (r_0 + F)} \right]}, \tag{7}$$

and by eliminating p_s from (5) and (7), we obtain the equation

$$K = \frac{p}{\dfrac{1}{k_1} + \dfrac{RT}{D_1} \left[\dfrac{\alpha r (r_0 - r)}{r_0} + \dfrac{F \cdot r^2}{r_0 (r_0 + F)} \right]}. \tag{8}$$

Let N be the number of briquettes in the unit volume, and the rate of oxidizing reaction μ_1 (mol/cm³. sec) will be expressed as

$$\mu_1 = N a \pi r^2 K / p. \tag{9}$$

As it is possible to express N with the void of the packed bed v by making use of the relation

$$N = \frac{3 (1 - v)}{a \pi r_0^3}, \tag{10}$$

we get the expression

$$\mu_1 = \frac{3(1-v)}{\dfrac{r_0^3}{k_1 \cdot r^2} + \dfrac{RT}{D_1}\left[\dfrac{\alpha(r_0-r)r_0^2}{r} + \dfrac{F \cdot r_0^2}{r_0+F}\right]},\qquad(11)$$

by substituting the equations (8) and (10) into (9).

In the case of the oxidizing reaction, i. e., $C + O_2 \rightarrow CO_2$, the velocity of the chemical reaction at temperatures higher than $800°$ is so great that μ_1 is entirely governed by diffusion,[4] and therefore the first term in the denominator of the equation (11) can be neglected, so that the expression for μ_1 becomes

$$\mu_1 = \frac{3D_1(1-v)}{RT\left[\dfrac{\alpha(r_0-r)r_0^2}{r} + \dfrac{F \cdot r_0^2}{r_0+F}\right]}.\qquad(12)$$

This denotes that the rate of oxidizing reaction μ_1 is proportional to $(1-v)$ and is inversely proportional to the square of the radius of the briquette r_0 as long as the values of D_1, T and $(r_0/r-1)$ can be regarded as constant, the thickness of the boundary layer F being neglected as it is much smaller as compared with the radius of the briquette r_0.

Obviously, in the reducing zone, the above equation (11) holds good also for the expression of the rate of the reaction $C + CO_2 \rightarrow 2CO$.[5]

Then we obtain the equation for the rate of reduction of carbon dioxide μ_2 (mol/cm³. sec)

$$\mu_2 = \frac{3(1-v)}{\dfrac{r_0^3}{k_2 r^2} + \dfrac{RT}{D_2}\left[\dfrac{\alpha(r_0-r)r_0^2}{r} + \dfrac{F \cdot r_0^2}{r_0+F}\right]},\qquad(13)$$

in which k_2 is the reaction constant and D_2 the coefficient of interdiffusion of carbon mono- and dioxides.

However, at the temperature as low as $1100°C$ the rate of this chemical reaction is so slow that the term for the diffusion can be omitted. Hence, the expression for μ_2 becomes

$$\mu_2 = \frac{3k_2(1-v)}{r_0\dfrac{r_0^2}{r^2}},\qquad(14)$$

which means that μ_2 is closely correlated with the value of $\dfrac{(1-v)}{r_0}$. Basing his research on the experimental data, Mayers[2] comes to the same conclusion.

Having been able to express μ_1 and μ_2 in terms of chemical and diffusional resistance, we are now in a position to discuss problems of the composition of gases in a packed fuel bed.

Let us concentrate our attention on the following main reaction : $C+O_2 \rightarrow CO_2$, $C+CO_2 \rightarrow 2CO$ and $2CO+O_2 \rightarrow 2CO_2$. These reactions proceed under partial pressures p_1, p_2, p_3 of oxygen, carbon dioxide, and carbon monoxide respectively, at any point in a fuel bed.

Although, usually, the reactions $C+O_2 \rightarrow CO_2$ and $C+CO_2 \rightarrow 2CO$ are treated as those of the first order according to the stoichiometric relations, the reaction $2CO+O_2 \rightarrow 2CO_2$ is known to be more complicated and proceed through complex chain mechanism.[6] However, the authors have assumed that these series of partly still unknown chain reactions can be represented by an ordinary second order reaction, because it is simpler and accurate enough for the present purpose.

Hence, as the rate of decrease of the concentration of oxygen along the axial distance of a packed bed $G\dfrac{dp_1}{dx}$ must be equal to the rate of oxygen consumption according to the first and last equations, we have

$$G\frac{dp_1}{dx} = -(\mu_1 p_1 + k_3 p_1 p_3).\tag{15}$$

In the same way we have the relations

$$G\frac{dp_2}{dx} = -\mu_2 p_2 + \mu_1 p_1 + 2k_3 p_1 p_3,\tag{16}$$

and

$$G\frac{dp_3}{dx} = 2\mu_2 p_2 - k_3 p_1 p_3,\tag{17}$$

in which G is the quantity of air supply, x the thickness of the oxidizing layer measured upwards from the lower end, k_3 is the reaction constant of the reaction $2CO+O_2 \rightarrow 2CO_2$. Formally, we are able to get the values of p_1, p_2 and p_3 by integrating the above simultaneous equations, but the actual calculations can not be carried out so simply, because μ_1, μ_2 and k_3 may have different values at every point in the fuel bed.

Substituting the equations (11) and (13) in (15), (16) and (17), we obtain the relations

$$G\frac{dp_1}{dx} = -\frac{3(1-v)p_1}{\dfrac{RT}{D_1}\left[\dfrac{a(r_0-r)r_0^2}{r}+\dfrac{F\cdot r_0^2}{r_0+F}\right]+\dfrac{r_0^3}{k_1 r^2}} - k_3 p_1 p_3,\tag{18}$$

$$G\frac{dp_2}{dx} = \frac{3(1-v)p_1}{\dfrac{RT}{D_1}\left[\dfrac{a(r_0-r)r_0^2}{r}+\dfrac{F\cdot r_0^2}{r_0+F}\right]+\dfrac{r_0^3}{k_1\cdot r^2}}$$

$$-\frac{3(1-v)p_2}{\dfrac{RT}{D_2}\left[\dfrac{a(r_0-r)r_0^2}{r}+\dfrac{F\cdot r_0^3}{r_0+F}\right]+\dfrac{r_0^3}{k_2\cdot r^2}} + 2k_3 p_1 p_2,\tag{19}$$

and

$$G \frac{dp_3}{dx} = 2 \frac{3(1-v)p_2}{\frac{RT}{D_2}\left[\frac{a(r_0-r)r_0^2}{r} + \frac{Fr_0^3}{r_0+F}\right] + \frac{r_0^3}{k_2 \cdot r^2}} - k_3 p_1 p_2. \tag{20}$$

By this means, we can eliminate the unknown μ_1 and μ_2.

On the other hand, as it is clearly seen from the equations $C+O_2 \rightarrow CO$, $C+CO_2 \rightarrow 2CO$, one molecule of oxygen or carbon dioxide reacts upon one atom of carbon so that the rate of the decrease of carbon $\frac{dr}{dx}$, in the present case, can be expressed by the equation

$$\frac{dr}{dx} = \frac{12}{u \cdot f \cdot \rho}\left[\frac{3(1-v)p_1}{\frac{r_0^3}{k_1 \cdot r^2} + \frac{RT}{D_1}\left[\frac{a(r_0-r)r_0^2}{r} + \frac{Fr_0^2}{r_0+F}\right]} + \frac{3(1-v)p_2}{\frac{RT}{D_2}\left[\frac{a(r_0-r)r_0^2}{r} + \frac{Fr_0^2}{r_0+F}\right] + \frac{r_0^3}{k_2 \cdot r^2}}\right], \tag{21}$$

whose first and the second terms in the blacket correspond to the carbon consumption by the oxidizing and the reducing reactions, respectively. In the equation, f represents the content of fixed carbon, ρ the apparent density, and u the rate of translational movements (cm/sec) of coke briquettes.

The thickness of the boundary film F can be obtained from the relation

$$F = \frac{D_m \cdot P}{R \cdot T \cdot k_g \cdot p_f}, \tag{22}$$

in which D_m is, for the present case, the mean value of coefficient of interdiffusion in the systems CO_2–O_2 and CO_2–CO, p_f the logarismic mean of the concentration of gas at the inner- and outer surfaces of the boundary film,[7] P the total pressure of gases, and R and T are, as usual, gas constant and absolute temperature, respectively. The mass transfer coefficient of the gas film k_g in a packed bed, which appears in the above equation, can be calculated in the following manner:[8]

The mass-transfer factor j_d is usually expressed by the equation

$$j_d = \left(\frac{k_g \cdot M \cdot p_f}{G}\right)\left(\frac{\mu}{d \cdot D_1}\right)^{2/3}, \tag{23}$$

and for $(D_p G/\mu) < 350$

$$j_d = 1.82 \left(\frac{D_p \cdot G}{\mu}\right)^{-0.41}, \tag{24}$$

therefore, we can calculate k_g, using j_d as an intermediate, if other values in the equations are ready to hand.

The figures, such as M, the mean molecular weight of air, G, the quantity of air supply, μ, the viscosity of gases, d, the density of gases, and D_p, the effective diameter of the briquette can be regarded as known. Hence, from the known

value of the modified Reynolds number $\left(\dfrac{D_p \cdot G}{\mu}\right)$ we can get the value of j_d and, by substituting this in the equation (23), the necessary value k_g can readily be obtained.

By solving the equations (18), (19), (20) and (21) simultaneously by the method of numerical integration, we obtain the values of partial pressure of oxygen and carbon dioxide at any point of the fuel bed. The following experiments have been carried out in the hope of finding out how the calculated values agree to the experimental data.

2. Experiments

Coke and clay powder, which had passed through the 60 meshes of the standard sieve, were mixed in various proportions and kneaded well with a proper amount of water. Then the mixture was made into cylindrical briquettes of 2 cm in height and in diameter by means of a small auger machine. The technical analysis of coke gave the results; water 2.2, volatile matter 7.1, fixed carbon 80.9, ash 9.8%..

In Fig. 2 is shown a sketch of the apparatus used for the present experiments. A small cylindrical furnace, F, of 60 cm high and 13 cm in inner diameter was charged with about 700 pieces of briquettes, and after they had been ignited on the grate B, air was supplied from under the grate so that the combustion proceeded upwards. The temperature of the central axis of the packed fuel bed, which changes according to the displacement of the combustion zone, was measured every five minutes with Pt-Pt·Rh thermo-couples fixed at the position (1)~(4) and (6).
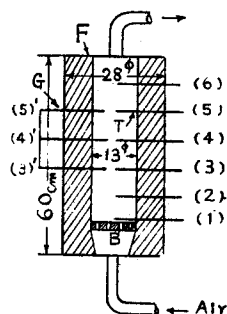

Fig. 2. Diagram of Experimental Apparatus.

B; Grate, G; Gas Sampling Tube, T; Thermocouple, F; Furnace.

For the purpose of measuring the radial temperature distribution, the thermocouple (5) was moved in the protecting tube and the reading was taken at the five fixed points. The protecting tube of the thermo-couple (4) was furnished by the necessary equipments so that it can also be used as a suction pyrometer for the measurements of gas-temperature.

The furnace was provided with three sampling holes (3)′, (4)′ and (5)′, from which the gases in the fuel bed were drawn out every ten or twenty minutes according to the state of combustion and analysed by the method of Hempel.

The conditions of the experiments are tabulated in Table 1.

Table 1.

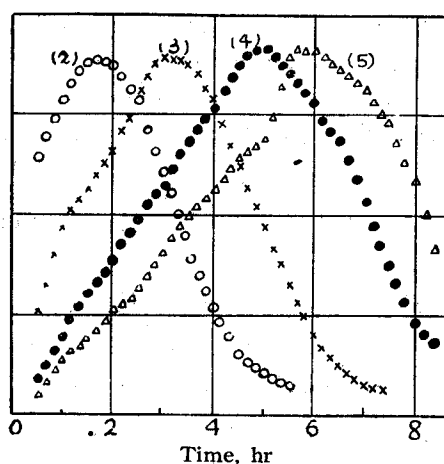| Experiment No.	Fixed carbon in briqutte %	Apparent density of briquette	Rate of air flow, kg/m². hr	Volume of voids in bed
1	66.0	1.34	190	0.43
2	60.0	1.32	190	0.43
3	52.0	1.35	190	0.43
4	60.0	1.32	313	0.43
5	60.0	1.32	246	0.43

The series of curves in Fig. 3, (a), (b) and (c) illustrate typically the general feature of the progress of temperature change when the burning zone passes
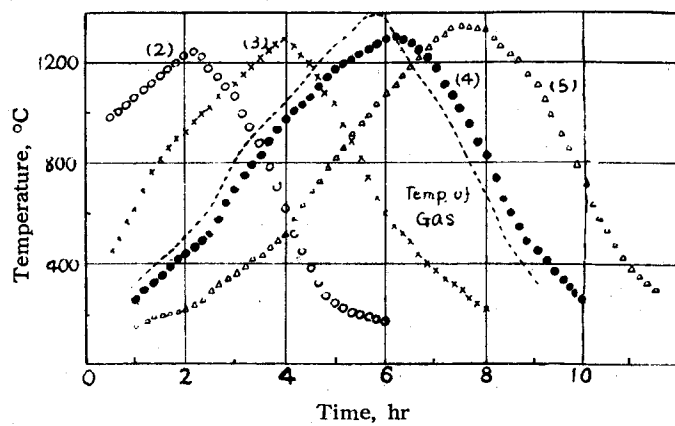
(a) Exp. No. 2.
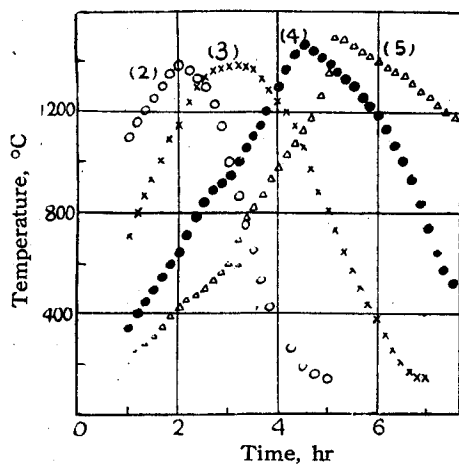
(b) Exp. No. 4. (c) Exp. No. 5.

Fig. 3. Experimental Temperature-time Curves.

through successively the points from (2) to (5). Also a curve for the gas temperature at the point (4) is drawn in dotted line, which may serve as a reference to estimating the difference of solid and gas-temperature. The relative positions of the curves will indicate the rate of "burning up" of briquettes and also thickness of the burning zone.

The results of gas analysis are represented graphically in Fig. 4, which disclose the change of CO–,
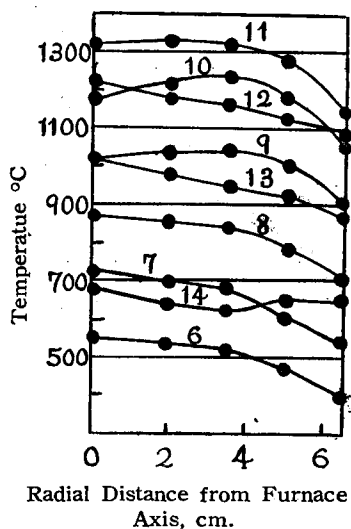

At the position (3)′ (4)′ (5)′
CO₂ —O— —□— —⊙—
O₂ ---●--- ---✕--- ---△---
CO --⊗-- --▲-- --⊟--

Exp. No. 2

Exp. No. 5
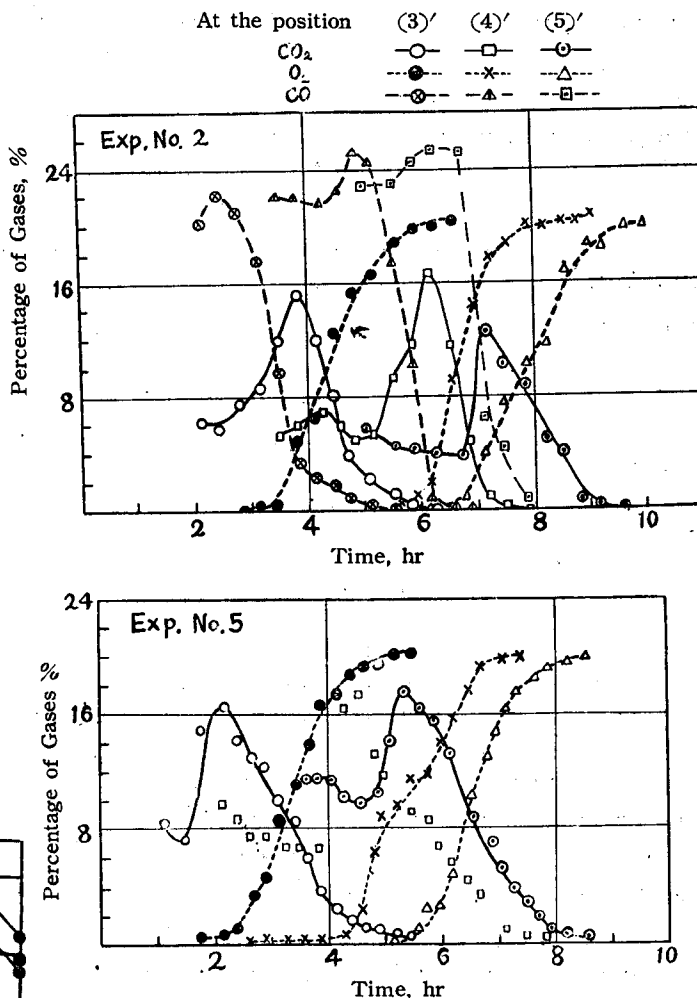
Fig. 4. Composition of Gases in the Coke Bed.

Fig 5. Temperature Distribution at the Plane (5).

CO_2– and O_2 content of the gases in the fuel bed during the burning up of briquettes.

The radial temperature distribution at the plane (5) is given in Fig. 5, in which each curve represents the distribution at the time t (hr) indicated on the curve.

The temperature range of the reducing and oxidizing zones of the fuel bed can be estimated by comparing the curves in Figs. 3 and 4.

It can be pointed out that the oxidizing reaction

begins to predominate at the point where the temperature is still a little lower than the maximum, and ends at the point of about 500°C where the oxygen content amounts to the normal value of 21%. On the other hand, in the present cases, the reducing reaction seems to begin at about 950°C corresponding to the point of maximum of CO content. These relations have already been given in Fig. 1 example.

The maximum temperature and the time necessary for completing the reaction at serveral positions in the furnace under different experimental conditions are summarized in Table 2.

Table 2.

Exp. No.	Maximum temperature in °C			Time necessary for completing the reaction in min			
				Oxidizing reaction		Reduding reaction	
	Measured at the position (3)	(4)	(5)	(4)′	(5)′	(4)′	(5)′
1	1230	1250	1320	190	190	140	150
2	1290	1320	1350	170	170	140	140
3	1220	1320	1360	150	160	140	130
4	1390	1460	1480	130	120	90	80
5	1430	1450	1350	160	160	110	100

The increase of air blast accelerates the burning velocity and consequently the larger number of briquettes enter simultaneously into the reaction which results in the building up of a thicker reaction zone. The richer in carbon content are the briquettes, the longer will be the time necessary for their burning out, which fact means that the velocity of burning up of the reaction zone is slow.

From the curves in Fig. 3, it can be found out that the temperature of gas is about 50°C higher than that of solid when the green briquettes enter into the reaction. This difference broadens gradually up to the maximum value of 150°C, and then narrow until finally the curves representing gas- and solid-temperatures cut each other at some point before the solid-temperature reaches the maximum and then both curves run almost pararell until the briquettes completely burn out.

The radial temperature gradient is confirmed to be comparatively small as long as the reaction between solid and gas phases goes on.

3. Comparison of Calculated Values with Experimental Data

As all measurements have been carried out with the furnace of the fixed fuel bed having no continous charge and discharge system, the steady state required

in our simplified calculations can not be obtained, and consequently both results, the experimental and theoretical, are not to be compared as they stand. However, if we assume the charge and discharge are going on constantly with the velocity equal to the mean velocity u (cm/sec) of the burning up of briquettes calculated from the experimental data, it would be possible to realize the steady state in which all other figures are practically the same as in the present experiments.

The mean velocities, which act as intermediate between steady and non-steady states, are as follows:

Experiment No.	1	2	3	4	5
$u \times 10^3$ (cm/sec)	1.14	1.35	1.6	3.0	2.2

The coefficient of diffusion D and velocity constnat k of chemical reaction which appear in the equations (18), (19) and (20) can be expressed as $D = D_0 \left(\dfrac{T}{273} \right)^n$, $k = \dfrac{c'}{\sqrt{T}} e^{-\frac{E}{RT}}$, respectively, in which D and D_0 are the coefficient of interdiffusion at T° and $273^\circ K$, n is a constant having the values between 1.5–2.0, R the gas constant, E the activation energy, and c' a constant.

The numerical values of D_0, E, c' and n for the reactions $C + O_2 \rightarrow CO$, $C + CO_2 \rightarrow 2CO$ and $2CO + O_2 \rightarrow 2CO_2$ are given in Table 3.

Table 3.

	Reactions		
	$C + O_2 \rightarrow CO_2$	$C + CO_2 \rightarrow 2CO$	$2CO + O_2 \rightarrow 2CO_2$
D_0 (cm²/sec)	0.168	0.137	—
E (Kcal)	20	53	20
c'	1.04×10^6	8.9×10^5	10
n	1.6	1.5	—

Obviously, $u = \dfrac{dx}{dt}$. Therefore, by means of the relations given by (18), (19), and (20), we can calculate the values of the partial pressure of gases in the fuel bed at any moment during the experiment and thus compare them with the experimental data. In our calculations, we used the following numerical values: coefficient of diffusional resistance α, thickness of gas film F, cinder loss L, partial pressure of carbon dioxide p_2 at the end of the reducing zone, modified Reynolds number, and mass-transfer factor j_a as shown in Table 4.

Table 4.

Exp. No.	α	F (cm)	L (%)	p_2	R_e	j_a
2	1.73	0.24	0.8	0.04	26.4	0.34
4	1.73	0.20	0.8	0.06	43.0	0.25

Needless to say, both D and k are the functions of temperature. The numerical integrations, however, can be carried out without difficults, when we assume that the temperature was constant during the short period of $\Delta t = 2000$ sec. and would be the same as the mean value of the corresponding temperatures of solid phase obtained by direct measurements (Fig. 3).

In Fig. 6, the values calculated by the method of Runge-Kutta are compared with the results of the measurement. It will be seen that the agreement of both values is good enough. Hence, the basic equations (18), (19), and (20) can be regarded as expressing correctly the physical and chem-

Fig. 6. Composition of Gas in the Combustion of Coke.

(a) Exp. No. 2.   (b) Exp. No. 4.

ical changes occuring in the fuel bed, although a great drawback in practical use is that the temperature at every point be known beforehand. However, the materials contained in this paper will throw light on the analysis of the complicated phenomena which must be taken into account for discussing these reactions.

The problems of temperature distributions in the fuel bed will be treated in our papers which will appear in succession.
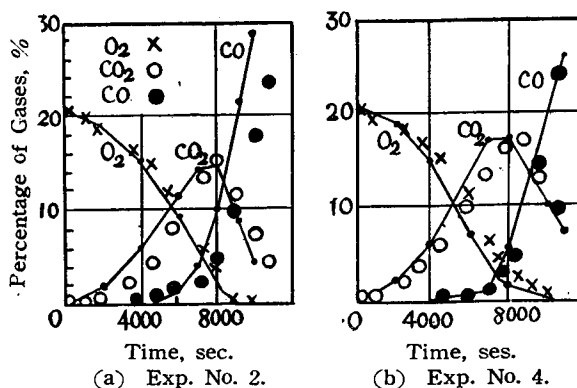
Summary

The results of this investigation may be summarized as follows:

(1) A quantitative formulation of the reaction rate of coke upon air in the packed bed has been presented under the conditions, under which both diffusion and chemical reaction may affect the reaction rate.

(2) By using the theoretical formulas for the rate of reactions, $C + O_2 \rightarrow CO_2$ and $CO_2 + C \rightarrow 2CO$, we could calculate the percentages of CO_2, CO and O_2 in the packed bed. Comparing the calculated values with the experimental results, we found the agreement satisfactory.

Acknowledgment

References

1) M. A. Mayers ; Trans. Am. Soc. Mech. Eng., 279 (1937), Ind. Eng. Chem., **32**, 563 (1940).

2) M. A. Mayers : Fuel, **21**, 4 (1942).

3) O. A. Hougen; Chem. Process Principles, 1068 (1947).

4) H. C. Hottel ; Ind. Eng. Chem. **26**, 749 (1934).

5) I. Sawai, M Kunugi; Memoirs of. Faculty of Engineering Kyoto Univ., **12** (4), 87 (1950).

6) B. Lewis & G. von Elbe ; Combustion, Flames and Explosion of Gases (1939).

7) O. A. Hougen; Chem. Process Principles, 932 (1947).

8) O. A. Hougen; Trans. Am. Inst. Chem. Eng., **41**, 445 (1945), Chem. Process Principles, 985 (1947).