The Combustion Process Effectiveness Factor of Oil Shale Char Particles

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ABSTRACT

According to the definition of the effectiveness factor for porous catalyst particles, a combustion process effectiveness factor has been suggested in combination with the features of shale char combustion. Unlike the effectiveness factor used in catalytic reactions, which is based on gas concentration and temperature at the surface of catalyst, the effectiveness factor for combustion process is based on concentration and temperature in the bulk gas phase, which do not change during the combustion reaction.

A mathematical expression for the combustion process effectiveness factor has been derived in terms of a shrinking-core model with the particle size unchanged. The expression of the location for the minimum value of combustion process effectiveness factor in the particle is presented. The criterion for the shrinking-core model also has been derived.

The combustion process of Fushun and Maoming oil shale char particles was analyzed with the effectiveness factor defined. Experimental results compare fairly well with results obtained from the theoretical effectiveness factor.

INTRODUCTION

The resource of oil shale found in China is rich, especially in Fushun and Maoming (Hou, 1985). It is the main heating resource in the shale oil retorting process where shale oil char gasifies and burns. Therefore, it is important to investigate oil shale char combustion (Wang and Wang, 1987; Wang and others, 1989).

The effectiveness factor is an important design consideration in the investigation of catalytic reaction kinetics for solid-gas porous catalyst particles. Considerable work has been done regarding the effectiveness factor of the solid-gas catalytic reaction (Aris, 1975; Rester and Aris, 1969; Carberry and Kulkarini, 1973; Weisz and Hicks, 1962; Yun and Ding, 1985; Ye and Gu, 1986). However, only few investigations have examined the combustion effectiveness factor of the solid-gas noncatalytic reaction between carbon in the porous char particle and oxygen in the air. For the special situation of oil shale char burning, the effectiveness factor of the solid-gas noncatalytic reaction has been investigated according to the definition of effectiveness factor for porous catalyst particles.

THEORETICAL CONSIDERATIONS

Combustion Process Effectiveness Factor

According to the definition of the effectiveness factor (n) for porous catalyst particles:

$$n = \frac{\text{actual reaction rate}}{\text{ideal reaction rate}} \tag{1}$$

The combustion process effectiveness factor of oil shale char particles can be defined as:

$$n = \frac{\text{actual reaction rate}}{\text{reaction rate obtained when gas concentration at the surface of reaction is the same as that in the bulk gas phase}} \tag{2}$$

Thus:

$$n = \frac{4\pi r_c^2 k_g C_{Ac}}{4\pi r_c^2 k_g C_{Ag}} \tag{3}$$

According to the oil shale char-particle character, the distribution of reacting concentrations, C_{Ac} and C_{Ag}, can be given (Wang and others, 1989) as:

$$\frac{C_{Ac}}{C_{Ag}} = \left[\frac{1 - k_g R}{D_e (1-x)^{1/3} \left[1 - (1-x)^{1/3}\right]} + \frac{k_g}{k_f}(1-x)^{2/3} \right]^{-1} \tag{4}$$

The combustion process effectiveness factor of oil shale char particles then becomes:

$$n = \frac{1}{1 + N_c(1-x)^{1/3}[1-(1-x)^{1/3}] + \dfrac{N_c}{N_{sh}}(1-x)^{2/3}} \quad (5)$$

where:

$$N_c = \frac{k_g R}{D_e} \quad (6)$$

$$N_{sh} = \frac{k_f R}{D_e} \quad (7)$$

or:

$$N_c = \frac{\text{diffusion resistance in char layer}}{\text{reaction resistance at interface}}$$

$$N_{sh} = \frac{\text{diffusion resistance in char layer}}{\text{diffusion resistance in gas film}}$$

Using the relationship between conversion and reacting surface:

$$1 - x = (r_c/R)^3 \quad (8)$$

the combustion process effectiveness factor of oil shale char particle can be given as:

$$n = \frac{1}{1 + N_c \frac{r_c}{R}\left(1 - \frac{r_c}{R}\right) + \frac{N_c}{N_{sh}}\left(\frac{r_c}{R}\right)^2} \quad (9)$$

Shrinking-Core Model

As may be expected, the minimum value of the combustion process effectiveness factor is found by differentiating equation 9 and setting

$$dn/d(r_c/R) = 0 \quad (10)$$

The location of the minimum point of the combustion process effectiveness factor can be given as follows:

$$\frac{r_c}{R} = \frac{1}{2\left(1 - \frac{1}{N_{sh}}\right)} \quad (11)$$

and the minimum value of the combustion process effectiveness factor is as follows:

$$n_{min} = \frac{4(N_{sh}-1)^2}{4(N_{sh}-1)^2 + N_c N_{sh}(3 - N_{sh})} \quad (12)$$

From equations 5 and 9, we know that the combustion process effectiveness factor is a function of N_c, N_{sh}, and x or r_c/R, but its minimum value involves only N_c and N_{sh}, and the location of the minimum point is related to N_{sh} only.

It can be seen from equation 11 that when N_{sh} increases, the diffusion resistance in the gas film decreases—that is, the increase in diffusion resistance in the char layer leads to a decrease in r_c/R. This means that the location of minimum point of the combustion effectiveness factor will move toward the particle center. As N_{sh} approaches infinity, r_c/R approaches a value of 0.5. This means that the location of the minimum point of the combustion process effectiveness factor cannot exceed one-half the particle radius.

From equations 2 and 5, note that when diffusion resistance in the gas film becomes negligible, N_{sh} approaches infinity, and the minimum value of the combustion process effectiveness factor becomes a function only of reaction resistance at the interface and diffusion resistance in the char layer (N_c). Thus, the minimum value of n becomes:

$$n_{min} = 1 - \frac{N_c}{4} \quad (13)$$

By analyzing equation 11, we see the following:

1. When $0 < N_{sh} < 1$, then $r_c/R < 0$, and the shrinking-core model cannot be used.
2. When $1 < N_{sh} < 2$, then $r_c/R > 0$, and the reaction becomes homogeneous.
3. When $N_{sh} > 2$, then $1 > r_c/R > 0$, in which case the shrinking-core model can be used.

Therefore, $N_{sh} > 2$ can be taken as the criterion of the shrinking-core model (SCM). Our experiment shows that combustion of Fushun and Maoming oil shale char particles is characterized by a shrinking-core reaction, which can described by the SCM.

Effect of Reacting Conditions

The reacting conditions (temperature, gas flow rate, and particle diameter) affect the kinetic parameters (such as k_f, k_g, and D_e) of oil shale char-particle combustion, and these parameters can be expressed by N_c and N_{sh} (equations 6 and 7). Figures 1 and 2 show the variation in combustion process effectiveness factor with N_c and N_{sh}. From these plots, it can be seen that:

1. When N_c is unchanged, n increases as N_{sh} increases.
2. When N_{sh} is unchanged, n decreases as N_c increases.

Comparing the curves between Figures 1 and 2, it was found that N_c is more important than N_{sh} to variations in combustion process effectiveness factor.

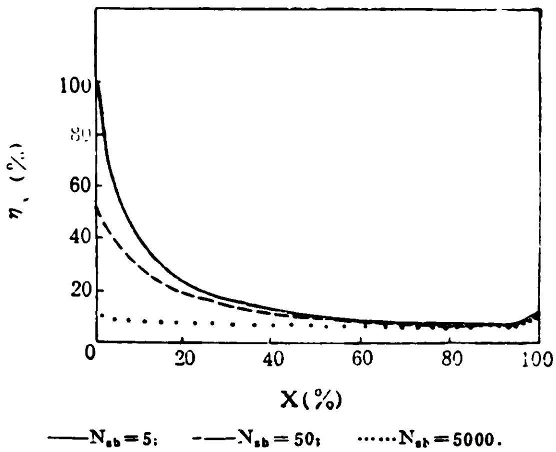


Figure 1. Relation between effectiveness factor and conversion under different combustion conditions (N_c constant).

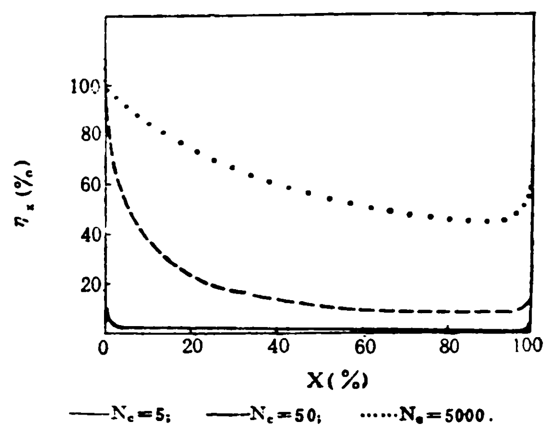


Figure 2. Relation between effectiveness factor and conversion under different combustion conditions (N_{sh} constant).

EXPERIMENTAL

Properties of Samples

The raw oil shale particles of different sizes were calcined in a Fischer assay apparatus from room temperature to 540°C at a constant heating rate of 5C°/minute, and retorted at the final temperature for 3 hours to prepare the char particle samples for combustion testing. The properties of the samples are listed in Table 1.

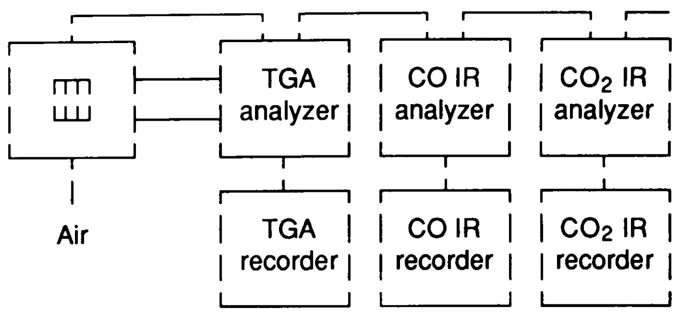
Experimental Apparatus and Procedures

The apparatus used to investigate the combustion of oil shale char particles has been described by Wang and others (1989). In addition, a separate measurement of the reaction rate was obtained by sampling the gases exiting the reactor by means of online CO_2 and CO analyzers.

Table 1. Characteristics of shale char.

Property	Fushun Sample*	Maoming Sample
Particle size, mm	7–14.5	6.5–14
Total carbon, %	4.95	12.65
Organic carbon, %	4.79	12.37
Apparent density, g/cm^3	2.01	1.38
Effective density, g/cm^3	2.36	2.36
Total porosity, cm^3/g	0.0744	0.303
Specific surface, m^2/g	10.7	13.7
Void fraction, %	14.9	41.7
Equivalent radius, Å	138	442

* Sample is of low grade and has low pore volume.



All the experiments were made under isothermal conditions. The samples were heated at a rate of 30C°/minute in a nitrogen stream. At the desired temperature, the nitrogen flow was replaced by air. During combustion, the weight of the sample and the CO_2 and CO concentrations were recorded continuously until sample weight remained constant.

RESULTS AND DISCUSSION

The chemical reaction rate constant (k_g), the diffusion parameter in the ash layer (D_e), and the diffusion parameter in the gas film (k_f) can be obtained in our experiments (Wang and others, 1989). The dimensionless N_c and N_{sh} values for Fushun and Maoming oil shale chars, involving k_g, D_e, and k_f, are summarized in Table 2.

As shown in Figures 3 through 6, the combustion process effectiveness factor of Fushun and Maoming oil shale char particles varies with the conversion. From these plots, it can be seen that n quickly abates until carbon conversion reaches about 90%. Combining this situation with equation 8, we see that when the reacting surface nearly reaches one-half the particle radius ($r_c/R = 50\%$), the combustion process effectiveness factor has a minimum value (Figures 7 through 10).

In Figures 3 through 6, the rapid decline in combustion process effectiveness factor means that combustion of

Table 2. N_c **and** N_{sh} **values of Fushun and Maoming oil shale chars under different combustion conditions.**

Test No.	Temperature (°C)	Air Flow Rate (ml/min)	Particle Size (cm)	N_c	N_{sh}
		Fushun Chars			
F-1	586	535	0.94	11.8	121
F-2	588	205	1.42	96.5	249
F-3	608	205	0.88	82.3	67
F-4	610	105	0.88	101	70
F-5	613	76	0.89	94.0	49
F-6	627	110	0.65	149	119
F-7	632	110	1.40	139	93
F-8	705	205	0.92	612	77
F-9	781	76	1.16	248	37
F-10	816	205	0.96	77.0	30
F-11	929	205	0.95	324	31
		Maoming Chars			
M-1	570	555	0.88	87.9	68.9
M-2	578	205	0.68	22.6	172
M-3	588	205	1.12	121	325
M-4	593	205	1.39	233	119
M-5	593	76	0.89	70.4	56.1
M-6	603	209	0.86	45.8	56
M-7	685	205	0.92	1,760	40
M-8	798	205	0.87	5,692	43.1
M-9	843	76	0.69	5,191	51.3
M-10	876	205	0.88	7,235	116

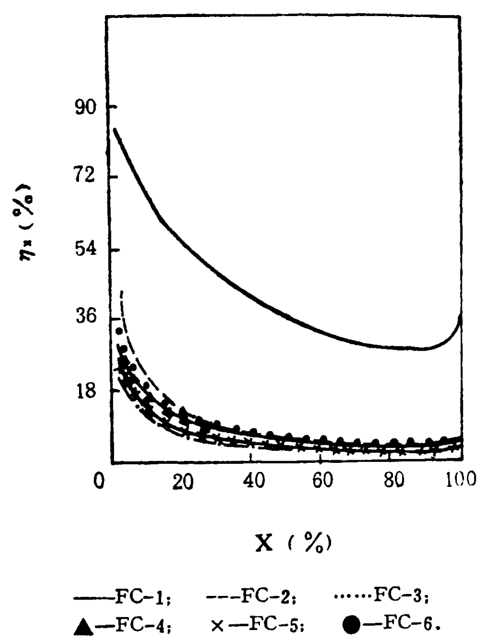


Figure 3. Effect of carbon conversion on effectiveness factor for combustion of Fushun shale char (<630°C).

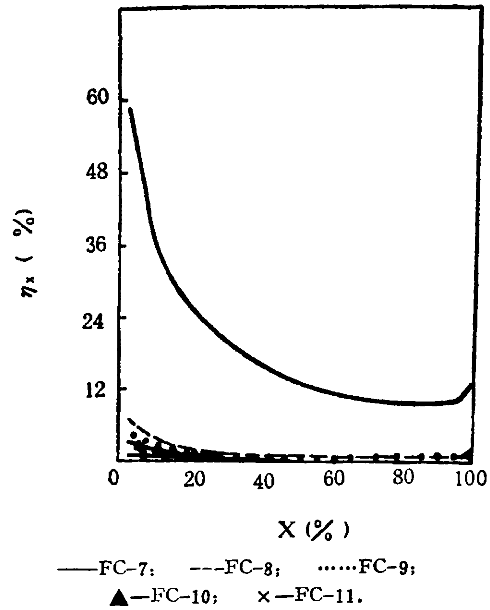


Figure 4. Effect of carbon conversion on effectiveness factor for combustion of Fushun shale char (>630°C).

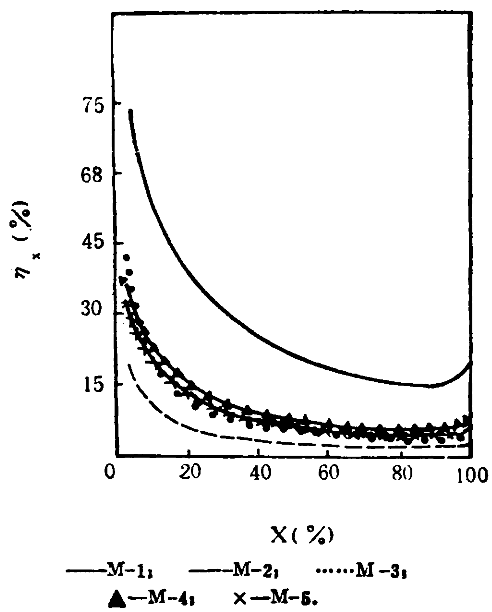


Figure 5. Effect of carbon conversion on effectiveness factor for combustion of Maoming shale char (<600°C).

Fushun and Maoming shale char particles is strongly affected by the physical transfer process.

In porous catalytic reaction engineering, the catalyst effectiveness factor is classified with the reacting activeness. According to the combustion reaction activity, we believe that the combustion process effectiveness factor of Fushun and Maoming shale char particles can be classified as a new catalog.

According to equations 5, 9, and 13, we know that the combustion effectiveness factor of these char particles must have a minimum value, whose location depends only on N_{sh}—that is, on diffusion resistance in the gas film and in the char layer. Together with our analysis of combustion process resistance of Fushun and Maoming oil shale char particles (Wang and others, 1988), we believe this is caused by the fact that related resistance in the gas film, in the char layer, and at the interface reaction alters in the combustion process.

CONCLUSIONS

1. $N_{sh} > 2$ can be taken as the criterion of the shrinking-core model.

2. The location of the minimum point of the combustion process effectiveness factor cannot exceed one-half the particle radius.

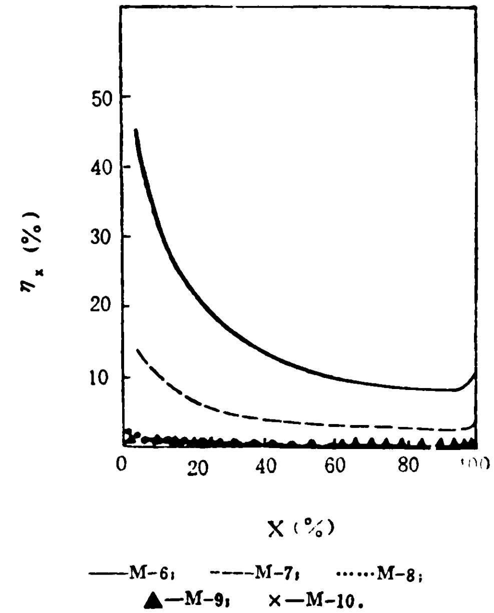


Figure 6. Effect of carbon conversion on effectiveness factor for combustion of Maoming shale char (>600°C).

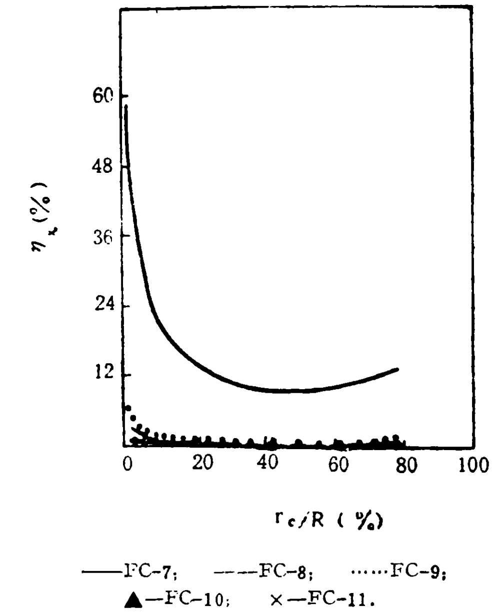


Figure 8. Relation between effectiveness factor and reaction front for combustion of Fushun shale char (>700°C).

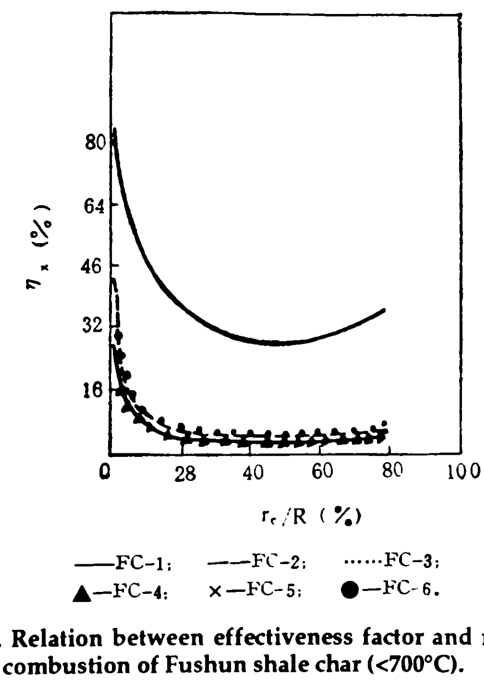


Figure 7. Relation between effectiveness factor and reaction front for combustion of Fushun shale char (<700°C).

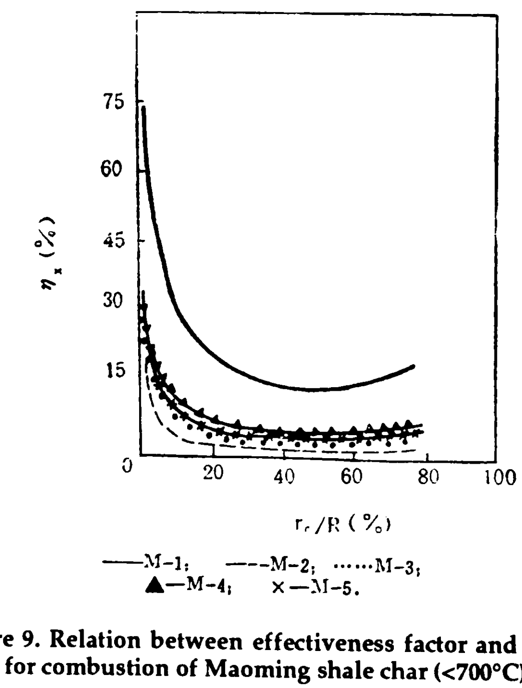


Figure 9. Relation between effectiveness factor and reaction front for combustion of Maoming shale char (<700°C).

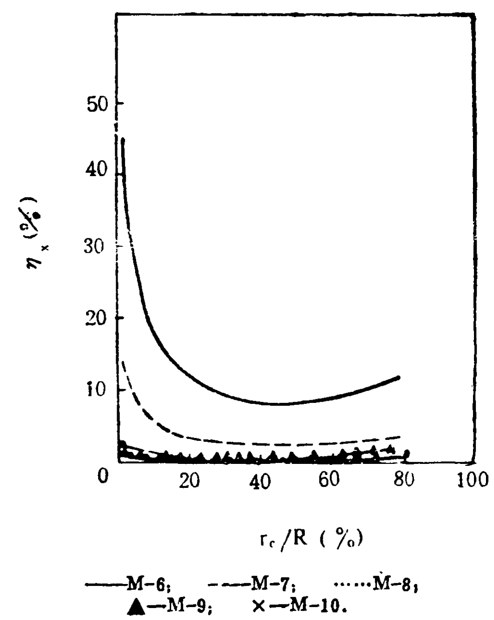


Figure 10. Relation between effectiveness factor and reaction front for combustion of Maoming shale char (>700°C).

3. The combustion process effectiveness factor of Fushun and Maoming oil shale char particles decreases as the conversion increases, which can be classified as a new catalog.

4. The combustion process of Fushun and Maoming oil shale char particles is strongly affected by physical transfer processes.

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REFERENCES

Aris, Rutherford, 1975, The mathematical theory of diffusion and reaction in permeable catalysts: Oxford, Clarendon Press, v. 1.

Carberry, J.J., and Kulkarni, A.A., 1973, Nonisothermal catalytic effectiveness factor for monolith supported catalysts: Journal of Catalysts, v. 31, no. 1, p. 41–50.

Cannon, K.J., and Denbigh, K.G., 1957, Studies on gas-solid reactions, I—The oxidation rates of zinc sulphide: Chemical Engineering Science, v. 6, nos. 4/5, p. 145.

Hou, X.I., ed., and others, 1985, Chinese shale oil industry: Petroleum Industry Press.

Ishida, M., and Wen, C.Y., 1968, Comparison of kinetic and diffusional models for solid-gas reactions: AIChE Journal, v. 14, no. 2, p. 311–317.

Lin, M., 1987: Beijing Graduate School, University of Petroleum, M.S. thesis.

Rester, S., and Aris, R., 1969, Communication on the theory of diffusion and reaction, II—The effect of shape on the effectiveness factor: Chemical Engineering Science, v. 24, no. 4, p. 793–795.

Wang, J.Q., and Wang, X.Q., 1987: Acta Petrolei Sinica (Petroleum Processing Section), v. 3, no. 3, p. 1.

Wang, Xianqing, Lin, Min, Qian, Jialin, and Zhu, Yajia, 1988, A study on the combustion kinetics of Fushun and Maoming shale char particles, *in* Zhu Yajia, ed., Proceedings, International Conference on Oil Shale and Shale Oil, in conjunction with the 21st Oil Shale Symposium: Beijing, China, Chemical Industry Press, p. 495–505.

Wang, X.Q., Lin, M., Qian, J.L., and Zhu, Y.J., 1989: Journal of Fuel Chemistry and Technology, v. 17, no. 2, p. 118–125.

Weisz, P.B., and Hicks, J.S., 1962, The behaviour of porous catalyst particles in view of internal mass and heat diffusion effects: Chemical Engineering Science, v. 17, p. 265–275.

Ye, M.H., and Gu, Q.W., 1986: Physical Chemistry Sinica, v. 2, no. 5.

Yun, N.J., and Ding, F.X., 1985: Acta Petrolei Sinica (Petroleum Processing Section), v. 1, no. 1, p. 25.

Nomenclature

C_{Ac} O_2 concentration in the surface of unreacted core (mol/cm^3)
C_{Ag} O_2 concentration in bulk gas (mol/cm^3)
D_e diffusion parameter in ash layer (cm^2/s)
k_f diffusion parameter in gas film (cm^2/s)
k_g chemical reaction rate constant (cm/s)
n combustion process effectiveness factor
N_c dimensionless group
N_{sh} dimensionless group
R particle radius (cm)
r_c radius of unreacted core (cm)