여러 CO_2-O_2 혼합기체에서 인도산 분말숯의 등온 연소반응

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Combustion Kinetics of Pulverized Indian Coal-Char in Different CO_2-O_2 Mixture Isothermally

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요약. 여러 CO_2-O_2 혼합기체에서 인도산 분말숯의 연소반응실험을 수행하였다. 샘플을 분쇄하여 58 마이크론보다 작은 채로 거르고 질소분위기에서 숯으로 만들었다. CPRI 방갈로에 있는 열분석기 (TGA-50)을 사용해 실험을 하였다. CO_2-O_2 혼합기체는 몰비로 (80-20, 60-40, 40-60, 20-80)을 사용하였다. 활성화에너지 (E) 및 지수앞자리인자 (A)을 통합접근 및 수정된 Arrhenius식을 사용해 계산하였다.

주제어: 연소반응, 인도산 분말숯, CO_2-O_2 혼합기체

ABSTRACT. Experimental work was carried out to study the combustion kinetics of the Indian coal-char in the varying mixture of carbon dioxide-oxygen (CO_2-O_2). The coal sample was pulverized and sieved to less than 58 microns and charred using volatile furnace by passing the nitrogen gas. The experiments were carried out using the Thermo Gravimetric Analyzer (TGA-50) at CPRI, Bangalore, different proportions of (CO_2-O_2) gas was allowed in to the TGA-50 (80-20, 60-40, 40-60, 20-80) mole basis were used to study the combustion kinetics of coal Isothermally, kinetic parameters like Activation energy (E) and the pre-exponential factors (A) are calculated using the unification approach and modified Arrhenius equation.

Keywords: Combustion kinetics, Pulverized Indian coal-char, CO_2-O_2 mixture

INTRODUCTION

Many researchers in the past have studied the combustion kinetics of the coal-chars either by isothermal or non-isothermal analysis,[1-7] the reaction kinetics of coal-chars concerns correlation with char morphology, pore structure (porosity), surface area. Surface area and porosity of the prepared coal-char was determined using BET nitrogen gas adsorption. To estimate the combustion kinetics of coal-char, we need to consider the reactions occurring on surfaces (external and internal) of solid particles. There are different types of models farmed to study the kinetics of coal-chars, one such model is shrinking unreacted core model (SCM).[1,3,5] In this model chemical reaction occurring at the pore surface is the rate controlling step at low temperatures, here reaction starts on the outer surfaces and later ash layer is formed and then the reaction processed inside core of the particle leaving behind the ash or unreacted minerals, hence at any time during the reaction their exit a unreacted core which shrinks

in size during the reaction hence the model named as shrinking unreacted core model.[1,3]

The aim of this paper is to estimate the overall reaction rate, which is the product of conversion factor (f (X)) and intrinsic reaction rate (r_s). The activation energy (E) and pre-exponential factor (A) are determined by a unification approach using Random Pore Model (RPM), for experiments conducted isothermally using Thermogravimetric analyzer (TGA) for different CO_2-O_2 proportion mixtures viz (80-20, 60-40, 40-60, 20-80), were the oxygen concentration was maintained constant for all the cases.

EXPERIMENTAL PROCEDURE

Char preparation and Coal properties

Pulverized coal sample was heated in volatile furnace Leco (U.S.A), in flowing nitrogen gas environment at 950 °C at a rate of 20 liters/min and socked for 60 min, after 60 min the furnace was cooled to room temperature in flowing nitrogen gas environment and later the resulted coal-char was homogenized and stored for combustion studies in TGA. The char and coal samples, were analyzed for proximate, ultimate, particle size shown in *Table* 1

and BET nitrogen surface area, are shown in *Table* 2.

Experimental work

Thermogravimetric analyzer (TGA) used here was TGA-50 model. Different proportions of (CO_2-O_2) gas mixtures were fed to TGA at room temperatures and pressure more than atmospheric pressure (1.1 - 1.2 atm). The pre-mixed and calibrated (CO_2-O_2) mixture cylinders were used for analysis. The oxygen concentration for all the case was maintained constant by mainly fixing the flow rate of the oxygen same for the cases i.e. (10.5 mL/min). Isothermal experiments were carried out with prepared coal-char (15 - 18 mg) in the presence of the (CO_2-O_2) mixtures with constant heating rate 20 °C/min for different temperatures 500, 525, 550, 575 and 600 °C respectively. Flow rate of the gas mixtures were varied by keeping oxygen flow rate constant at 10.5 mL/min.

ISOTHERMAL METHOD FOR EVALUATION OF MODEL AND ARRHENIUS PARAMETERS

A description of isothermal method used for our calculation, was earlier used by[1,9,10,11] with applica-

Table 1. Proximate and Ultimate analysis of coal and char samples

Samples	Proximate Analysis (dry basis), %			Ultimate analysis (dry basis), %					Particle size D (V, 0.9) (microns)
	Volatile Matter	Ash	Fixed Carbon	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen	
Coal-A	25.6	40.6	33.8	42.2	3.4	1.3	0.31	12.19	33.2
Char-A	1.7	62	36.3	37.2	0.22	0.1	0.28	0.20	26.0

Table 2. BET surface area analysis of char samples

Samples	Porosity, %	External surface area, m^2/m^3	Total pore length, m/m^3	Structural parameter (Ψ)
Char-A	43.3	8.0	11.6	1.30

Table 3. Activation energy and lumped Pre exponential factor for different gas environment

Samples	Activation energy, KJ/Kmol				Lumped Pre-exponential factor, (1/min) pa^{-n}			
	CO_2-O_2 in Mol.Vol.Percent				CO_2-O_2 in Mol.Vol.Percent			
	80 - 20	60 - 40	40 - 60	20 - 80	80 - 20	60 - 40	40 - 60	20 - 80
Char-A	119	102	87	80	2.7×10^4	3.9×10^3	523.0	237.0

tion to char combustion with mixture of (N_2-CO_2) or pure CO_2 using Random pore model (RPM). The overall reaction rate or rate of the reaction incorporating the conversion factor f (X) is given by

$$\frac{dX}{dt} = r_s(T, P_{O_2})f(X) \qquad (1)$$

Were, r_s is the intrinsic reaction rate (m/min). From RPM, conversion in terms of dimension less time is given by[9,10]

$$X = 1 - \exp\left\{-\tau\left(1 + \frac{\tau.\psi}{4}\right)\right\} \qquad (2)$$

on differentiating equation (2), we get

$$\frac{dX}{d\tau} = (1-X)\sqrt{1 - \psi \ln(1-X)} \qquad (3)$$

After integrating equation (3), the time constant

$$\tau = \frac{2}{\psi}\left[\sqrt{1 - \psi \ln(1-X)} - 1\right] \qquad (4)$$

Time factor, $\quad \dfrac{\tau}{t} = t_f = \dfrac{r_s S_0}{1 - \varepsilon_0} \qquad (5)$

Were, $\quad r_s = K P_{O_2}{}^n \qquad (6)$

But according to Arrhenius equation the reaction rate constant 'K' is given by

$$K = A\exp(-E/RT) \qquad (7)$$

Substituting equation (7) in to equation (6)

$$r_s = A\exp(-E/RT)P_{O_2}{}^n \qquad (8)$$

Substituting equation (8) in to equation (5)

$$t_f = \left(\frac{AS_0}{1 - \varepsilon_0}\right)P_{O_2}{}^n \exp(-E/RT)$$

In the above equation $\{(AS_0)/(1-\varepsilon_0)\} = K_0$. Were K_0 is the lumped pre exponential factor.

There fore, $\quad t_f = K_0 P_{O_2}{}^n \exp(-E/RT) \qquad (9)$

Taking logarithm of equation (9)

$$\ln t_f = \ln K_0 + n\ln P_{O2} - (E/RT) \qquad (10)$$

Partial pressure of oxygen (P_{O2}) is constant for a particular temperature. The order of the reaction can be obtained by plotting $\ln t_f$ *vs.* $\ln P_{O2}$. Further, plotting $\ln t_f$ *vs.* 1/T, the E and K_0 will be obtained from the slope and intercept respectively.

Replace $d\tau$ with dt in equation (2)

$$\frac{dX}{dt} = K_o^! P_{o2}^n \exp(-E/RT)f(X) \qquad (11)$$

Where: $f(X) = (1-X)\sqrt{1 - \psi \ln(1-X)}$ for RPM model.

RESULTS AND DISCUSSION

Property of coal char

Char prepared from volatile furnace was subjected to proximate (TGA-600, Leco), ultimate (CHNS-2000, Leco), particle size (Malvern particle size analyser) and BET nitrogen adsorption analysis (Micrometrics GEMINI 2360). The results are given in *Table* 1.

The particle size of parental coal and its respective char was analysed using the Master sizer X (Malvern make), which works on the principle of laser ensemble light scattering technique.

A pore size distribution data were obtained from BET analysis using BJH approach this measurement was uniform and repeatable results were obtained, using this data we plotted a graph of pore radius against the pore volume is shown to get 2nd order polynomial equation of pore volume in terms of pore radius which up on the integration will give the porosity ε_o, External surface area per unit volume S_o and pore length per unit volume L_o using the following relation given by Bhatia.[9,10]

$$\varepsilon_0 = \int_0^\infty V(r)dr \tag{12}$$

$$S_0 = 2\int_0^\infty \left(\frac{V(r)}{r}\right)dr \tag{13}$$

$$L_0 = \pi\int_0^\infty \left(\frac{V(r)}{r^2}\right)dr \tag{14}$$

Conformation of model and determination of reactivity constants (isothermally)

The experiment was carried out with the char prepared in volatile furnace from the data obtained conversion on (ash dry free basis) as the ash is the minerals left out and will not take part in the combustion was calculated. Conversion X is calculated by

$$X = \frac{W - W_0}{W - W_\infty} \tag{15}$$

The equation (11) was used for validating the shrinking core unreacted model (SCM) and the Random pore model (RPM), from BET results we can observe that the porosity values of the char sample was very high around 45%. Hence the SCM is not suitable model to calculate kinetics of the char because the SCM model does not take in to the account of the structural properties of the char, the reactivity of the char is confined to availability of the surface area. i.e. initially the pore surface area will grow therefore the rate of reaction will increase but latter due to the overlapping of growing surfaces will decrease the rate of reactions, this concept is very well explained in the 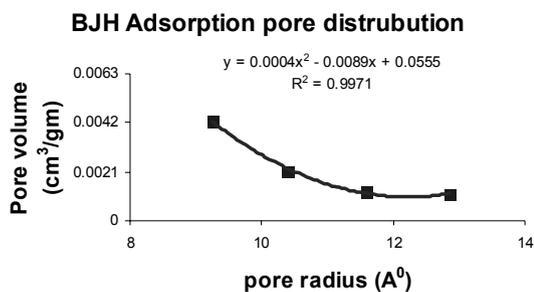RPM, therefore the RPM is used to calculate the kinetic parameters. The complete conversion was not able to be at temperatures 500 and 525 ^{o}C, hence the Arrhenius plot was plotted for 50% conversion. We have got different activation energy (E), lumped pre-exponential factor (K_0) and pre exponential factor (A) for different (CO_2-O_2) mixtures which are in range with earlier works.

CONCLUSION

The combustion profiles of the char in CO_2-O_2 mixtures for temperatures 600, 575 and 550 ^{o}C showed the influence of CO_2 concentration over the reactivity. The overall reactivity increases when the concentration of CO_2 decreases in the CO_2-O_2 mixture for the constant O_2 concentration which indicates that the CO_2 have some cooling effect on the reactivity of char, because of which the differential weight loss with respect to time is slowed as concentration of CO_2 is increased even after maintaining same amount of O_2 concentration as shown in weight loss patterns at different temperatures in *Fig.* 2, 3 and 4.

Here we have used a different approach to determine the Arrhenius parameters like activation energy (E) and lumped Pre exponential factor (K_0) experimentally which are very important inputs for numerical analysis of burning profiles of coal-chars in different (CO_2-O_2) gas-environments using Computational Fluid Dynamics (CFD). The E and K_0 values were determined using the modified Arrhenius equation (10), were the partial pressure of the O_2 is constant through out the experiment for particular temperature, therefore lnP_{O_2} term in the

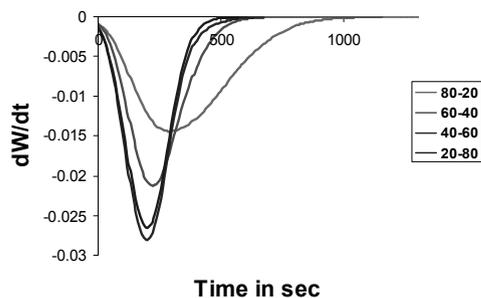Fig. 1. BJH adsorption pore distribution curve for char-A.

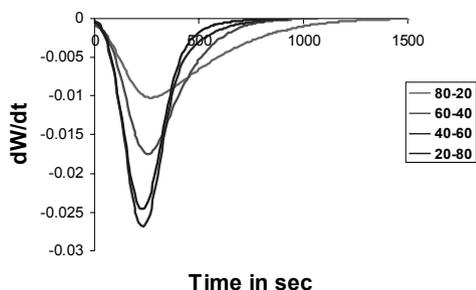Fig. 2. Rate of weight loss with time for char-A at 600 ^{o}C.

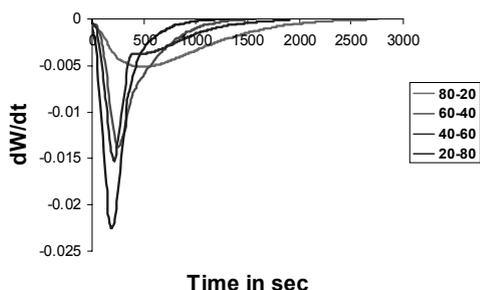*Fig*. 3. Rate of weight loss with time for char-A at 575 °C.

Fig. 4. Rate of weight loss with time for char-A at 550 °C.

equation (10) will be constant for a particular temperature, if we plot the graph of $\ln t_f$ versus $1/T$ the negative slope of the line give the Activation energy (E) in terms of KJ/mole and intercept will give the lumped pre-exponential factor (K_0) in terms of (1/min) pa^{-n}. The E and K_0 values decreases as the concentration of CO_2 decreases which means as the peaking temperature comes down the activation energy required for the reaction to initiate decreases. The values experimentally determined are in range with the previous experimental results of other researchers.
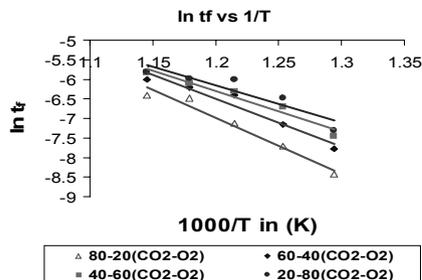

Fig. 5. Determination of activation energies and lumped pre-exponential factors for char-A for 50% conversion.

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Nomenclature			
E	Activation energy, kJ/ mole	t_f	Time factor, 1/min.
f(X)	Conversion factor	V	Pore volume adsorbed in m³/g
A	Pre exponential factor, (m/min) (Pa)$^{-n}$.	W	Weight of char in mg at time t sec
K	Reactivity or reaction rate constant, (m/min) (Pa)$^{-n}$	W_0	Initial weight of char in mg
K_0	Lumped pre-exponential factor, (1/min) (Pa)$^{-n}$.	$W\infty$	Weight of non-combustible matter after complete combustion in mg.
n	Order of reaction.	X	Fractional conversion of carbon
L_o	Total pore length per unit volume, m/m³.	t	Time, sec
PO_2	Partial pressure of reacting gas, kPa.	T	Temperature, K
R	Universal gas constant, 8.213 kJ/mol K.	T_o	Initial Temperature, K
r_s	Intrinsic reaction rate, m/min	ε_o	Initial porosity
r	Pore radius in A^0	ρ	Density of solid, g/m3
So	External pore surface area, m2/m³.	ψ	Structural parameter.
		τ	Dimension less time in case RPM