

Comparative Studies on the Combustion Kinetics of Chars Prepared from Brown and Bituminous Coals under Air (O₂/N₂) and Oxy-fuel (O₂/CO₂) Conditions

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This paper deals with the application of a solid-gas reaction model which can describe the combustion and gasification mechanism for air (O₂/N₂) and oxy-fuel (O₂/CO₂) conditions. Loy Yang brown coal was used as a sample after pyrolysis, together with Newlands coal as bituminous coal for comparison of coal ranks. By carrying out the thermogravimetric analysis (TGA) run under non-isothermal conditions, chemical reaction rates of partial oxidation reaction and gasification reaction were estimated. Heat and mass transfer between the single pulverized char particle and gas were numerically simulated, thus, overall reaction rate including mass transfer rate, chemical reaction rate could be evaluated. In the low temperature region, the reaction rate is mainly controlled by the chemical reaction, on the other hand, it becomes dominated by mass transfer, (diffusion as well as convection effects), in high temperature region. Using this solid-gas reaction model, burn-off time of each char was also estimated under the various conditions, i.e., air (5% O₂/N₂) and oxy-fuel (5% O₂/CO₂) conditions with consideration of absence and presence of CO₂ gasification reaction effect.

1. Introduction

Although a future energy mix of fossil fuels and renewable energies is considered as one of the pragmatic scenarios, there are still restrictions in that there are limited fossil fuel deposits and undeveloped technologies for extraction and power generation. Coal, especially low-rank coals, which are particularly abundant, is considered to be included in the future energy mix. However, coal has many disadvantages, for example, firing of coal results in emissions that contain many contaminants and especially greenhouse gases, CO₂.

CO₂ generated from coal combustion in air comprises approximately 15% of the flue gas, and it would not be economically advantageous to separate this CO₂ from flue gas because of its relatively low concentration. Pure oxygen can be used as an oxidant, however, it causes a high adiabatic flame temperature. To address these problems, a new method has been developed, so called oxy-fuel combustion. Unlike conventional boilers, during oxy-fuel combustion, a combination of highly pure oxygen, nearly 95%, and recycled flue gas is used to control the flame temperature and to make up the missing N₂. In addition, the main components in oxy-fuel-generated flue gas are CO₂ and steam, and the concentration of CO₂ can be as high as 98%¹⁾.

Therefore, there is a need to evaluate char-O₂ as well as char-CO₂ reaction rates in the oxy-fuel system by comparison with that of combustion in usual boilers operated

using O₂/N₂. Usually, the activation of char with oxidant, O₂ or CO₂, is heterogeneous gas-char reaction and pore structure and surface area of the char particles are changing with the reaction. These structural variations and other phenomena such as mass transfer, pore diffusion, and chemical reaction have to be considered simultaneously in the kinetic modeling of the reaction²⁾. In the case of char-O₂ reaction, for particles below 50 μm, the reaction rate is determined by the slowest rate of the reaction step, whereas for particles larger than 100 μm the diffusion limits the combustion rates. For the char-CO₂ reaction, for char particle sizes (< 300 μm) and lower temperature (< 1,000 °C), gasification rate is normally controlled by the chemical reaction rate and occurs nearly uniformly throughout the interior surfaces of the char particles^{1,3-5)}. However, for smaller pulverized char particles (< 100 μm) at higher temperatures (> 1,000 °C) pore diffusion becomes important⁶⁻⁷⁾.

The motivation for this study is to focus on comparing the partial oxidation reaction rate, gasification reaction rate and mass transfer rate of oxygen in N₂ and CO₂ according to the presence or absence of CO₂ gasification.

2. Experimental

Loy Yang brown coal and Newlands bituminous coal, for comparison of coal ranks, were used as samples and the proximate and ultimate analyses of these samples are shown in Table 1.

Table 1 Proximate and ultimate analyses of samples

Proximate analysis (wt. %)				
Sample	M(db)	Ash(db)	VM(db)	FC(db)
Loy Yang	-	1.16	52.25	46.59
Newlands	-	15.14	28.20	56.67

Ultimate analysis(wt. % daf)					
Sample	C	H	O	N	S
Loy Yang	70.85	4.56	23.69	0.63	0.26
Newlands	84.63	4.69	8.69	1.70	0.29

M: Moisture, VM: Volatile material, FC: Fixed carbon, db: dry basis, daf: dry ash free.

Although, various types of apparatus have been used for the kinetic study of gasification reaction, TGA(Thermogravimetry analysis) has been most widely used because of its advantages such as rapid analysis, cost effectiveness, and applicability of various parameters to the observed data. Hence this study was also carried out by TG-DTA (TG-DTA 2000SA, Bruker AXS) for the estimation of heterogeneous chemical reaction rate of char-O₂ and char-CO₂ by using Eq. (1).

$$\frac{dX}{dt} = k_0 \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot (1-X)^n \quad (1)$$

where, X is the conversion rate of char particle, *i.e.*, $1-m/m_i$, k_0 is the pre-exponential factor, E_a is the activation energy, R is the gas constant, T is the temperature, n is the reaction order.

Table 2 Experimental conditions

Parameter	Condition
Char particle size	125~150 μm
Gas concentration	21% O ₂ in N ₂ (Air) 100% CO ₂
Sample mass	0.5 mg
Heating rate	50 K/min
Maximum temperature	1) 1,473 K for air atmosphere 2) 1,873 K for CO ₂ atmosphere

3. Numerical simulation

3.1 Reaction models for char partial oxidation and gasification

The most widely used heterogeneous partial oxidation reaction and gasification reaction are based on a simple global reactions.



These equations can be written in Arrhenius form as follows:

$$r_c = k_0 \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot m_p \cdot p_{\text{oxi}} \quad (2)$$

where, r_c is the chemical reaction rate, m_p is the particle mass, P_{oxi} is the partial pressure of oxidant⁸⁾.

The mass transfer rate, r_c^M , of oxidant to the surface of char particle is estimated from Mulcahy's models based on some assumptions⁹⁾.

$$r_c^M \cong \left(\frac{D_{\text{Oxi},0}}{0.5d_p}\right) \left(\frac{\tilde{n}_0}{M}\right) \left(\frac{T}{T_0}\right)^{0.75} \left[\frac{-\ln(1-\gamma f_{v,\text{Oxi}})}{\gamma}\right] \cdot S_p \cdot \frac{M_C}{\nu_{\text{Oxi}}} \quad (3)$$

where, $D_{\text{Oxi},0}$ is the diffusion coefficient of oxidant at the standard conditions, d_p is the particle diameter, ρ_0 is gas density around the particle, \bar{M} is the averaged gas molecular weight, T, T_0 are gas temperature and its standard temperature, $f_{v,\text{Oxi}}$ is mole fraction of oxidant, S_p is surface area of particle, M_C is molecular weight of char, and ν_{Oxi} is stoichiometric coefficient of the oxidant. These models have been previously validated by Matsushita et. al.¹⁰⁾

In addition, γ is non-dimensional parameter which can describe the convection as well as diffusion behavior of CO, which is the product of reaction (R-2). In the case of combustion this parameter is equal to -1, whereas, in the case of CO₂-gasification it varies with volume fraction of oxidant¹¹⁾.

Using the chemical reaction rate, r_c , together with the mass transfer rate, r_c^M , it is possible to determine the overall reaction rate, r_o , as follows:

$$\frac{1}{r_o} = \frac{1}{r_c} + \frac{1}{r_c^M} \quad (4)$$

3.2 Governing equation

To estimate the burn-off time, heat and mass transfer around a single char particle were considered as a balance equation. Variation of char particle temperature during the partial oxidation reaction has been simulated under the assumption that the total heat transfer is completely controlled by three terms, convective heat transfer, Q_{conv} , radiation heat transfer, Q_{rad} , and reaction heat transfer, Q_{reac} :

$$Q_{\text{Total}} = Q_{\text{conv}} + Q_{\text{rad}} + Q_{\text{reac}};$$

$$m_p C_p \frac{dT_p}{dt} = h(T_g - T_p) \cdot A_p + \varepsilon \sigma (T_w^4 - T_p^4) \cdot A_p + \sum \xi \Delta H \cdot r_o \quad (5)$$

where, m_p is the mass of char particle, C_p is the specific heat, t is reaction time, h is convective heat transfer coefficient, T_p and T_g are temperature of char particle and gas temperature, respectively, A_p is the surface area of char particle, ε is the emissivity of char particle, σ is the Stefan-Boltzmann's constant, ξ is the contribution ratio of reaction heat, (0.5), ΔH is the formation heat of prod-

uct, r_o is the overall reaction rate.

In addition, the char consumption rate, or the reduction rate of char particle mass, can be expressed as:

$$\frac{dm_p}{dt} = -r_{O_2}^{O_2} - r_{CO_2}^{CO_2} \quad (6)$$

where, $r_{O_2}^{O_2}$ and $r_{CO_2}^{CO_2}$ are the overall reaction rate of partial oxidation reaction of char with oxygen and carbon dioxide as an oxidant, respectively.

As mentioned in previous section, to estimate the burn-off time, the numerical simulation was limited to the chemical and mass transfer rate under the following additional assumptions.

1. The shape of char particle is spherical.
2. There is no temperature distribution inside the char particle.
3. There is no reaction in pores of the particle, or the particle is assumed as non-porous spherical particle.
4. The temperatures of gases and the wall of the gasifier are constant.
5. The char is fully devolatilized, thus, there is no volatile matters in the particle.
6. The contribution percentage of reaction heat, ζ , generated on the particle surface is set as 50%, in other words, the heat generated by the reaction is equally distributed to solid and gas phases.

It can be seen that there will be some errors in calculation due to the above assumptions, in particular, the oversimplification of the particle shape. Despite these shortcomings, the application of this solid-gas reaction model remains applicable due to the dominance of surface reactions over reactions in the pores of the char particles.

To evaluate the influence of oxidant types (O₂ and CO₂) on the partial oxidation characteristics, and to estimate the behaviors of O₂ in different bath gases such as N₂ and CO₂, the calculations were carried out under the conditions shown in Table 3.

Table 3 The calculation conditions

Parameter	Condition
Char particle diameter	150 μ m
O ₂ concentration in N ₂	5% / 95%
O ₂ concentration in CO ₂ (Gasification reaction effect was ignored)	5% / 95%
O ₂ concentration in CO ₂	5% / 95%
Initial particle temperature	300 K
Gas temperature	a) 1,500 K
Wall temperature	a) 1,200 K

4. Results and discussion

4.1 TG results and evaluation for estimating the chemical reaction rate

Using Eq. (1) from the results of TG-DTA, pre-exponential factor, k_0 , and the activation energy, E_a were ob-

tained. Note that the chemical reaction was assumed to be the first-order reaction.

In the case of partial oxidation reaction in N₂, for Loy Yang char, since it appeared that the conversion rate, X was affected by the mass transfer of oxidant at $X > 0.4$, of the data obtained at $X = 0.15-0.4$ ($T = 760-775$ K) was designated as the chemical reaction range for fitting. For Newlands char, the conversion rate appeared to be unaffected by the mass transfer over the entire range of conversion, so the whole data at $X = 0.0-1.0$ ($T = 814-1,105$ K) were used for the numerical fitting. In the case of gasification reaction in CO₂, these ranges were set as 0.02-0.98 ($T = 912-1,186$ K) and 0.2-0.6 ($T = 1,102-1,180$ K) for Loy Yang char and Newlands char, respectively. Fig. 1 shows the Arrhenius plots fitted according to the method mentioned above and Table 4. shows k_0 and E_a for each coal.

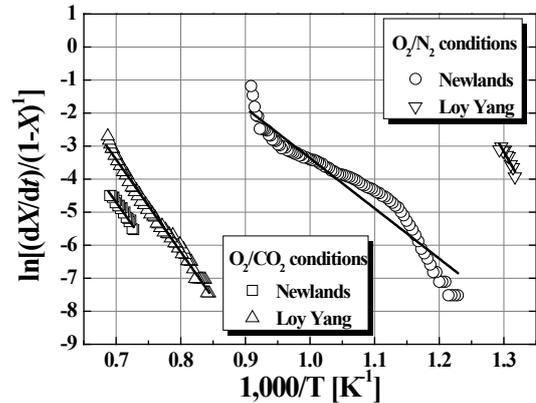


Fig. 1 Arrhenius plots for each of the coals under air and oxy-fuel conditions.

Table 4 Estimated Arrhenius parameters for reaction rate

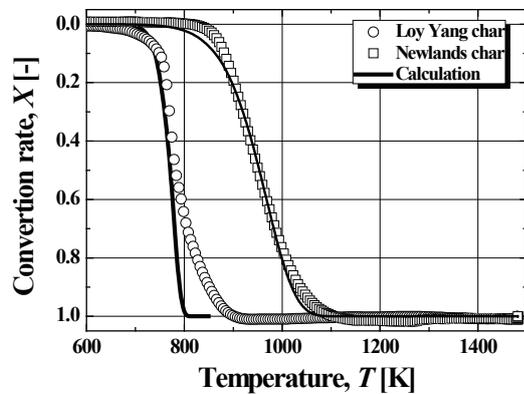
Condition	Sample	k_0 [sec ⁻¹]	E [J/mol]
Char-O ₂	Loy Yang	1.07×10^{18}	2.86×10^5
	Newlands	2.17×10^5	1.30×10^5
Char-CO ₂	Loy Yang	1.06×10^7	2.33×10^5
	Newlands	2.15×10^6	2.29×10^5

Results of partial oxidation reaction carried out by TG for two coals were examined as shown in Fig 2 (a) with dotted lines. Reaction initiation temperature of Loy Yang char is 150 °C lower than that of Newlands char, and the higher slope of reaction rate for Loy Yang char is observed in comparison to that for Newlands char. Above tendencies show that the reactivity of Loy Yang coal as brown coal is larger than that of Newlands bituminous coal. It can be seen that there is difference between two partial oxidation processes, Loy Yang char has two stages: chemically rate determining step and mass transfer rate determining step, which can be verified by

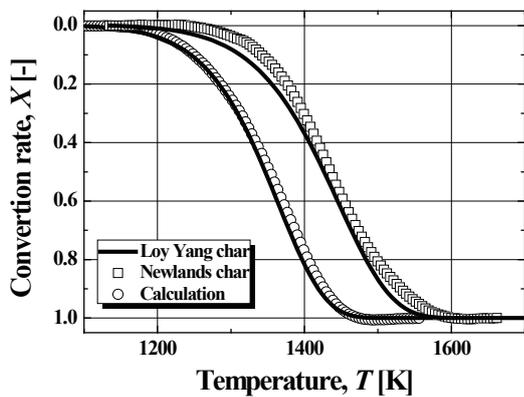
the change of slope around at $X = 0.4$. On the other hand, for Newlands char, the rate of change in weight loss, *i.e.*, change of the slope, is almost the same from initiation to completion of the reaction, which means that there is only one stage, chemically rate determining step.

The graphs drawn with solid line are analyzed data using factors described in Table 4 and show good agreement with TG results. Note that the chemical reaction is assumed to be a first-order reaction and analyzed.

On the other hand, in the case of CO_2 gasification reaction, there is no rapid slope change region in the progress of reaction regardless of coal ranks as shown in Fig 2 (b).



(a)



(b)

Fig. 2 Comparison of TG results and analyzed data between (a) partial oxidation and (b) gasification reaction.

4.2 Calculation results and discussion

Chemical reaction rate denoted by Eq. (2), mass transfer rate of oxidant to char particle surface by Eq. (3) and their overall reaction rate by Eq. (4) for Loy Yang coal and Newlands coal in the air and oxy-fuel conditions are shown in Fig. 3. Since the same chemical reaction model is employed for the air and oxy-fuel conditions, there are

no differences in the oxidation and gasification reaction rate of each coal. The difference of overall reaction rate of oxygen, $r_{\text{O}}^{\text{O}_2}$, in N_2 (air) and CO_2 (oxy-fuel) conditions is attributed only to the difference of the mass transfer rate, more exactly due to the difference in γ and D values, or model parameter and diffusion coefficient in Eq.(3). Note that being evaluated the reaction rate of oxygen, r^{O_2} , in CO_2 , the gasification reaction was ignored to focus on the comparison of oxygen behavior in different atmosphere gases.

The transition from chemical to mass transfer control region for Loy Yang char begins at around 800 K, whereas for Newlands char it begins at 1,200 K, indicating that the reactivity of Loy Yang char is greater than that of Newlands char. These results are consistent with the weight loss results.

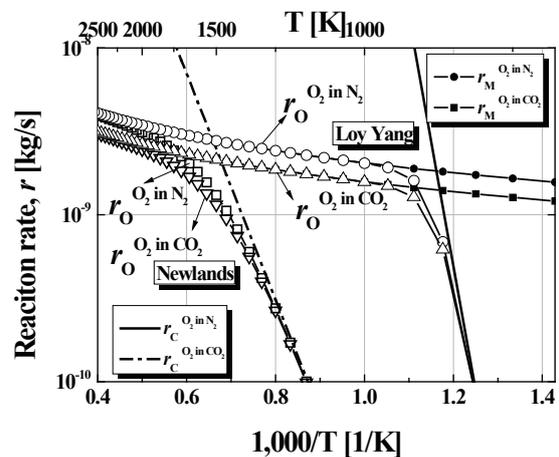


Fig. 3 Comparison of partial oxidation rates in 5% O_2/N_2 with those in 5% O_2/CO_2 for Loy Yang char and Newlands char: It was assumed that there was no CO_2 gasification reaction effect in 5% O_2/CO_2 conditions.

Fig. 4 shows the particle weight loss as well as char particle temperature with elapsed time for two coals calculated under conditions shown in Table. 3. Time required to achieve maximum temperature is about 0.05 s. As mentioned above, the transition temperature from chemical to mass transfer control region of r^{O_2} are 800 K and 1,200 K for Loy Yang and Newlands char, respectively, and for partial oxidation reaction by oxygen both in N_2 , CO_2 conditions, the char particle temperature, T_p , reaches above these transition temperature ranges, thus the initiation of weight decrease could be observed.

The difference in weight decrease rate in (a) and (b) in Fig. 4 is mainly attributed to the lower diffusivity of O_2 in CO_2 in comparison to the diffusivity in N_2 which can affect the transport of O_2 to the surface of the char particle leading to the reduced partial oxidation reaction rate.

As evaluated in previous section, in Fig. 4, because the char particle temperature, T_p is an important factor that

determines the reaction rate, there was a need to estimate the energy balance of a single char particle as shown in Fig 5.

Total energy balance was achieved around 0.05 s after heating up according to the setting values, especially gas temperature, T_g , and wall temperature, T_w . In the initiation step, the heating sources were convection and radiation, however, as reaction proceeds reaction heat became more important.

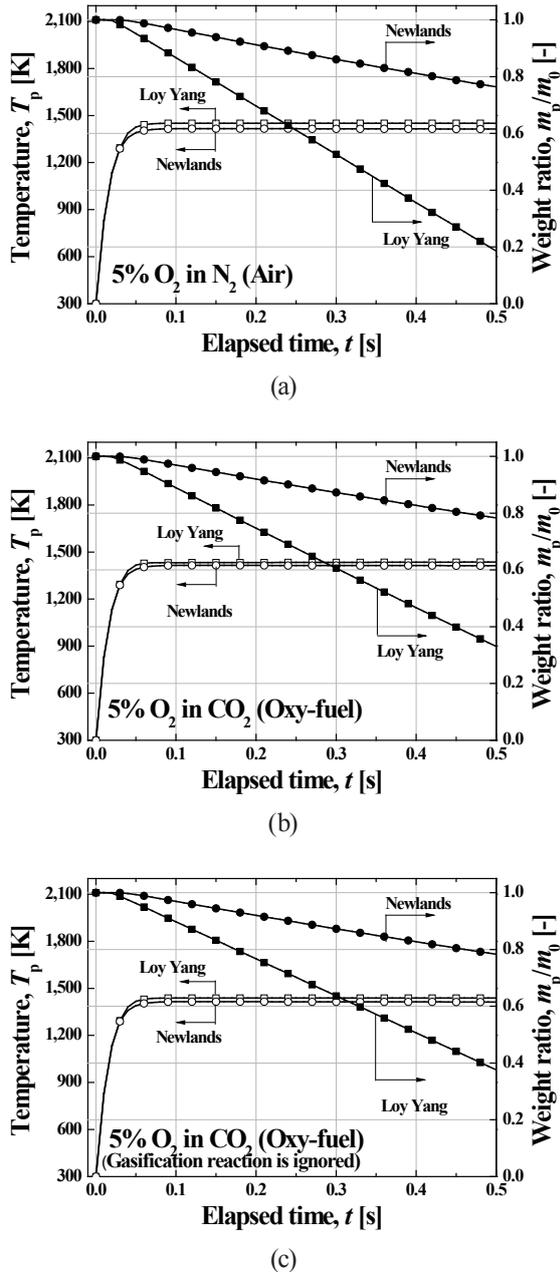


Fig. 4 Weight losses and particle temperatures with elapsed time for Loy Yang char and Newlands char: (a) 5% O_2 in N_2 (air condition), (b) 5% O_2 in CO_2 (oxy-fuel conditions regardless of gasification reaction), (c) 5% O_2 in CO_2 (oxy-fuel condition).

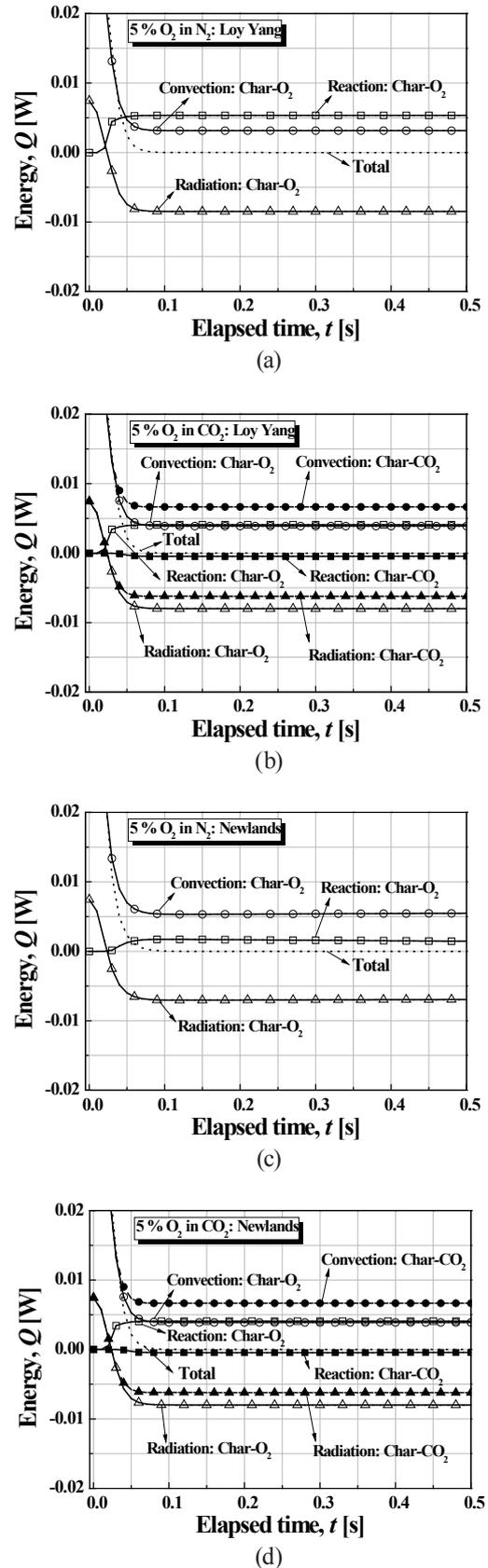


Fig. 5 Contributions of energies and their balances under Char- O_2/N_2 , and Char- O_2/CO_2 , Char- CO_2 conditions for each coal: (a), (b) Loy Yang char, (c), (d) Newlands char.

Especially outstanding differences in reaction heat were revealed between partial oxidation reaction, char-O₂/CO₂ and gasification reaction, char-CO₂, as shown in Fig. 5 (b), (d). This difference was mainly due to the endothermic gasification reaction leading to the reduction of char particle temperature.

For Loy Yang char, when compared the reaction heat of char-O₂/N₂ with that of char-O₂/CO₂ in Fig. 5 (a), (b), the variation of reaction heat is also noticeable. This is attributed to the difference of diffusivity, as it were, the larger diffusivity of O₂ in N₂ in comparison to CO₂ causes comparatively higher mass transfer rate of oxidant to the surface of char particle, and therefore increases the reaction rate. On the other hand, this tendency was not as significant for Newlands char ((c), (d) in Fig. 5) when compared to that of Loy Yang char. In addition, the difference in reaction heat of char-O₂/N₂ between Loy Yang char and Newlands char is significant and the reaction rate of Loy Yang char is higher than that of Newlands char in both cases, partial oxidation and gasification, indicating that apart from the differences in burning conditions, the coal rank may be an important factor in reactivity and this is consistent with the results of burn-off time.

Another aim of this study is to derive the burn-off time along with the variation of burning conditions, which leads to find out the difference in air and oxy-fuel conditions. The burn-off times of two coals were thus estimated and depicted in Fig. 6.

The burn-off times of Loy Yang char are about 8-10 times shorter than those of Newlands char. Due to the difference in diffusivities of O₂ in N₂ and in CO₂, the burn-off times were also slightly affected as shown in the cases of Char-O₂/N₂ and Char-O₂/CO₂ without consideration of effect of gasification reaction.

Although it may appear that the burn-off time in char-O₂/CO₂ should be shorter in comparison to that of char-O₂/N₂ due to the synergy effect between char-O₂ and char-CO₂ separately, the effect of combining the two reactions increases the burn-off time due to the endothermic gasification reaction as shown in Fig. 6.

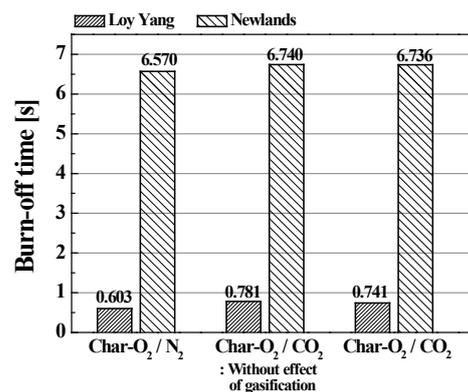


Fig. 6 Comparison of burn-off time between Loy Yang char and Newlands char: (Char-O₂/N₂) vs (Char-O₂/CO₂ regardless of gasification reaction) vs (Char-O₂/CO₂).

5. Conclusions

Within the limits of the current experimental conditions, the following conclusions were made:

1. The transition from chemical to mass transfer control region for Loy Yang char begins at approximately 800 K, whereas for Newlands char it begins at 1,200 K, indicating that the reactivity of Loy Yang char is greater than that of Newlands char.
2. The overall reaction rate of carbon dioxide, $r_o^{CO_2}$, under N₂ is much slower than that of oxygen, $r_o^{O_2}$, under the same conditions due to the difference in the mass transfer rate, more exactly, because of the difference in D , γ values, i.e., diffusion coefficient and model parameter.
3. The most dominant factor affecting the particle temperature which determines the reaction rate ultimately is reaction heat. Although it may appear that the overall reaction rate in char-O₂/CO₂ should be faster than in char-O₂/N₂ by virtue of char-CO₂ gasification reaction, the effect of combining the two reactions decrease the burn-off time due to the endothermic gasification reaction.

Nomenclature

A_p	surface area	[m ²]
C_p	specific heat	[J/(kg K)]
d	diameter	[m]
D	diffusion coefficient	[m ² /s]
E_0	activation energy	J/mol K
f	fraction	[-]
H	formation heat	
k_0	pre-exponential factor	[1/s]
\bar{M}	average molecular weight	[kg/kmol]
m	mass	[kg]
n	reaction order	[-]
P	partial pressure	[atm]
R	universal gas constant	[J/mol K]
r	reaction rate	[kg/s]
S	surface area	[m ²]
t	reaction time	[s]
T	temperature	[K]
X	conversion rate of char particle, (1- m/m_i)	[-]
Q	heat	[W]

Greek symbols

ν	stoichiometric coefficient	[-]
ρ	gas density	[kg/m ³]
γ	non-dimensional parameter	
ε	emissivity	
σ	Stefan-Boltzmann's constant	
ζ	the contribution ratio of reaction heat	
Δ	the difference between reactant and product	

Subscripts

con	convective
g	gas
m	mass
M	mass transfer
o	oxidant
p	char particle
rad	radiation
reac	reaction
Total	sum of items
v	mole
0	standard condition

References

- 1) M. F. Irfan, M. R. Usman, *Energy*, **36**, 12 (2011).
- 2) J. H. Zou, Z. J. Zhou, F. C. Wang, W. Zhang, Z. H. Dai, H. F. Liu, Z. H. Yu, *Chem. Eng. Proc.: Process Intensification*, **46**, 630 (2007).
- 3) X.-Z. Sha, Y.-G. Chen, J. Cao, Y. M. Yang, D. Q. Ren, *Fuel*, **69**, 656 (1990).
- 4) L. Shufen, S. Ruizheng, *Fuel*, **73**, 413 (1994).
- 5) C.-Y. Wen, S. Dutta, in *Coal conversion technology*, eds, by C.-Y. Wen, E. S. Lee, Addison-Wesley, New York, p. 57 (1979).
- 6) G.-su Liu, A. G. Tate, G. W. Bryant, T. F. Wall, *Fuel*, **79**, 1145 (2000).
- 7) M. F. Irfan, M. R. Usman, K. Kusakabe, *Energy*, **36**, 12 (2011).
- 8) M. A. Field, *Combust. Flame*, **13**, 237 (1969).
- 9) M. F. R. Mulcahy, I. W. Smith, *Rev. Pure and Appl. Chem.*, **19**, 81 (1969).
- 10) Y. Matsushita, K. Yoshida, H. Aoki, T. Miura, *Proc. 4th ECM* (2009).
- 11) H.-S. Kim, Y. Matsushita et al, *Kagaku Kogaku Ronbun* (2012). Under review.