Research Report

Introduction

Concerns over the role of greenhouse gases in forcing global warming have led to international agreements that have set targets for controlling carbon dioxide emissions. Achieving these goals will require emissions trading, increasing energy efficiency, fuel substitution, and changes in combustion practice. Coal is an abundant, low cost fuel but with a high ratio of carbon to hydrogen, making control of CO₂ a major concern for the future use of coal. As stationary sources emitting large amounts of CO₂, pulverized coal fired power stations could be the best candidates to install CO₂ capture system. In lieu of our growing energy demands, carbon sequestration provides an alternative to sharply reducing coal use. Carbon sequestration can be defined as the capture and secured storage of the carbon that is emitted as a result of human activities as well as the carbon that is already present in the atmosphere. However, it is necessary that the concentration of CO₂ in the gas or liquid stream be more than 90% before it can be injected into the oceans or deep underground geological formations.

The carbon-CO₂ reaction is of great importance in coal gasifiers and in numerous industrial operations hence this gasification process has been examined extensively by many investigators. Turkdogan and Vinters reported the effect of CO₂ concentration on the carbon-CO₂ reaction rate. The reaction rate of the C-CO₂ reaction with respect to CO₂ concentration is approximately first order at low pressures (pressures much below atmospheric) but approaches zeroth order at high pressures (pressures above 15 atm). The carbon-O₂ is also important in overall gasification scheme because the reaction is rapid even with chars, exothermic and not limited by equilibrium. Thus some char is reacted with O₂ to produce the heat and temperature required to drive the carbon reaction. Moreover, prior to or concurrent with the other reactions in a gasifier, pyrolysis of coal takes place. As the behavior of pyrolysis is not yet properly established but however, it is known that the rate of pyrolysis and the amount and composition of volatile products from a given sample of coal or char depends upon several factors such as heating rate, final decomposition temperature attained, vapor residence time, the environment under which the pyrolysis takes place, pressure coal particle size and coal type. The char-CO₂ reaction, after the pyrolysis reaction is completed, takes place on the char surface and is essentially a carbon-CO₂ reaction. As the later starting only after the former stage is essentially completed and as the pyrolysis process is completed at high temperature so it is better to gasify the coal at oxy-fuel combustion conditions by which the internal surface area increases markedly.

Oxy-fuel combustion technology could be successfully used to retrofit existing coal fired power plants or alternatively be used to design and build new coal fired power plants with almost zero emissions. In a recent review, oxy-fuel combustion technology for coal fired power generation has been described in detail and demonstrated to be a cost effective method of CO₂ capture. However differences in thermal properties of N₂ and CO₂ make oxy-fuel combustion quite different from conventional air combustion. Buhre also reported that the presence of CO₂ in high concentrations during oxy-fuel combustion affects the heat transfer, flame ignition, coal burn out, emissions, and ash properties. Comparison of the reactivity of coal/char in air and oxy-fuel combustion environments under various O₂/N₂ and O₂/CO₂ conditions have been studied and number of factors have been identified to cause the difference. This difference in reactivity are due to the differences in properties of bulk gases, the lower rate of diffusion of oxygen through CO₂ and the higher specific heat capacity of the CO₂ and may be the coal type also play a significant role in the reactivity and hence burnout.

The aim of the present study is to see the effects of different combustion environments of bulk gases, oxygen and CO₂ concentrations, pyrolysis conditions and different heating rates on coal gasification reaction. Most importantly the simultaneous processes of pyrolysis and gasification reactions have been studied on coal. Different models have been applied and from them different activation energies values have been calculated at different heating rates for different weight fractions of the coal.
2. Experimental

2.1 Material and its characterization

A coal imported from China, Datong coal, was selected for the thermo-gravimetric analysis experiments. The raw coal was first crushed and pulverized firstly using the mortar & pessell in the laboratory and then sieved using screen vibrator. The proximate and ultimate analyses of coal sample are summarized in Table 1.

Table 2 shows the physical properties of the resulting coal.

Table 1: The proximate and ultimate analyses of Datong coal sample

<table>
<thead>
<tr>
<th>Coal Analysis</th>
<th>Proximate analysis (dry %)</th>
<th>Ultimate analysis (dry %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>3.89</td>
<td>C 73.92</td>
</tr>
<tr>
<td>VM</td>
<td>27.28</td>
<td>H 3.82</td>
</tr>
<tr>
<td>F C</td>
<td>61.54</td>
<td>O 10.24</td>
</tr>
<tr>
<td>Ash</td>
<td>11.18</td>
<td>N 0.27</td>
</tr>
<tr>
<td>Total S</td>
<td></td>
<td>Comb. S 0.61</td>
</tr>
<tr>
<td>Uncomb. S</td>
<td></td>
<td>Na 470 (mg/kg)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K 1600 (mg/kg)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hg 0.07 (mg/kg)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Se 0.0001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd 1 (mg/kg)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>As 0.0002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B 0.0011</td>
</tr>
</tbody>
</table>

Table 2: The physical properties of the Datong coal sample

<table>
<thead>
<tr>
<th>Property</th>
<th>Datong Coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m²/g)</td>
<td>5</td>
</tr>
<tr>
<td>Pore volume (cm³/g)</td>
<td>0.016</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>13.2</td>
</tr>
<tr>
<td>Particle size (µm)</td>
<td>100 – 300</td>
</tr>
<tr>
<td>Specific density (-)</td>
<td>1.47</td>
</tr>
<tr>
<td>Heat capacity (J/Kg K)</td>
<td>1170</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1490</td>
</tr>
<tr>
<td>Softening point (°C)</td>
<td>1290</td>
</tr>
<tr>
<td>Calorific value (kJ/Kg)</td>
<td>28.780</td>
</tr>
</tbody>
</table>

2.2 TGA measurement and analysis

Pyrolysis and CO₂ gasification experiments were carried out in a TGA apparatus connected with the computer having thermo plus 2 software for analyzing the coal sample. The procedure can be summarized as follows: about 10 mg of the sample having a particle size range of 100 – 300 µm in diameter was placed in a quartz pan. The sample was packed loosely and placed the pan over the TG holder of which one end was suspended and another was attached to the microbalance. The temperature of the sample was measured by a thermocouple placed at the beneath of the holder. The coal sample was heated at a heating rate of 10 K/min from room temperature to 1273 K in the mixture of O₂/N₂ or O₂/CO₂ with various oxygen concentrations from 2% to 100% for combustion tests and different pyrolysis tests using N₂ or CO₂. Pyrolysis and gasification processes were also taken place simultaneously. Initially, the system was purged with high purity nitrogen at heating rate of 10 K/min and then the flow of N₂ was switched to different mixtures of O₂/CO₂ at the same heating rate of 10 K/min. In order to verify the influence of heating rate, the non-isothermal tests runs proceeded at different heating rates of 10, 15, 20 and 50 K/min. For all the experiments, the gas flow rate was kept at 50 cc/min. The weight change of the sample, time and temperature were recorded simultaneously for all the experiments.

3. Results and Discussion

3.1 Coal combustion in different environments

This Fig. 1 shows the comparison of coal pyrolysis experiments in different gas environments with the variation of gas temperatures by thermo gravimetric analysis technique. In case of pure streams of CO₂ and N₂ environments, the mass loss rate of coal pyrolysis in the presence of N₂ was lower than that in pure CO₂ environment at both high and low temperature regions but
this difference is marginal at high temperature. This may be understood by the stages of coal pyrolysis process. In case of 100% N₂ environment, the coal pyrolysis process has two stages: release of moisture content and devolatilization but the process of coal pyrolysis in high 100% CO₂ environment can be divided into three stages: moisture release, devolatilization and char gasification by CO₂ in high temperature zone. Also, this difference may be explained due to the density difference and transport properties of these gases which are quite different (the mass of the CO₂ molecule is different from that of N₂). Moreover, the formation of char particles is larger and its surface area is also higher than that of the N₂ char particles as observed by Rathnam. In high concentration of O₂, all the coal was fully combusted immediately and sharply lost its weight and reached to the ignition point immediately which is around 417 °C as shown in Table 3 and also indicated as a horizontal peak in the Fig. 1.

Different mixtures of these gases were also investigated as shown in Fig. 1 and it can be clearly seen that the difference among them is very meager i.e. almost same except at high temperature zone where there some difference is found.

It is seen in Fig. 1 that at high temperature region the weight loss in O₂/CO₂ environment is little bit less than O₂/N₂ environment that may be due to the thermophysical difference of combustion mixtures and due to the lower rate of diffusion of oxygen through CO₂ but this difference is so small that can be ignored. This meager difference can be explained by this way that, the presence of the same concentration of O₂ in the gas mixture dominates the combustion process over the pyrolysis process and hence the individual effect of CO₂ and N₂ gases in the mixtures becomes insignificant and as a result TGA profiles show the same curves. On the other hands, Li claimed that, in O₂/CO₂ mixture, the loss rate of coal sample is little smaller than that in O₂/N₂ condition and the burning time is little longer hence the replacing of N₂ only by CO₂ is unfavorable to the burning and burn-off of the coal char. But this paper deals with the reaction of coal with CO₂ in order to overcome the environment issues as the increase of CO₂ concentration causes a global warming. However, this combustion performance in the presence of CO₂ can be improved by increasing oxygen concentration in the gas mixture as described in the next section.

### 3.2 Effect of different O₂/ CO₂ mixtures

During non-isothermal heating process, the normalized TG curves in different combustion environments are shown in Fig. 2. It can be seen that the rate of mass loss increases with the increase of oxygen concentration in O₂/CO₂ mixture. When the concentration of oxygen is so high then the TG profiles decreased sharply and reached to the ignition point immediately. The details of ignition points with the use of different oxygen compositions are shown in Table 3.

As mentioned in above section that the coal reactivity in O₂/CO₂ environment is little smaller than that in O₂/ N₂ environment at the same oxygen concentration, but coal reactivity increases with the increase of oxygen concentration and that is found to be proportional to the O₂ concentration in O₂/CO₂ environment. In fact, under oxygen enriched char combustion conditions, CO oxidation in the boundary layers of char particles and the gasification of the char by CO₂ becomes significant and that pulverized coal char particles burn under increasing kinetic control in elevated oxygen environments, despite the higher burning rates. It is also seen in the combustion profiles that each profile shows a peak which appears at about 350 °C i.e. before ignition temperature for all the TGA profiles. In fact, TGA profiles must show the decreasing trend of loss of volatile matters but instead of decreasing, it indicating the increase of coal mass. This increase in coal mass may be due to the reaction of oxygen with the functional groups present in the coal sample. In order to support this point, it is clearly seen from the Fig. 1 that when there is no oxygen in the gas stream then there is no peak which can cause the increase of mass. So it can be claimed that this increase in mass is due to the reaction of oxygen with the functional group present in

<table>
<thead>
<tr>
<th>Comp.</th>
<th>100% O₂</th>
<th>20% CO₂ /80% O₂</th>
<th>50% CO₂ /50% O₂</th>
<th>70% CO₂ /30% O₂</th>
<th>79% CO₂ /21% O₂</th>
<th>79% N₂ /21% O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>I T °C</td>
<td>417</td>
<td>421</td>
<td>434</td>
<td>472</td>
<td>479</td>
<td>488</td>
</tr>
</tbody>
</table>

![Fig. 2. TG curves of Datong coal combustion in a mixture of different gases at heating rate of 10 K/min.](image)
the coal sample. This Fig. 2 also contains one small Fig which is required to find out the optimum value of O₂ i.e. how much oxygen is stoichiometrically needed to react with the present functional groups in the coal sample. It is clearly indicated in the small Fig. that with the use of 2% & 6% O₂ there is absolutely no peak appears but with the increase of oxygen concentration from 6 to 8% O₂, then the peak starts to appear so this shows that 8% O₂ appears to be optimum value. However, the use of lesser amount of O₂ shifted the TGA curves to the higher temperature zone and as a result the burning rate of coal is decreased and the burnout time is also delayed.

3.3 Effect of different pyrolysis temperatures

The figures 3, 4 and 5 show the influence of different pyrolysis temperatures on coal sample in both isothermal and non-isothermal conditions. The Fig. 3 showed different TGA profiles with the effect of different pyrolysis temperatures on coal sample. In this experiment, the coal was first pyrolysed at different temperatures started from 300 to 825 °C and then gasified with 21% O₂/79% CO₂ gas mixture. The mass loss rate profiles after 500 to 825 °C when gasified dropped down sharply as they were already reached at or beyond the ignition points as mentioned in the Table 3. But in case of 300 and 400 °C, when gasified, the mass rate loss decreased slightly up to the ignition temperature and then dropped down sharply to complete the combustion reaction. As the ignition point lies between 400 and 500 °C, so as a result, the prior use of gasify medium is useless. So there is need to perform pyrolysis from room temperature to 400 or 500 °C, either at isothermal or non-isothermal conditions.

Fig. 4 (a,b) showed the pyrolysis process at 400 and 500 °C at non-isothermal condition with heating rate of 10 K/min with different compositions of oxygen and carbon dioxide. It can be seen from Fig. 4(a) that TGA curves slightly moved ahead up to the ignition point and completed the gasification reaction smoothly except at the high composition of oxygen and carbon dioxide (i.e. 50%).

At high ratio of O₂/CO₂, the TGA curve first moved ahead slightly as rest of the TGA curves but at a sudden lost its weight and immediately reached to its ignition point due to the excess amount of oxygen and then smoothly decreased and completed the gasification reaction. On the other hand, in Fig. 4(b), it can be seen that all the TGA curves were dropped immediately as these were already beyond the ignition point but at high concentration of oxygen 30% and 50% the curves were moved back and reached up to their respective ignition points and finally completed the gasification reaction. On comparing with Fig. 4(a) and Fig. 4(b), it can be claimed that weight loss in both the figures is almost same or may be weight loss is very slightly less in former Fig than the later one but at relatively low temperature. This claim can be explained...
from Fig. 4(c) which is located within the Fig. 4(b). Fig. 4(c) showed the comparison of coal sample with the char sample at different pyrolysis temperatures. The weight loss of coal sample under non pyrolysed condition and the sample pyrolysed at 400 °C were almost same but comparatively at less temperature than the coal sample pyrolysed at 500 °C. There are number of advantages of this prior process of pyrolysis than to the gasification process:

1) Simultaneous production of fresh char in one continuous process by removing the moisture content and volatile matters
2) Avoiding the excess use of gasifying medium
3) No increase of coal sample mass as there is no reaction between oxygen and the present functional group. However, it doesn’t affect significantly on the combustion reaction mechanism.

Fig. 5 (a,b) shows the influence of pyrolysis process with the extension of heating rate at isothermal condition for particular period of times.

In this coal sample was first pyrolysed up to 400 °C at a heating rate of 10 K/min and then keep the sample at 400 °C for different times from 0 to 90 min and then the coal sample was gasified with the mixture of 79% CO₂/ 21% O₂ at a heating rate of 10 K/min. These experiments were performed just to remove more volatile matters from the coal samples but these experiments having constant heating rate at isothermal conditions were found to be not attractive because of excessive time and may be due to need of multiple experiments. It is seen in Fig. that the weight loss is almost same as that of Fig. 4(a) except the length of experiments performed. So these experiments seem not to be fruitful because of the passage of excessive time.

3.4 Effect of heating rate on combustion characteristic of coal

Coal combustion experiments were also carried out at four different heating rates (10, 15, 20 and 50 K/min) from room temperature to the final temperature i.e. 1000 °C and their combustion profiles were presented in Fig. 6.

It is shown in figure that with the increase of heating rate, TGA curves shift to higher temperature zone. As the heating rate increases from 10 to 20 and finally to 50 K/min, the weight loss rates at respective heating rates were also decreased. In case of 10 to 20 K/min heating rates, the weight loss rates were almost same but on the other hand at 50 K/min the weight loss rate was comparatively less. It may also indicate that the increase in heating rate only shortens the time approaching the final temperature but little influence on its combustion mechanism. On these
heating rates, values of activation energies at different weight fractions were also found by different correlations at non-isothermal analysis condition as shown in Fig. 7.

In case of non-isothermal analysis, the temperature changes at a constant positive rate. Brown\(^{22}\) developed a rate equation of weight loss in the differential form.

\[
\frac{dx}{dT} = \frac{A(1-\alpha)}{\beta} \exp\left(\frac{-E}{RT}\right)
\]

Integrate this equation using initial conditions \(\alpha = 0, T = T_o\)

\[
\ln(1-\alpha) = -\frac{A}{\beta} \int T \exp\left(\frac{-E}{RT}\right)
\]

As the ignition point lies after 400 °C hence the limits of the integral are conventionally changed to

\[
\int T \exp\left(\frac{-E}{RT}\right)
\]

hence the function \(p(x)\) may be introduced such that:

\[
p(x) = \frac{AE}{\beta R} \int \frac{e^{x}}{x^2} \, dx
\]

where \(x = E/RT\), hence eq (a) becomes

\[
\ln(1-\alpha) = \frac{AE}{\beta R} p(x)
\]

where \(\alpha = \frac{m_i - m_f}{m_i - m_f}\)

\(m_i\) is the initial mass of coal, \(m_f\) is the mass of coal at a time \(t\) and \(m_f\) is the final mass of coal after the reaction and \(\beta\) is the heating rate.

The problem with this equation is that this equation is not analytically solvable. The function \(p(x)\) however can be expressed by some approximate equation. There are many approximations have been derived but in this paper two simple approaches have been used: Doyle’s\(^{23}\) and Coats-Redfern’s\(^{24}\) approximations. These are selected for their simplicity and resulting ease of manipulation of eq (b) into linear forms.

Doyle’s approximation of \(p(x)\) is derived by observing a linear relationship between \(\ln p(x)\) and \(x\):

\[
p(x) = \exp\left(-5.33-x\right)
\]

Hence eq (b) comes out to be

\[
\ln[\ln(1-\alpha)] = \ln\left[\frac{AE}{\beta R}\right] - 5.33 - 1.052\left(\frac{E}{RT}\right)
\]

Hence for a given heating rate, \(E\) and \(A\) values can be estimated by plotting the \(\ln[\ln(1-\alpha)]\) versus \(1/T\). In case of Coats-Redfern approach only the first term of an asymptotic expansion of \(p(x)\) is retained:

\[
p(x) = \frac{e^x}{x^2}\left[1 - (2/3)x + (3^2/4!x^2) - (4^2/5!x^3) + \ldots\right]
\]

So \(p(x)\) comes out to be \(p(x) = e^{x^2}/x^2\)

Hence the equation may be incorporated into a linear equation as

\[
\ln[\ln(1-\alpha)/T^2] = \ln\left[\frac{A}\beta R\right] - \frac{E}{RT}
\]

The values of \(E\) and \(A\) may be estimated from the intercept and slope respectively of a plot of \(\ln[\ln(1-\alpha)/T^2]\) versus \(1/T\). Further, the \(E\) and \(A\) values may also be calculated from very well known correlation i.e. Freeman-Carroll method:\(^{25}\)

\[
\Delta\log\frac{da}{dt} = n\Delta\log(1-\alpha) - \frac{E}{2.303R}\Delta\left(\frac{1}{T}\right)
\]

The plot of \(\log\frac{da}{dt}\) vs \(1/T\)

gives the value of \(E\) and \(A\) from the curve.

It is also seen in Fig. 6 that activation energies appear to decrease with increasing heating rates\(^{26}\). There is a difference of about (40 kJ/mol) in the values of \(E\) from using 10 and 50 K/min heating rates. As observed in Fig. 6, at 600 °C, more than 80 % of the material was reacted at a heating rate of 10 K/min whereas around 50% of the original material was reacted at a heating rate of 50 K/min.

At different heating rates, different methods such as Freeman-Carroll method, Doyle’s and Coats-Redfern’s approaches were used for the determination of activation energies. These values were found to be at different weight fractions starting from 90% of the original coal material to the 15% of the retained coal material within the temperature range of about 400 to 600 °C. This range of temperatures and weight fractions have only been selected because the main reaction i.e. gasification lies within these temperature ranges and weight fractions. At each heating rate, the values of \(E\) calculated by Coats-Redfern and Doyle’s approaches were found to be high and close enough to each other but on the other hand the values of \(E\) calculated by Freeman-Carroll method were found to be lower. Moreover, the activation energy profiles obtained by each method showed the same trend i.e. parabolic curve. For these methods, the maximum values of \(E\) were found to be between the weight loss fractions of 30 to 40% at 10 K/min but these \(E\) values were shifted to lowest weight fractions from 20 to 30% when heating rate of 20 K/min was applied and so on. It is clearly seen from the Fig. 7 that parabolic curves of these values of \(E\) were obtained by all the calculation methods. These parabolic curves may be explained by this way that at the...
start, the lower activation energy values were due to the
combination of fixed carbon and volatile matters present
in the coal and then these curves showed maximum peaks
which may indicate the presence of high concentration
of fixed carbon and almost zero concentration of volatile
matter for the gasification reaction and then again the
activation energy values go down may be because of the
combination of low concentration of fixed carbon and
comparatively high quantity of ash contents.

4. Conclusions

Gasification of coal/char in a CO₂ atmosphere can be
divided into two stages, the first stage due to pyrolysis
(removal of moisture content and devolatilization) which
is comparatively at lower temperature and char gasification
by different O₂/CO₂ mixtures at high temperature. In N₂
and CO₂ environments from room temperature to 1000
°C, the mass loss rate of coal pyrolysis in N₂ is lower than
that of CO₂ may be due to the difference in properties of
the bulk gases. The gasification process of pulverized coal
in O₂/CO₂ environment is almost same as compared with
that in O₂/N₂ at the same oxygen concentration but this
effect is little bit delayed at high temperature. This may be
due to the lower rate of diffusion of oxygen through CO₂
and the higher specific heat capacity of CO₂. However
with the increase of O₂ concentration the mass loss rate of
coal also increases and hence it shortens the burn out time
of coal. The optimum value of O₂/CO₂ for the reaction of
O₂ with the functional group present in the coal sample
was found to be about 8%. The combination of pyrolysis
and gasification process can be the unique and fruitful
 technique as it can save the prior use of gasifying medium
and gasification process can be the unique and fruitful

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