Investigation of co-pyrolysis characteristics of high-ash Indian coal and rice husk

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Abstract. This study investigates the non-isothermal pyrolysis characteristics of a low-grade, high ash Indian coal, and rice husk using a thermogravimetric analyzer (TGA). A series of thermo-gravimetric experiments are conducted to examine the effects of coal and biomass blending on their thermal degradation behavior and synergetic effects in the nitrogen atmosphere. The thermo-gravimetric (TG) curves show two distinct tips where the larger tip is obtained for biomass as compared to the coal. The thermogravimetric study does not demonstrate any significant synergetic interaction between the biomass and high ash coal in the blends, and the additive rule describes the behavior of their combined pyrolysis. The activation energy and preexponential factor for coal and biomass are calculated based on the TGA data using the Friedman method. The corresponding calculated mean activation energy values for the biomass and Indian low-rank coal were found to be 203.463 KJ/mol, and 66.97 KJ/mol respectively.

1. Introduction

Due to global warming concerns, renewable energy resources are getting more attention in the present global energy scenario. Fossil fuel-based processes contribute about 80% of the share in primary energy production globally however they pose serious environmental concerns including emissions of harmful pollutants and greenhouse gases. Biomass stock originated from lingo-cellulosic sources is a sustainable renewable energy source that can replace fossil fuels and be converted into energy, power, liquid fuels, and other useful chemicals [1]. Bioenergy is also considered carbon-neutral as CO₂ released during biomass combustion returns to the atmosphere and is used by plants during photosynthesis. Thermo-chemical conversion of biomass into clean products such as gases and/or liquid fuel is more efficient and economical than its direction combustion. Among available methods to transform biomass thermochemically, pyrolysis and gasification of biomass are the most promising. Pyrolysis is the solid fuel feedstock's thermal decomposition into smaller fragments such as gases, liquid, and solid char under a medium temperature, and an inert environment. The major advantage of the pyrolysis process is the reduction in the transportation cost of the liquid fuel when compared to the gasification products [2]. Bio-char obtained from pyrolysis could be applied as an alternative modifier of soil due to its substantial absorbing characteristic. Also, the sequestration of biochar can significantly reduce the CO₂ concentration in the environment and can prove to be an important role-playing entity in the market of carbon capture setup worldwide. Even after years of research, the
fundamental scientific understanding of biomass pyrolysis is not matured enough primarily due to the absence of detailed models that can describe its chemistry and transport phenomena. The major challenges in the development of these descriptions arise due to the multiphase, multi-scale conversion techniques, and the complexity of feedstock. A thorough understanding of the mechanism of elementary reactions can open new avenues for process optimization in an accurate sense, and adaptability of feedstock.

Coal pyrolysis has been used efficiently for the generation of bio-oil and syngas for more than 100 years although considerable efforts to optimize the yield of liquids, solids, and gas fractions are given in the last few decades. Biomass pyrolysis is a relatively new research topic where a significant amount of work has been done only in recent years. Coal has a small H/C and O/C ratio as compared to biomass [3]. During co-pyrolysis of biomass with coal, the higher hydrogen donor ability, and high oxygen content of biomass facilitate reactivity of coal pyrolysis reaction. Thus, the process of co-pyrolysis of biomass with coal may be a useful way for the improvement of product yield particularly in the case of a low-grade coal feedstock. Various researchers have reported on the enhancement and synergetic effects of different types of coal and biomass feedstock. It is found out that the interaction of biomass-coal may improve the product yield obtained from the pyrolysis of coal alone [4]. Wu et al. [5] studied the interaction of bituminous coal with various biomass varieties like pine sawdust and residue straw using the Thermo-gravimetric analyzer (TGA) and concluded that using biomass blending with the coal enhanced the product yield. The synergetic effects are also confirmed by Senobe et al. [6] in the co-pyrolysis investigation utilizing lignite coal and corncob biomass using a reactor of fixed bed type. The occurrence of synergy in TGA and the fixed-bed reactor was observed by Park et al. [7] utilizing different blends of sub-bituminous coal and sawdust. Apart from the pyrolysis characteristics of a feedstock, its kinetic parameter also plays an important role to estimate its efficient utilization. Thermogravimetric analysis (TGA) is precisely a reliable technique of studying the kinetics of coal, thermal events, and biomass which mainly provides measurements of loss in terms of sample weight as a function of temperature and time. Various methods are proposed by researchers for the estimation of kinetic variables from curves and datasets related to TGA. These methods can be broadly divided into model-free and model-fitting methods where model-fitting method are not particularly useful for non-isothermal TGA data as it gives one order higher values [8]. The characteristics of pyrolysis and kinetics of high-ash Indian coal and Lignocellulosic biomass are investigated in the present work using TGA under the inert atmosphere. Using single first order reaction model (Friedman method), kinetic parameters like frequency factor ($A$) and activation energy ($E_a$) are obtained. The study's findings may be used to optimize the thermochemical conversion processes, including pyrolysis and gasification, and for the development of suitable technologies.

2. Materials and methodology

Indian sub-bituminous coal is used as the feedstock for the experimental investigations in the thermogravimetric analyzer. The coal feedstock was received in the size of 20-100 mm, which is ground in a hammer mill and sieved using a vibratory sieve shaker up to the maximum particle size of 150 µm. Rice husk is used as the biomass, which is ground using a mixer to a suitable distribution of particle size (<150 µm). The coal and biomass blends are prepared in blending ratios of 0:100, 25:75, 50:50, 75:25, and 100:0 in terms of weight percentage. Table 1 listed the data of proximate and ultimate analysis of coal and biomass. The higher calorific value (HHV) of the coal is calculated using Dulong and Petit equation as; $HHV = 33823C + 144249(1 - O/8) + 9418 \times S_{kg}/kg$. Here, the mass fractions (%) of carbon, hydrogen, oxygen, and sulfur, are represented by C, H, O, and S respectively which are taken from ultimate analysis (Table 1).
Table 1. Proximate and ultimate analysis of the biomass and the coal (As received)

| Proximate analysis | Biomass (% wt.) | Coal (% wt.) | Ultimate analysis | Biomass (% wt.) | Coal (% wt.) |
|--------------------|-----------------|--------------|-------------------|-----------------|--------------|
| Moisture           | 7.36            | 2.0          | Carbon            | 39.061          | 48.37        |
| Volatiles          | 73.33           | 7.1          | Hydrogen          | 5.567           | 1.23         |
| Fixed carbon       | 6.48            | 45.6         | Oxygen            | 34.27           | 1.65         |
| Ash content        | 12.83           | 45.3         | Nitrogen          | 0.911           | 1.11         |
| HHV                | 17868.96        | 15062.68     | Sulphur           | -               | 0.34         |

The pyrolysis experiments are performed in a Thermo-Gravimetric Analyzer (make: TGA/DSC METTLER TOLEDO). Figure 1 shows the TGA experimental setup. For carrying out a typical experimental run, 15±0.2 mg samples were placed and the rate of heating was maintained at 10°C/min from ambient temperature to 1000°C in N₂ environment at a constant purge rate of 4 mL/min. Lab facilities at the CESE, IIT Kanpur, India are used to conduct experiments. Experiments are carried out at different temperatures (30–1000°C) and blending ratios (0, 25, 50, 75, and 100 %) of coal and biomass. The temperature range is selected such that it covers drying and devolatilization processes till the ash softening temperature suitable for fluidized beds.

Figure 1. Photograph of the Thermo-Gravimetric Analyzer used in the study.

3. Kinetics parameters
The pyrolysis process of coal and biomass is assumed by a series of first-order reactions. Therefore, the following equation is used to calculate the reaction rate using the Arrhenius equation concerning a heterogeneous medium:

\[
\frac{dx}{dt} = Ae^{-\frac{E_a}{RT}} f(\alpha)
\]

(1)

Here in Eq. (1), the conversion degree is represented by \( \alpha \), the reaction temperature is represented by \( T \), and time is represented by \( t \). Notations \( R \), \( E_a \), and \( A \) represents the ideal gas constant (8.314 J/mol K), activation energy, and the pre-exponential factor. The reaction model
function is denoted by $f(\alpha)$, and the fuel's combustion rate at the temperature $T$ is denoted by $\alpha(T)$, and it is evaluated by data obtained from TG analysis using the following equation:

$$\alpha = \frac{m_o - m_f}{m_o}$$  \hspace{1cm} (2)

Here, $m_o$ and $m_f$ denote the solid fuel sample's initial and final mass, and the sample's mass at temperature $T$ is denoted by $m_f$. The function $f(\alpha)$ can be represented by Eq. (3).

$$f(\alpha) = (1 - \alpha)^n$$  \hspace{1cm} (3)

where, $n$ denotes the reaction order. For an experiment of non-isothermal type with a constant heating rate ($\beta = \frac{dT}{dt}$), rate of reaction as a function of temperature can be written in the form of Eq. (4);

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E_a}{RT}} f(\alpha)$$  \hspace{1cm} (4)

For the estimation of activation energy, the Friedman method is used. This Friedman analysis can be expressed with the help of the following equation:

$$ln(\beta \frac{d\alpha}{dt}) = ln(Af(\alpha)) - \frac{E_a}{RT}$$  \hspace{1cm} (5)

The activation energy values can be obtained from the slope of $ln(\beta \frac{d\alpha}{dt})$ with $-1/T$ (K).

4. Results and discussion

4.1 Pyrolysis characteristics of coal and biomass

Figure 2. The DTG (left), and the TG (right) curves for coal pyrolysis at a heating rate of 10°C/min.

The DTG and the TG curves of coal are shown in figure 2. The used coal has small moisture and volatile content which is evident from the significantly lower weight loss observed from the TG plot. No drastic change is visible in the TG curve and a gradual, continuous decay is observed which corresponds to the moisture removal and devolatilization processes. A well-known three-stage analysis technique for low-rank coal pyrolysis is widely recognized. Surface moisture/water removal is considered as the first stage; which occurs mainly due to some depolymerization conversion reactions. In the second stage also called the reaction stage, 70%– 80% of weight losses occur followed by the third stage where the residue decomposition rate is even smaller. From the TG curve for coal, it may be said that the moisture discharge happens between the temperature limit of 100°C to 215°C. The value of residue ratio which remains constant after the moisture removal process can be observed from the TG curve. For a specific value of temperature, the DTG curve plot can be used to assess the value of the weight loss rate. DTG curve peak value denotes the temperature which accounts for the
maximum loss in weight of the sample. It can be observed from figure 2 that, the maximum weight loss occurs around 510°C temperature for high-ash coal. The temperature of more than 250°C marks the beginning of thermal decomposition of the sample whereas a continuous decomposition takes place at higher temperatures till the maximum examined value of the temperature (~1000°C). The final weight of sample residue obtained during the pyrolysis is the result of both entities, that is, the partial oxidation of the sample material and the volatile released from the sample.

![Figure 3. The DTG (left), and the TG (right) curves for biomass pyrolysis at the heating rate 10°C/min.](image)

The effects of temperature on rice husk pyrolysis behavior are shown in figure 3. DTG and TG curves are plotted to determine the drying and devolatilization characteristics of lignocellulosic biomass material. Two distinct weight loss curves are visible for rice husk pyrolysis from the TG curve as shown in figure 3, which can be associated with the drying and the devolatilization. The start of the first major weight-loss event mainly due to the drying process can be distinguished around the temperature of 100°C, which becomes constant after 150°C. The second drastic weight loss event takes place around the temperature of 250°C. Hemicellulose decomposition begins to take place after 200°C and can go up to the temperature of 310°C, whereas cellulose decomposition occurs after a temperature of 310°C. The slope of the DTG curve changes at 390°C, which signifies the maximum rate of lignin decomposition [9], or we can say that the maximum weight loss for rice husk takes place at this temperature.

4.2 Pyrolysis characteristics of biomass-coal blends

Figure 4 shows the DTG & TG curves of various values of rice husk and coal blends. The obtained curves of DTG and TG for pure biomass and coal are also shown here. TG analysis shows that by increasing the biomass content in the coal-biomass blends, the fraction of residual weight decreases. The biomass portion present in the blend influences the liquid, solid, and gas distribution. Char yield decreases with the blending ratio of coal-biomass, whereas the yield of gas and liquid content increases. Whereas the yield of gas and liquid content increases. The immobile structural coal phase is generally composed of aromatics with cross-links joined together by C=C bonds of heavy strength and 1000 KJ/mol bond energy [10].
The breakage of these bonds is easier in the presence of the macromolecular structure of hemicelluloses, cellulose, and lignin present in the biomass, comparing heating it alone. The biomass components are bonded with each other by relatively weak ether bonds with an approximated bond energy of 380–420 KJ/mol, which results in a much quicker decomposition of biomass than coal [10]. TG curve explains these characteristics where a higher weight loss occurs in the case of higher values of blending ratios. The DTG curve displayed higher peaks for larger values of coal/biomass blending ratio.

4.3 Synergetic or Additive behavior

To examine whether any synergy occurred or not, the weight loss (TG) curve obtained from blending experiments is compared with that obtained from the individual biomass and coal feedstock experiments multiplied with their respective fractions. The weight loss ($W_{cal}$) due to the additive rule can be written as follows;

$$W_{cal} = m_c W_C + m_b W_B$$

where $m_c$ and $m_b$ are mass fractions of coal and biomass in the blends, whereas, $W_C$ and $W_B$ represents the weight losses of coal and biomass during their separate pyrolysis. The weight loss ($W_{cal}$) of the blend is calculated for 25C:75B, 50C:50B, and 75C:25B blends, and its comparison of TG curve with that obtained directly from blend pyrolysis experiments is shown in figure 5. The comparison between the two TG curves depicts slight differences, and there seems to be a little interaction between coal and biomass in the blend during heating. The low heating rate (<50°C) during the experiments could be the main reason for the insignificant interactions between the two blends. Lower heating rates inhibit interactions of the different blend components and separate their devolatilization process.

Table 2. Kinetic parameters for the pyrolysis of biomass and high-ash Indian coal.

| Rate of Heating | $E_a$ (KJ/mol) | $A$ (min$^{-1}$) | $E_a$ (KJ/mol) | $A$ (min$^{-1}$) |
|----------------|--------------|----------------|--------------|----------------|
|                | Biomass      | Coal           | Biomass      | Coal           |
| 10°C per min   | 205.45       | 3.103 E4       | 68.23        | 187.37         |
| 20°C per min   | 203.38       | 3.213 E4       | 67.45        | 188.43         |
| 30°C per min   | 201.56       | 3.116 E4       | 65.23        | 187.29         |

Figure 4. DTG (left), and TG (right) curves for different coal-biomass blends pyrolysis at the heating rate 10°C/min.
4.4 Estimation of kinetic parameters
An iso-conversational model-free technique known as the Friedman method is used to estimate the kinetic parameters for pyrolysis of biomass and high-ash Indian coal in an inert atmosphere of nitrogen at three distinct heating rates. In the present study, we apply this model-free technique in the form of a reaction with first-order kinetics. So, the graph shows a straight-line relationship in between $\ln(\beta \frac{d\alpha}{dt})$ and $-1/T$ (K). The mean estimate, when calculated for activation energy for biomass, was found to be in the range of 203.463 KJ/mol, whereas, for coal, the mean activation energy lies around 66.97 KJ/mol. Table 2 shows the values of frequency factor and activation energy that are calculated for biomass and coal samples at three different heating rates. It is found that the activation energy of both fuels decreases with the heating rate. The values of activation energy and correlation coefficient ($R^2$) with conversion degree (ranges from 0.1 to 0.9) for biomass and high-ash coal are listed in Table 3. The high value of correlation coefficient ($R^2$) suggests that our model fits the data well. The variation of the activation energy with the conversion degree ($\alpha$) is shown in figure 6.
Table 3. Activation energy ($E_a$) and Coefficient of determination (R-Square) values with conversion degree (α).

| Conversion degree (α) | Biomass $E_a$ | R² | Coal $E_a$ | R² |
|-----------------------|--------------|----|------------|----|
| 0.1                   | 187.3        | 0.996 | 64.23      | 0.997 |
| 0.2                   | 203.45       | 0.997 | 62.45      | 0.998 |
| 0.3                   | 204.56       | 0.996 | 65.78      | 0.997 |
| 0.4                   | 204.32       | 0.998 | 65.34      | 0.997 |
| 0.5                   | 204.23       | 0.997 | 66.78      | 0.998 |
| 0.6                   | 203.87       | 0.997 | 67.23      | 0.998 |
| 0.7                   | 203.65       | 0.998 | 68.34      | 0.996 |
| 0.8                   | 205.45       | 0.997 | 69.23      | 0.997 |
| 0.9                   | 210.45       | 0.996 | 71.23      | 0.996 |

Figure 6. The activation energy of biomass (left), coal (right) as a function of conversion degree.

5. Conclusions

Thermogravimetric analysis is carried out to examine pyrolysis characteristics of blended biomass and coal in different proportions. Rice husk is used as the biomass with a low-grade, high-ash Indian coal. Pyrolysis characteristics are evaluated in terms of weight loss and differential weight loss curves. Synergetic interactions due to blending are examined by comparing them with the TGA data obtained from unary biomass and coal pyrolysis. During the individual pyrolysis of the coal and biomass, it is found out that the high-ash Indian coal incurs a very low weight reduction with no distinct peaks visible in the DTG curve. In contrast, biomass demonstrated a high reduction in the weight with an increase in temperature accompanied by the presence of well-defined devolatilization peaks. For both the fuels, the pyrolysis conversion increased as the temperature increased. For the biomass-coal blends, the TG curve showed that the weight reduction increased with increasing biomass content in blends. The calculated and experimental TG curves of the blends indicated that no significant synergetic interactions take place between both the fuels. The mean value of coal activation energy for coal were estimated as 66.97 KJ/mol which suggest High-ash Indian coal can be used for power generation and in industrial operation.
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