Thermogravimetric Analysis of Pinus Wood For Kinetic Analysis by Using Coats and Redfern Method

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ABSTRACT

Pinus wood is selected for this study because it is freely available near to Punjab in Jammu & Kashmir region. Kinetic studies are extremely useful for the interpretation of reaction mechanism and catalytic phenomenon, optimization, behavior on molecular basis and build-out of new chemical processes. This study is highly focused to characterize the pinus wood by using proximate analysis, FTIR analysis, calorific value and TGA. In this study kinetics evaluation performed by using Coats and Redfern method, this method is non-isothermal type and throughout this study it was observed that pinus wood has the high thermal stability and it can be used for the applications for the production of clean and eco-friendly energy.

Keywords: Pinus wood, TGA, Activation energy, thermal stability, kinetic parameters

1. INTRODUCTION

The Pinus wood was selected for this study because it is coniferous forest, resinous, evergreen trees of the *Pinaceae* family. It is an important pine in the northern Himalayas and a sticky flammable. The main significance of utilizing kinetic analysis is to take out the valuable information on the pyrolysis through various forms of kinetic models and their correlations [1-2]. This study indicates the thermal stability of pinus wood by using thermo-gravimetric analysis. Thermogravemetric analysis provides the complete thermal analysis of the biomass material, in TGA method biomass weight losses occurs with temperatures. Wood can be degraded into the form of volatiles and charcoal and ash contents. Biomass consists cellulose, hemicellulose and lignin content, cellulose and hemicellulose is the fibrous part of the biomass materials and during the heating process volatile matters depends on the (cellulose + hemicellulose) holocellulose. TGA provides the weight losses at different temperature zones and by the analyses it can be predicted that which biomass need how much energy for the combustion. Biomass contains cellulose, hemicellulose and lignin contents, moisture can be removed at 100-110 °C temperature and weight losses starts at 200-220 °C temperature. Holocellulose (cellulose + hemicellulose) cracked at 220-400 °C temperature and ash content achieved after the complete combustion of the biomass at around 600-1000 °C (temperature range depends on biomass materials). Ash contents depend on the amount of lignin content [3-4].
2. MATERIAL AND METHODS

The physico-chemical properties of the selected sample were characterized by using different ASTM methods by using CHNS analyzer, FTIR analyzer and TGA analyzer.

3.0 EXPERIMENTAL

This article’s calculations highly based on TGA analysis, for this analysis pre-weighed biomass sample taken into silica crucible and it was burned into the N₂ environment into the TGA analyzer by using controlled heating rate 10 °C/min.

3.1 KINETIC CALCULATIONS

By using TGA thermogram, kinetics factors were determined by using Coats and Redfern non-isothermal equation [5-7].

Coats and Redfern equation can be determined as

$$\ln \left[ 1 - \frac{(1-x)^{(1-n)}}{(1-n)} \right] = \ln \left( \frac{AR}{\beta E} \right) \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{RT} \quad (\text{for } n \neq 1)$$

and for n=1, Coats and Redfern equation is

$$\ln \left[ \frac{\ln(1-x)}{T^2} \right] = \ln \left( \frac{AR}{\beta E} \right) \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{RT}$$

Where, \(x\) = fractional weight loss of the wood sample

$$x = \frac{(W_i - W_t)}{(W_i - W_f)}$$

\(W_i\) = Initial weight of the biomass material
\(W_t\) = weight of the biomass at time t
\(W_f\) = final weight of the biomass

and \(E\) = activation energy, \(T\) is the temperature and \(n\) is the number and \(R\) is the gas constant = 8.31 J/mol.K.
4.0 RESULTS AND DISCUSSION

4.1 Proximate analysis and calorific value of sample

Table 1, indicates the high volatile matter in to the wood sample (80.88%) due to the higher cellulose and hemicellulose and low ash content (1.47%) because of low lignin content and high calorific value 4360 Kcal/kg indicates high thermal stability of wood.

| S.No. | Proximate analysis          | Value (%) |
|-------|----------------------------|-----------|
|       | Moisture                   | 4.9       |
|       | Volatile matter            | 80.88     |
|       | Fixed carbon ( calculated by difference) | 12.75 |
|       | Ash content                | 1.47      |
|       | C                          | 52        |
|       | H                          | 4.8       |
|       | N                          | 0.85      |
|       | S                          | 0         |
|       | O (calculated by difference ) | 42.35 |
| Density of p.wood | Kg/m³ | 395 |
| Calorific value | (Kcal/kg) | 4360 |

Stability of wood indicates it can be used as a solid fuel into the various applications gasification, pyrolysis for high energy production.
4.2 FTIR ANALYSIS OF PINUS WOOD:

Fig. 1 FTIR analysis of pinus wood
Table 2 FTIR analysis of the pinus wood

| S.NO. | peak     | Intensity | Functional groups and chemical bonds                                      | Ref. |
|-------|----------|-----------|--------------------------------------------------------------------------|------|
| 1     | 414.71   | 93.318    | C-C bonding                                                              | [8]  |
| 2     | 459.07   | 95.299    | C-C bonding                                                              |      |
| 3     | 505.37   | 95.249    | C-C bonding                                                              |      |
| 4     | 555.52   | 95.82     | C-C bonding                                                              |      |
| 5     | 1026.16  | 95.347    | C-O stretching [carboxylic acid, phenol, alcohol]                         | [9]  |
| 6     | 1151.54  | 97.271    | COC stretching vibration [pyranose ring skeletal]                        |      |
| 7     | 1267.27  | 97.516    | C-O-C stretching [aryl-alkyl ether-linkage]                              |      |
| 8     | 1454.38  | 98.071    | O-CH3 [methoxyl-O-CH3]                                                   |      |
| 9     | 1693.56  | 97.627    | C=O stretching [ketones, aldehydes, carboxylic acids]                    |      |
| 10    | 2004.11  | 98.718    | N=H stretching, O=H stretching                                           |      |
| 11    | 2202.78  | 99.041    | C-H stretching                                                           |      |
| 12    | 2931.9   | 98.224    | Methyl C-H stretch [alkyl, aliphatic, aromatic]                          |      |

Above Table 2, identified the various chemical bonding and type of chemical compounds, at peak 2931 cm\(^{-1}\) C-H bonds are found in methyl groups also in methylene groups identifying of aliphatic, alkyl and groups having ring structure, at peak 1693 cm\(^{-1}\), C=O stretching is present, for the detection of ring structure and benzene bond C-O is used. 1151 intense peak has been investigated -C-O-C- stretching bonds identification of Pyranose ring skeletal, from peaks 414-555 cm\(^{-1}\), -C-C bonding found in region from 0 to 1500 cm\(^{-1}\). 2004 cm\(^{-1}\)-peak identified N=H stretching, O=H stretching, at peak 1454 cm\(^{-1}\) found O-CH\(_3\) identified Methoxyl-O-CH\(_3\), for peak 2202 cm\(^{-1}\) has been investigated C-H stretching. O, CH reformation of hemicelluloses and cellulose determined O-CH\(_3\) chemical molecules, for the peak value 1454 cm\(^{-1}\) O-CH\(_3\) found, ring like structure skeletal-vibration merge and reformation plane is done with C-H bond and identification of methoxyl–O–CH\(_3\)[8].
4.3 TGA ANALYSIS FOR EVALUATION OF THE KINETIC PARAMETERS

TGA Thermogram of wood:

![Fig.2 TGA thermogram of pinus wood](image)

TGA study has been performed in the temperature range (ambient to 1000 °C) at 10 °C/min. After the testing it had been found that the thermal stability of pinus wood sample is higher and its activation energy calculated (125.52 KJ/mole). The measure weight losses occurred in between 300-600 °C temperature range. At 300 °C temperature 19 % weight degraded and at 600 °C temperature 86 % weight degraded in the pinus wood and after 600 °C temperature constant weight losses occurred. Results presented in Table 3.

Table 3 Kinetic parameters of pinus wood

| Heating rate (β) | Temperature (K) | Frequency factor (A) | Kinetic rate constant (K) | E (KJ/mole) | R² |
|------------------|-----------------|----------------------|--------------------------|-------------|----|
| 10 °C/min.       | 873             | 0.032                | 0.24                     | 125.52      | 0.98 |

Activation energy is calculated by plotting of the above equation (between 1/T and F(x)). Table 3 presents kinetics parameters that are activation energy and frequency factor of wood sample. Thermogravimetric results of the pinus wood sample indicated the threshold energy or activation energy (125.5 KJ/mole) for the combustion of biomass material. According to the high calorific value (4360 Kcal/Kg) and activation energy (125.5 KJ/mole) wood material has the high thermal stability so it can be used for the higher application for energy production by using thermochemical
methods pyrolysis, gasification, combustion, biogasification and liquefaction. All these methods are providing the promising and cost feasible options for clean energy production.

5.0 CONCLUSION

Pinus wood found in large quantity in Jammu and Kashmir region so it is selected for this study and thermogravimetric results of the pinus wood sample indicated the threshold energy or activation energy (125.5 KJ/mole) for the combustion of biomass material. According to the high calorific value (4360 Kcal/Kg) and activation energy (125.5 KJ/mole) wood material has the high thermal stability so it can be used for the higher application for energy production by using thermochemical methods pyrolysis, gasification, combustion, biogasification and liquefaction. All these methods are providing the promising and cost feasible options for clean energy production. FTIR analysis it observed that various chemical functional groups identified for peak 2931 cm⁻¹, C-H bonds are found in methyl groups also in methylene groups identifying of aliphatic, alkyl and groups having ring structure aromatic, at peak 1693 cm⁻¹ C=O bonding is present for the detection of ring structure and benzene -C-O is used.

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