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Study on kinetic parameters of different biomass samples using thermo-gravimetric analysis



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ABSTRACT

In this study, thermogravimetric analysis of three different biomass samples such as rice husk, saw dust and wheat husk is carried out to understand its thermal behaviour. Analysis is carried out in an inert nitrogen atmosphere from ambient temperature to 800 °C at a heating rate of 10 °C/min. It is observed that all the three biomass samples displayed similar weight loss trend. Three reaction zones corresponding to dehydration, hemicellulose-cellulose degradation and lignin degradation are observed for all the three biomass samples. The kinetic parameters such as activation energy, pre-exponential factor and order of the reaction of samples are determined using modified form of equation.

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1. Introduction

Biomass conversion to convenient fuels by pyrolysis is a promising concept. Pyrolysis is a precursor process to all thermochemical processes such as combustion, gasification, liquefaction etc [1]. However, biomass pyrolysis is an extremely fiddly process which undergoes a sequence of reactions and its reaction kinetics being influenced by many factors [2–5]. It is thus critical to gain a comprehensive knowledge into the basics of biomass pyrolysis process.

Biomass is composed of three major components: cellulose, hemicellulose and lignin. These components usually exist in biomass in the range of 32–45%, 19–25% and 14–26% (by weight) respectively [6]. Previous attempts in biomass

pyrolysis have revealed that the thermal degradation of biomass components follows the following trend: moisture evolution, hemicellulose degradation, cellulose degradation and finally lignin degradation [7,8].

White et al. [9] identified some factors viz: physical and chemical nature of the biomass, heat and mass transfer limitations, operating conditions (heating rate, operating atmosphere) and methodical errors influencing the biomass reaction kinetics. Excluding the above, certain factors like biomass type, instrument employed and methodology adopted in analysing also have some influence on reaction kinetics.

Thermogravimetric analysis (TGA) is a testing method done on samples to determine change in weight with respect to change in temperature. TGA relies on critical measurements

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such as weight, temperature and time. The rate of change in weight which is also a vital measurement is derived from temperature (consecutive) measurements. TGA curve alone may not be sufficient to interpret the weight loss of sample. Hence, a derivative thermogravimetric (DTG) curve along with TGA curve is needed to determine the apparent weight loss of samples. These days, TGA apart from its usual application is also finding its claim in the study of kinetics of biomass materials [10–12]. TGA is generally preferred, because of its simplicity and its reliance on fewer observations to calculate the kinetics for the complete temperature range [13]. Some of the disadvantages of TGA include low heating rate, being time consuming and its ability to handle only small amount of samples.

Determination of kinetic parameters such as activation energy, pre-exponential factor and order of reaction are crucial in forecasting the thermal response of sample. Determination of activation energy helps in finding out the minimum amount of energy needed to initiate a chemical change. Pre-exponential factor and the order of reaction help in calculating the reaction rate. These kinetic parameters can be used in predicting the thermal behaviour of the samples and the outcome of the findings can be taken as the basis for pyrolysis studies.

Biomass samples such as rice husk, saw dust and wheat husk are taken for this study. The reason for studying these biomass is to find-out a better mean of utilization (biomass) as they are often used as direct fuels (low in energy density) and as cattle feeds. In addition to that, their availability is abundant in Trichy, Tamilnadu, South of India. Rice being the major crop in Trichy, the rice husk availability is guaranteed round the year. Similarly, saw mills in and around Trichy, provides the continuous source for saw dust. The collected saw dust is from *Tectona Grandis* (Teak) wood which is a tropical hardwood species. Though wheat is not cultivated in Trichy, wheat husk is being commonly used as food supplement for cattle.

Though previous literatures have thrown light on the TGA of different biomass samples, only few works have succeeded in determining all the kinetic parameters (activation energy, pre-exponential factor and order of reaction) of all the components of biomass. This work is an attempt made to find-out all the kinetic parameters of the biomass components.

1.1. Objectives

The specific objectives of the work include:

1To conduct TGA on three different biomass samples (rice husk, saw dust and wheat husk) at a heating rate of 10 °C/min in an inert nitrogen atmosphere. (A lower heating rate ensures that heat and mass transfer not to be rate limiting steps and facilitates to study true reaction kinetics. One more advantage is that slower heating rate provides distinct degradation zones of biomass components in the Thermogravimetric–Derivative Thermogravimetric (TG–DTG) curve) [14];

To determine the degradation temperature range of biomass components, their initial degradation temperature and their corresponding weight loss when the sample is heated from ambient temperature to 800 °C. (Increase in temperature beyond 800 °C does not contribute for further weight loss of sample [14]);

3To determine the residual weight of samples after its complete degradation;

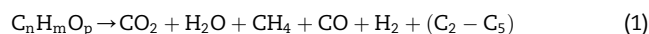
4To determine the kinetic parameters (activation energy, pre-exponential factor and order of reaction) for the samples.

1.2. Theoretical backdrop

The common pyrolysis mechanism while dealing with lignocellulosic biomass suggested by Babu and Mohan et al. [15,16], is briefed below

- i. Heat from a heat sources raises the inside temperature of the fuel.
- i. The commencement of primary pyrolysis reactions at higher temperatures leaves out volatiles and forms char
- ii. The movement of hot volatiles causes heat transfer between hot volatiles and cooler unpyrolysed fuel
- iii. Condensation of some of volatiles occurs when it contacts cooler parts of fuel, followed by secondary reactions generating tar
- iv. Parallel occurrence of autocatalytic secondary pyrolytic reactions and primary pyrolytic reactions
- v. More thermal decomposition, reforming, water gas shifts reactions, radical recombination and dehydration can also occur which are based upon process's residence time, temperature and pressure profile.

A generalised pyrolysis reaction can be given by the below equation [17].



Sequence of pyrolysis reactions at different temperatures is given in Table 1 [18].

Nachenius et al. [19] illustrated sequence of pyrolysis reactions using TGA. Their observations are briefed as below. Initially up to 100 °C biomass tend to lose its weight due to evaporation of water. Then till 160 °C, biomass weight loss is attributed due to bound water. The major biomass components cellulose, hemicellulose and lignin start to deteriorate above 180 °C. During their decomposition, biomass release non-condensable gases and condensable vapours. Above 400 °C, less volatile components are released producing a solid product rich in fixed carbon and less in volatile carbon content. The temperature above 600 °C makes the primary condensable components in gas phase to undergo cracking and polymerization reactions reducing bio-oil yield.

In this study, determination of the kinetic parameters from TGA technique is based on the modified form of Arrhenius equation proposed by Goldfarb et al. and Duvvuri et al. [20,21].

Global kinetics of the devolatilization reaction can be written as

$$-\frac{dX}{dt} = kX^n \quad (2)$$

Applying the Arrhenius equation,

$$k = Ae^{-E/RT} \quad (3)$$

Substituting the value of k in (1)

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