



## Kinetic studies on the pyrolysis of pinewood



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### HIGHLIGHTS

- Model free kinetic studies on pyrolysis of pine wood.
- Determination of kinetic triplet from TG analysis using isoconversional methods.
- Prediction of kinetic mechanism using master plots and compensation effect.
- Isothermal predictions from non-isothermal data for validation of kinetic results.

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### ABSTRACT

The kinetic study for pyrolysis of pine wood has been studied by a thermogravimetric analyzer in an inert atmosphere. Non isothermal model free kinetic methods were used to evaluate kinetics at six different heating rates of 5–40 °C/min. Three zones can be detected from the iso-conversional plot of pine with average activation energy values of 134.32 kJ/mol, 146.89 kJ/mol and 155.76 kJ/mol in the conversion range of 1–22%, 24–84% and 85–90%, respectively. The activation energy values were used to determine the reaction mechanism using master plots and compensation parameters. The results show that the pyrolysis process of pine wood can be described by two dimensional diffusion reaction mechanism in a wide range of conversion up to 0.7, followed by close to one and half order reaction mechanism. The kinetic results were validated by making isothermal predictions from non-isothermal data.

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### 1. Introduction

Biomass is a renewable resource, whose utilization has received great attention due to environmental considerations and the increasing demands of energy worldwide (Tsai et al., 2007). Biomass resources include wood and wood wastes, agricultural crops and their waste byproducts, municipal solid waste, animal wastes, waste from food processing, and aquatic plants and algae. Pyrolysis is one of the thermochemical biomass conversion methods with best industrial perspectives for biomass valorization, since the process conditions can be optimized to maximize the yields of gas, liquid and char (Czernik and Bridgwater, 2004). The pyrolysis behavior of lignocellulosic biomass depends on its three major building blocks: cellulose, hemicellulose and lignin. Forest biomass contains a high weight percentage of cellulose and lignin, whereas agricultural biomass contains a high weight percentage of cellulose and xylan (Cendrowska, 1997). Hardwoods have a higher proportion of cellulose and xylan than softwoods. The varying proportions of three key components affect the pyrolysis behavior of biomass

feedstocks and affect the yields of pyrolysis products both quantitatively and qualitatively.

Thermal analysis techniques such as thermogravimetric analysis (TGA) have been widely used to study biomass kinetics as they are high-precision methods and provide quantitative methods for examination of processes and estimation of effective kinetic parameters for various decomposition reactions. The actual reaction scheme of wood pyrolysis is extremely complex because of the formation of over a hundred intermediate products. The pyrolysis of wood is, therefore, generally modeled on the basis of apparent kinetics (Di Blasi, 2008). Numerous works on kinetic studies of wood have been reported in literature (Koufopanos et al., 1989; Matheus et al., 2012; Sbirrazzuoli, 2013; Tsai et al., 2007). Bamford et al. (1946) reported the first model of pyrolysis based on a single reaction scheme with first order kinetics. Di Blasi (2008) presented a review of the various studies on modeling of chemical and physical processes of biomass pyrolysis reported in literature. A majority of kinetic mechanisms consists of a single or three parallel reactions for the formation of the main product classes (one-stage or one-component mechanisms) following the proposal by Shafizadeh and Chin (1977) for wood (Di Blasi, 2008). These models come under the model fitting approach of

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kinetic analysis which suffers from several drawbacks. The forcible fitting of data leads to ambiguous kinetic predictions where more than one kinetic mechanism are likely to give good fits for same set of data. The most important feature of a reliable method of kinetic analysis is its ability to handle multi step processes (Vyazovkin, 2000). The isoconversional analysis provides a fortunate compromise between the oversimplified but widely used single step Arrhenius kinetic treatment and the prevalent occurrence of processes whose kinetics are multi-step and/or non-Arrhenius (Vyazovkin and Sbirrazzuoli, 2006). These methods allow estimates of the apparent activation energy at progressive degrees of conversion.

This paper focuses on determining the characteristics and kinetics that describes the thermal decomposition process of pine wood. The pyrolysis behavior of pine wood is studied using a thermogravimetric analyzer and the kinetic predictions are made using the non-isothermal model free kinetic methods. Generalized master plots and method of compensation effect are used to deduce the reaction mechanism governing the decomposition process. The selected methods for analyzing solid state kinetic data for pine wood pyrolysis are compared. The understanding of process is realized through kinetic equations that provides basis for further applications of the thermochemical conversion of pine wood as a potential feedstock.

## 2. Experimental method

### 2.1. Sample preparation and characterization

The pine wood sample used in the study was dried at room temperature. It was ground and sieved to an average particle size of 50  $\mu\text{m}$ . The ultimate analysis of pine wood sample showed that it contains 47.2% C, 7.7% H, and 44.9% O. It contains very less amount of sulfur (0.029%). The calorific value of pine sample was 17.34 MJ/kg, measured using a Parr 6300 bomb calorimeter. Proximate analysis of sample showed that it contains 13.58% moisture and about 95% volatiles (wet basis). It has a very less ash content of 0.835%. Moisture content of the feed has been obtained from the HR-83 Mettler Toledo Halogen Moisture Analyzer.

The trace metal analysis of pine sample has been carried out in the DRE, PS-3000 UV, Leeman Labs Inc., Inductively Coupled Plasma-Atomic Emission Spectroscopy. A high content of Potassium (1491 ppm), Calcium (841 ppm), and Phosphorus (314 ppm) is found in the sample with traces of Sodium, Iron, Aluminum, Zinc, etc.

### 2.2. Experimental techniques

The thermogravimetric analysis was carried out in DTG-60 unit (Shimadzu, Japan). Pine samples of average particle size of 50  $\mu\text{m}$  were taken in alumina crucibles with sample mass in the range of ca. 10 mg and were heated from room temperature to 700  $^{\circ}\text{C}$  at six different heating rates of 5, 10, 15, 20, 30 and 40  $^{\circ}\text{C}/\text{min}$ . Nitrogen gas at a flow rate of 100 ml/min was used as an inert purge gas to displace air in the pyrolysis zone, thus avoiding unwanted oxidation of the sample. The experimental results were tested to ensure repeatability.

## 3. Evaluation of pre-exponential factor and reaction mechanism $f(\alpha)$ for model free methods

A kinetic analysis is incomplete without the determination of pre-exponential factor and reaction mechanism. The analysis of  $E_{\alpha}$  dependencies helps in predicting kinetics and exploring the mechanisms of processes. Several methods have been proposed for evaluation of these parameters. A brief description of the methods used in the present study is as follows:

### 3.1. Using compensation parameters

Lesnikovich and Levchik (1983) reported that an apparent compensation effect is observed when a model fitting method is applied to a single-heating rate run. This compensation effect can be used for elucidating the reaction mechanism of the process using different reaction models. Substitution of different models  $f(\alpha)$  into a rate equation (Eq. (3)) and fitting it to experimental data yields different pairs of the Arrhenius parameters,  $A_i$  and  $E_i$ . The models  $f(\alpha)$  used in evaluation are given in Table 1. Eq. (3) has been provided in Supplementary information.

**Table 1**  
Expressions for  $f(\alpha)$  and  $g(\alpha)$  functions for some of the common mechanisms operating in solid state reactions.

S. No.	Model	Differential form $f(\alpha)$	Integral form $g(\alpha)$
<i>Nucleation models</i>			
P2	Power law	$(2/3) \alpha^{-1/2}$	$\alpha^{3/2}$
P3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
P4	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
P5	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
<i>Sigmoidal rate equations</i>			
A1	Avarami-Erofeev	$(3/2) (1 - \alpha) [-\ln(1 - \alpha)]^{1/3}$	$[-\ln(1 - \alpha)]^{2/3}$
A2	Avarami-Erofeev	$2(1 - \alpha) [-\ln(1 - \alpha)]^{1/2}$	$[-\ln(1 - \alpha)]^{1/2}$
A3	Avarami-Erofeev	$3(1 - \alpha) [-\ln(1 - \alpha)]^{2/3}$	$[-\ln(1 - \alpha)]^{1/3}$
A4	Avarami-Erofeev	$4(1 - \alpha) [-\ln(1 - \alpha)]^{3/4}$	$[-\ln(1 - \alpha)]^{1/4}$
F1	Prout-Tompkins	$\alpha(1 - \alpha)$	$\ln[\alpha/(1 - \alpha)]$
F2	Contracting area	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
F3	Contracting volume	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
F4	Random nucleation (1)	$(1 - \alpha)^2$	$1/(1 - \alpha)$
F5	Random nucleation (2)	$(1 - \alpha)^3/2$	$1/(1 - \alpha)^2$
<i>Diffusion models</i>			
D1	1D diffusion	$1/2\alpha$	$\alpha^2$
D2	2D diffusion-Valensi	$[-\ln(1 - \alpha)]^{-1}$	$(1 - \alpha) \ln(1 - \alpha) + \alpha$
D3	3D diffusion-Jander	$(3/2) (1 - \alpha)^{2/3} / [1 - (1 - \alpha)^{1/3}]$	$[1 - (1 - \alpha)^{1/3}]^2$
D4	3D diffusion-Ginstling	$(3/2) / [(1 - \alpha)^{-1/3} - 1]$	$1 - 2\alpha/3 - (1 - \alpha)^{2/3}$
<i>Reaction order models</i>			
R1	First order	$1 - \alpha$	$-\ln(1 - \alpha)$
R2	Second order	$(1 - \alpha)^2$	$(1 - \alpha)^{-1} - 1$
R3	Third order	$(1 - \alpha)^3$	$[(1 - \alpha)^{-2} - 1]/2$
R6	One and half order	$(1 - \alpha)^{3/2}$	$2[(1 - \alpha)^{-1/2} - 1]$

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