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### Reality in the Kinetic Modelling of Pyrolysis of Plant Fuels

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#### Abstract

This work investigated the physical nature of kinetic data for plant pyrolysis obtained by using global single component reaction model (GSCRM). The mass change and rate data of leaf and stem (twig) samples of 12 coniferous and broadleaf plant species were collected at a constant heating rate in an inert atmosphere. The kinetic data for pyrolysis of the plant samples were retrieved by using GSCRM, and then were compared with those obtained by the multi-component reaction model. It was found that the apparent activation energy for pyrolysis of leaf samples varies from 43 to 80 kJ mol<sup>-1</sup>, whereas that of the stems (twigs) ranges between 84 and 110 kJ mol<sup>-1</sup>. The activation energy determined for the decomposition of the hemicellulose, cellulose and lignin of the samples essentially fluctuates in narrow ranges. Further analysis revealed that the apparent activation energy obtained by the cellulose content of the samples, which does not correspond to the energy barrier of any reactions occurring during plant pyrolysis. Nevertheless, GSCRM is still useful in the theoretical modeling of plant pyrolysis because of its practicability and reasonable accuracy exhibited.

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Keywords: global single component reaction model; kinetic data; multi-component reaction model; plant species; pyrolysis reaction

#### 1. Introduction

The decomposition property of plant fuels has been deemed as the basic information for the design of their distillation processes and subsequent combustion systems in recently innovated bio-energy utilization industries [1]. As major fuels in wildland, plant leaves and twigs play a key role in the initiation and development of wildland fire.

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Thus, the kinetic data for plant pyrolysis reactions are essential to model the plant ignition and the sustainable combustion phenomena as well as fire initiation and development in wildland.

Kinetic analysis of plant pyrolysis is usually fulfilled by using either the global single component reaction model (GSCRM) or the multi-component reaction model (MCRM) [1-5]. By assuming the pyrolysis products only consisting of gaseous pyrolysate and char, the kinetic data can be retrieved to describe the performance of individual plants undergoing mass loss during pyrolysis [2]. The MCRM takes into account three components retained by plant fuels, i.e., hemicellulose, cellulose and lignin. The pyrolysis process is then considered to be the result of the parallel decomposition reactions of these components. The kinetic data obtained by MCRM displays certain constancy among different plant samples, and the pyrolysis process for individual plants can be well simulated on this basis [3-5]. However, due to the need to set the initial and final reactant mass for each component reaction, the MCRM is restricted in practical applications. In contrast, GSCRM is easy to use; thus, it is often applied in the theoretical modeling of plant combustion phenomena and the fire spread over wildland fuels [6, 7].

As reported in the literature, the magnitudes of the apparent activation energy (AAE) for the plant pyrolysis determined by GSCRM fall in the broad range of 69 to 140 kJ mol<sup>-1</sup> [2, 8]. So far, no detailed analysis has been done on the nature of the AAE for the global decomposition reaction of plant fuels. Kinetic parameters for individual plant pyrolysis are often evaluated by directly citing data from the literature, without considering the differences among the types of plant species as well as the parts obtained from individual plants. Therefore, the methods to evaluate the kinetic data for plant pyrolysis need to be examined.

#### Nomenclature

	A	pre-exponential factor, s <sup>-1</sup>
	Ε	activation energy for pyrolysis, kJ mol <sup>-1</sup>
	т	sample mass, kg
	п	reaction order
	$r^2$	correlation coefficient
	R	ideal gas constant, 8.314 J mol <sup>-1</sup> K <sup>-1</sup>
	t	time, s
	Т	sample temperature, K or °C
Greek symbols		
	a	conversion fraction
	β	heating rate, K $s^{-1}$
Subscripts		
	0	initial
		cellulose
	C d f	dried plant
	f	final
	H	hemicellulose
	L	lignin
	m	peak of the mass loss rate curve measured
	pk	peak of mass loss rate curve computed
	$P^{\prime\prime}$	pour of muss loss full our ve computed

In the present work, we studied the physical nature of the kinetic data for plant pyrolysis determined by GSCRM and examined the reliability of this model to predict the pyrolysis process of plant fuels. By determining the thermal decomposition kinetics of the leaf and stem (twig) samples of 12 plant species, the variation trends of the apparent kinetic data are analyzed, which enables an investigation into the mechanism responsible for the phenomena observed. Useful principles are also discussed for applying GSCRM to simulate the pyrolysis processes of different plant fuels.

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