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Prediction of product distribution in fine biomass pyrolysis in fluidized beds based on proximate analysis

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HIGHLIGHTS

- A model was developed to predict product distribution from biomass pyrolysis.
- The model is based on proximate analysis and hydrodynamics in fluidized beds.
- Relationships between product yields and fluidization condition were derived.
- Gas and char yields are a strong function of temperature and vapor residence time.

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ABSTRACT

A predictive model was satisfactorily developed to describe the general trends of product distribution in fluidized beds of lignocellulosic biomass pyrolysis. The model was made of mass balance based on proximate analysis and an empirical relationship with operating parameters including fluidization hydrodynamics. The empirical relationships between product yields and fluidization conditions in fluidized bed pyrolyzers were derived from the data of this study and literature. The gas and char yields showed strong functions of temperature and vapor residence time in the pyrolyzer. The yields showed a good correlation with fluidization variables related with hydrodynamics and bed mixing. The predicted product yields based on the model well accorded well with the experimental data.

1. Introduction

Pyrolysis is one of the most promising technologies of biomass utilization, which converts the biomass to bio-oil, char and gasses depending on the pyrolysis conditions. The pyrolysis is a thermal degradation of materials in the absence of oxygen. The pyrolysis can be a promising option for lignocellulosic biomass conversion because bio oils derived from biomass pyrolysis could act as feedstocks for producing hydrocarbons that may be readily integrated into existing petroleum refineries or future bio-refineries (Kim et al., 2013a).

In past decades, significant progress has been made in developing various pyrolysis technologies, and successfully testing them on laboratory, pilot and industrial scales. Recently, extensive research has been focused on fast pyrolysis using the fluidized bed process because of its high heat transfer and the short residence time for vapor to obtain a high yield of bio oil. Many studies have been carried out to determine the parametric influence of operating conditions on the yield of pyrolysis products of various biomasses for the design and optimum operating conditions of fluidized bed pyrolyzers. They found that the product distribution is affected by operating parameters as well as biomass type (Garcia-Perez et al., 2008; Lee et al., 2008; Heo et al., 2010).

The description of the pyrolysis process including product distribution is particularly challenging because it involves a great deal of physical and chemical transformations and produces a large number of product species. In spite of the technological progress and large amount of experimental data reported in the literature, there is still considerable debate over the reaction mechanism controlling the distribution of pyrolysis products (Garcia-Perez et al., 2008). As a result, existing models aiming to predict the rates or yields of the released pyrolytic volatiles are still supported by empirical data (Neves et al., 2011). Neves et al. (2011) suggested an empirical model to approximate the pyrolysis behavior of most biomass, where the product distribution is a function of temperature. However, the product distribution is affected by reactor type and geometry in addition to the chemical structure of the biomass

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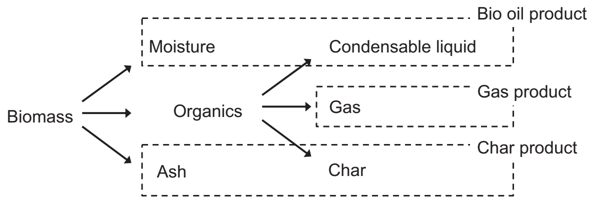

Fig. 1. Biomass pyrolysis concept for the predictive model in this study.

(Cao et al., 2004). Especially, the pyrolytic oil yield in a fluidized bed is affected by the fluidizing conditions, such as gas velocity, the physical properties of bed material and static bed height or vapor residence time (Cui and Grace, 2007). Therefore, biomass thermochemical conversion development requires methodologies for prediction of the product distribution, whereby an appropriate balance between empiricism and fundamentals related with characteristics of biomass and flow dynamics should be considered to describe the complex range of interrelated phenomena (Ioannidou et al., 2011).

When considering biomass thermal conversion, proximate analysis is one of the most important characterization methods. This consists of determining the moisture, ash, volatile matter and fixed carbon contents of the raw biomass. These values are essential as certain moisture, volatile matter and fixed carbon affect both thermal behavior and plant design (Garcia et al., 2013). Recently, a thermogravimetric model for pyrolysis product distribution in a captive batch reactor was proposed based on the proximate analysis of three agricultural residues (Ioannidou et al., 2011). The model enabled the possibility to evaluate a mass balance during the thermal treatment of the residue. However, the model did not take into account the possible activity of a second reaction (Ioannidou et al., 2011) which can possibly come from a variation in operating conditions. Also, it is still far from being applied in a fluidized bed pyrolyzer due to different operating principles between reactor types.

A predictive model was developed to describe the general trends of product distribution in fluidized bed for biomass pyrolysis. The model was made of mass balance based on proximate analysis and an empirical relationship with operating parameters. The empirical relationships between product yields and fluidization conditions in fluidized bed reactors were derived from the data in experiments of this study and literature, which address pyrolysis of fine biomass less than 2 mm to minimize the impact of internal heat transfer inside feedstock. A comparison between model results and experimental data was done to show its predictive capability for pyrolysis of various biomasses in fluidized beds.

2. Methods

2.1. Methodology and model structure

The biomass pyrolysis concept for this study is based on the fact that the precise mechanism is not clearly known because of extremely complex reactions that take place during the biomass pyrolysis process (Ioannidou et al., 2011). A simplified two-step concept of the pyrolysis was introduced to consider possible second-reaction which is affected by operating condition as Fig. 1. The concept assumes that biomass is composed of three components, i.e., organics (volatile and fixed carbon), moisture and ash based on proximate analysis. It is assumed that all organics and water are devolatilized from biomass and ash is left as part of solid residue as a first step in the pyrolysis process. The organics are partly converted into gas and char, depending on operating conditions in the second step of the pyrolysis process. Finally, unconverted organics, pyrolytic water and moisture are produced as bio oil or a liquid product from the fluidized bed reactor (Neves et al., 2011). The whole solid fraction of ash and pyrolytic char is produced as char, assuming that all the ashes in the feed material remain in the char. Taking into account the simplified concept and the proximate analysis results of the input material (moisture: M, volatile matter: VM, fixed carbon: FC and ash: A), it is possible to calculate mass balance as Eqs. (1)–(3).

$$\text{Feedstock} = M + OR + A \tag{1}$$

where OR is organics (volatiles and fixed carbon) as Eq. (2).

$$OR = VM + FC \tag{2}$$

$$\text{Product} = \text{bio oil} + \text{gas} + \text{char} \tag{3}$$

Assuming that each feedstock for pyrolysis in this model has the same content of moisture as the sample used in proximate analysis, the mass of bio oil is calculated as the sum of the moisture content and mass of unconverted organics obtained from char and gas yields as Eq. (4).

Table 1
Proximate analysis of a set of biomasses used in this study.

Raw material	Proximate analysis [wt%]				Reference
	Moisture	Volatile	Fixed carbon	Ash	
Jatropha seedshell cake	2.7	79.8	14.1	3.4	This study
Mallee *Eucalyptus loxophleba* (woody fraction)	0.0	81.9	17.6	0.5	Garcia-Perez et al. (2008)
Cassava stalk	0.0	79.9	14.1	6.0	Pattiya (2011)
Cassava rhizome	0.0	77.7	18.2	4.1	
Jatropha seedshell waste	2.7	79.8	14.1	3.4	Kim et al. (2013a)
Quercus acutissima	8.3	73.9	16.7	1.0	Lee et al. (2008)
Miscanthus sinensis	10.2	71.2	15.2	3.4	Bok et al. (2013)
Palm kernel shell	5.9	71.3	17.8	5.0	Kim et al. (2013b)
Jatropha seedshell cake	2.7	79.8	14.1	3.4	
Miscanthus sinensis var. purpurascens	8.0	74.9	15.7	1.4	Heo et al. (2010)
Sugar cane bagasse	6.8	76.9	10.8	5.3	Carrier et al. (2013)
Corn cob	4.6	79.9	13.7	1.6	
Corn stover	8.5	76.7	8.2	6.1	
Eucalyptus grandis	6.2	80.9	12.4	0.5	
Cassava rhizome	1.8	81.5	13.1	3.5	Pattiya and Suttibak (2012)
Cassava stalk	2.4	81.2	11.2	5.1	
Japanese larch	8.8	91.0[a]		0.2	Park et al. (2008a)
Radiata pine sawdust	7.6	92.2[a]		0.2	Park et al. (2008b)
Oriental white oak	10.4	87.6[a]		2.0	Park et al. (2009)

[a] Organics (sum of volatile and fixed carbon).