Kinetics of the release of elemental precursors of syngas and syngas contaminants during devolatilization of switchgrass

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A B S T R A C T

In this study, the results from laboratory measurements of the devolatilization kinetics of switchgrass in a rapidly heated fixed bed reactor flushed with argon and operated at constant temperatures between 600 and 800 °C was reported. Results indicate that switchgrass decomposes in two sequential stages during pyrolysis: stage I involves the evaporation and devolatilization of water and extractives and stage II involves that of hemicellulose, cellulose, and lignin. The estimated global activation energy for stage II increased from 52.80 to 59.39 kJ/mol as the reactor temperature was increased from 600 to 800 °C. The maximum conversion of carbon, hydrogen, oxygen, sulfur, and nitrogen ranged from 0.68 to 0.70, 0.90 to 0.95, 0.88 to 0.91, 0.70 to 0.80, and 0.55 to 0.66, respectively. The retention of alkali and alkaline earth metal (AAEM) species in the solid char after complete pyrolysis was significantly higher than in the original feed, indicating the importance of AAEM species in subsequent char processing.

1. Introduction

Pyrolysis and gasification are the two most common thermochemical conversion methods used to convert lignocellulosic biomass into fuels, chemicals, and materials to significantly displace the world demand for crude oil and coal (McKendry, 2002; Oyedeji et al., 2016). In the context of lignocellulosic thermochemical conversion, pyrolysis involves the thermal decomposition of biomass in the absence of oxygen to produce bio-oil as the major product, alongside biochar and pyrolytic gases (Basu, 2010). In contrast to pyrolysis, gasification is the thermal decomposition of biomass in the presence of limited and substoichiometric oxygen levels to yield producer gases as the major product followed by biochar (Abdoulmoumine et al., 2014). Although occurring in different environments, pyrolysis (also referred to as devolatilization) is the commencing chemical step during gasification which leads to the formation of volatiles that later undergo secondary reactions (intra- and extra-particle) to produce the final producer gases (McKendry, 2002).

Lignocellulosic biomass is a complex composite of water, volatiles, ash, and char from a thermochemical conversion standpoint. During pyrolysis, lignocellulosic biomass first reacts endothermically and

irreversibly to produce a mixture of primary gases (CO, CO_2, H_2O, H_2, and CH_4) and primary tars. Subsequently, the primary tar constituents are further cracked into secondary and tertiary tars as well as primary gases at temperatures typically observed for gasification (Fig. 1) (Milne et al., 1998). In addition to the production of primary constituents, gases generated during pyrolysis usually contain minor but significant quantity of undesirable contaminants. These contaminants include sulfur containing compounds (such as H_2S and COS), nitrogen containing compounds (such as NH_3 and HCN), and trace amounts of metals (such as K and Ca) (Abdoulmoumine et al., 2015). The presence of contaminant compounds in the main gas products is one of the major concerns for the commercial deployment of gasification technologies because they are difficult and expensive to remove (Heyne et al., 2013). A recent techno-economic analysis demonstrated that gas cleaning to remove contaminants accounts for the largest share of the capital cost and a significant share of the operating cost (Tan et al., 2015).

Thus, understanding biomass pyrolysis behavior and kinetics is essential to maximize desirable products and minimize contaminant compounds during biomass gasification. Hyphenated thermogravimetric analysis (TGA) techniques, such as TGA coupled with Fourier transform infrared (FTIR), gas chromatography (GC), or mass

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$$N_{species} + S_{species} + Metal_{species}$$

$$Volatile \rightarrow Primary\ Tar \rightarrow Secondary\ Tar \rightarrow Tertiary\ Tar$$

$$Biomass$$

$$CO + CO_2 + H_2O + CH_4 + H_2$$
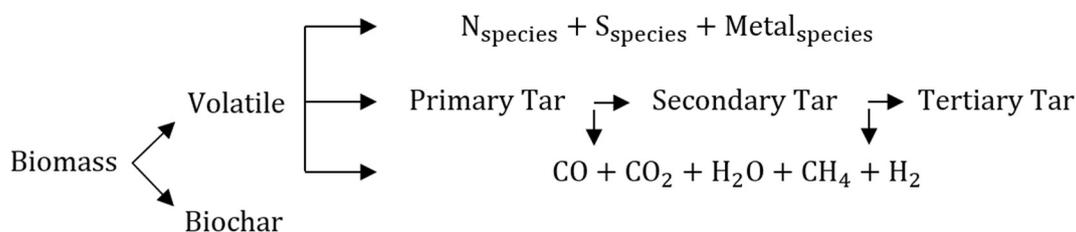
$$Biochar$$

Fig. 1. Biomass decomposition during pyrolysis.

spectrometry (MS), are common methods used to study the fundamentals of biomass pyrolysis. Such studies have been carried out with thin layered samples in mostly non-isothermal conditions (Bui et al., 2016; Di Blasi and Branca, 2001; Lv et al., 2004; Wang et al., 2007). Although TGA techniques are convenient for biomass pyrolysis modeling, resulting kinetic parameters have been criticized because of the inherent inability to accurately access the kinetic parameters obtained from TGA and the high sensitive of kinetic parameters to experimental noise (White et al., 2011).

Other investigators have utilized fixed-bed reactors to study biomass pyrolysis. Bilbao et al. (1995) achieved heating rates ranging from 2 to 53 °C/min during the pyrolysis of cellulose and pine sawdust in a tubular reactor. They found that gas yield increased as the pyrolysis temperature and heating rate increased. Raveendran et al. (1996) demonstrated that the distribution of pyrolysis products was unaffected by the interactions among individual biomass components by studying pyrolysis of several isolated biomass components (cellulose, lignin, hemicellulose, and extractives) and biomass feedstocks in a fixed-bed pyrolyser.

Several reaction kinetics models have been proposed for biomass pyrolysis. Radmanesh et al. (2006) employed a model with three independent parallel reactions to explain the production of char during the pyrolysis of Canadian beech wood, sawdust, and Chinese rice husk. The authors assumed a simple first-order rate equation to model the generation of H_2, CH_4, CO, and CO_2. Seo et al. (2010) also modeled the formation of gases from the pyrolysis of sawdust using the same kinetic model. In another study, Sadhukhan et al. (2008) proposed a parallel-series kinetic model to predict the pyrolysis behavior of coal–biomass blends. These and other similar models suffer from the fact that they do not resolve details about the species in the reaction products. Instead, they lump the pyrolysis products (e.g., light gases, oils, and char) because of the hundreds of molecular species that are produced (Tihay and Gillard, 2010). In some other cases, only the major gas products (CO, CO_2, H_2, and CH_4) were accounted for. Hence, it is not possible to derive any significant information about potential contaminant species that might be present in the initial pyrolysis products.

The objective in this study was to improve the understanding of the rates and distributions of syngas and contaminant precursor species that are released from switchgrass during pyrolysis. The methodology used was based on a twofold approach: i) to experimentally measure the release of selected elements during the pyrolysis of switchgrass that contribute to potential syngas and syngas contaminant species in the products and; ii) to develop global kinetic rate expressions for the release of these elements during experimental switchgrass pyrolysis.

This study was focused on the tracking of carbon, hydrogen, oxygen, nitrogen, sulfur, potassium, calcium, and magnesium due to their importance in syngas and syngas contaminant species in pyrolysis products or their derivatives.

2. Materials and methods

Fig. 2a illustrates the experimental flowchart followed in this study. Switchgrass (*Panicum virgatum*) was used for this work because of the forecasted importance of herbaceous biomass to a sustainable biomass supply system and its abundance in the United States. Switchgrass
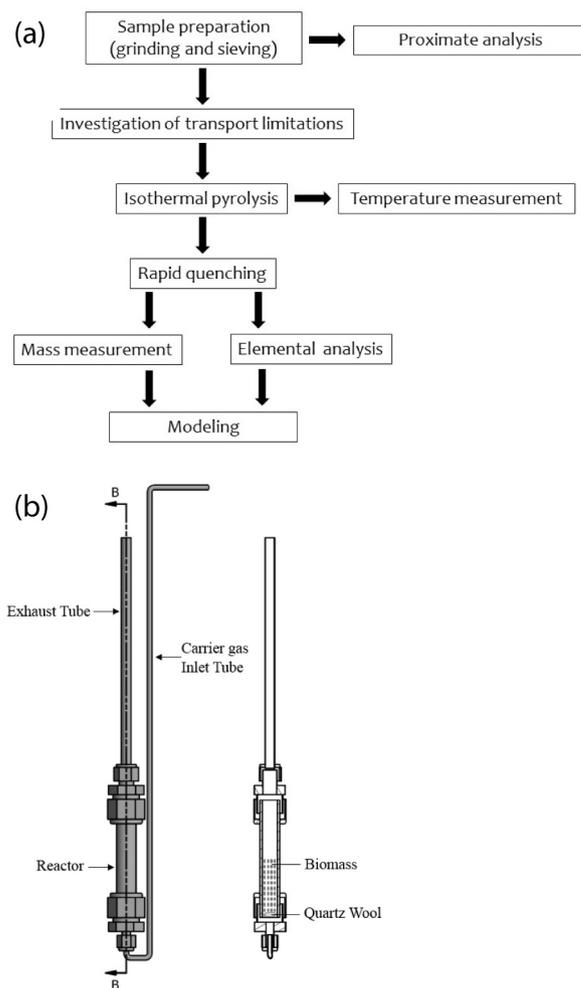
(a)

Sample preparation (grinding and sieving) → Proximate analysis

Investigation of transport limitations

Isothermal pyrolysis → Temperature measurement

Rapid quenching

Mass measurement   Elemental analysis

Modeling

(b)

Exhaust Tube

Carrier gas Inlet Tube

Reactor

Biomass

Quartz Wool

Fig. 2. a) The biomass pyrolyser used in this study and cross-sectional view of the reactor and b) experimental flowchart.

samples were ground with a knife mill (model No. 3, Thomas Wiley, Swedesboro, NJ) fitted with a 2 mm screen size. Then, the samples were sorted by size with a Ro-Tap screen shaker (model RX – 29, W.S. Tyler, Mentor, Ohio) fitted with 4 ISO screens (2.36 mm, 0.850 mm, 0.425 mm, and 0.180 mm).

The moisture content was determined following ASABE Standard S358.3 (ASABE, 2012) and was 4.34 wt% (wet basis) with a standard deviation of 0.17 wt%. Additionally, the volatile matter content was determined according to ASTM Standard D3175-11 (ASTM, 2011) and was 82.24 wt% (dry basis) with a standard deviation of 0.05 wt%. The ash content was measured according to NREL method (NREL, 2005) and was 4.31 wt% (dry basis) with a standard deviation of 0.09 wt%. Finally, the fixed carbon content was calculated by difference from the values of volatile matter content and ash content and was 13.45 wt% (dry basis) with standard deviation of 0.09 wt%.