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Modeling, experimental validation and optimization of Prosopis juliflora fuelwood pyrolysis in fixed-bed tubular reactor

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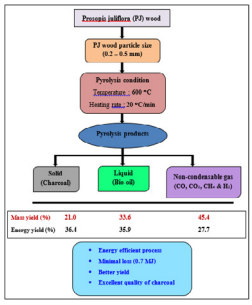
GRAPHICAL ABSTRACT



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ABSTRACT

This work studied the optimal conditions for pyrolysis of Prosopis juliflora wood in fixed-bed tubular reactor. The optimal conditions are measured by performing pyrolysis experiment with respect to wood properties such as particle size, moisture and pyrolysis condition such as, temperatures, heating rates. Higher solid yield (36.8%) was recorded for a slower heating rate of larger particle size at lower temperatures. Further, higher liquid yield (38.3%) was observed while maintaining high heating rate and temperature. It is observed that with increase in particle size, the yield of char and gas decreases and bio-oil increases. The literature reported biomass pyrolysis kinetic model is validated for Prosopis juliflora wood. The kinetic models are able to predict the performance of fixed-bed tubular reactor in terms of pyrolysis product properties. The validated kinetic model may be used for the design of commercial fixed bed pyrolysis reactor to process Prosopis juliflora wood.

1. Introduction

The prolonged use of fossil fuels has caused a greenhouse effect that induced the climate change and global warming. According to U.S. EIA's CO_2 emission data, the emissions level is projected to increase from 31.2 billion metric tons in 2010 to 36.4, 45.5 billion metric tons by 2020 and 2040 respectively (EIA, 2013). Further, to minimize the greenhouse effect there is an increasing focus on usage of the bioenergy. Bioenergy is proven for carbon-neutral energy sources. Prosopis juliflora (PJ) wood is considered as a potential source of biomass because they are abundantly available, low cost and sustainable to growth even in the adverse climatic conditions. It is an exogenous species and can grow faster and attain a yield of about 2.5 tons of wood/ha/year under drought and arid conditions (Pasha et al., 2008). PJ wood belongs to Leguminosae family, which has been widely disseminated over the past 150 years in India. Many products can be extracted from PJ wood, such as ethanol from stem wood (Naseeruddin et al., 2017), bio-oil from branches (Suriapparao et al., 2015) and polymer composites

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from bark (Saravanakumar et al., 2013).

Biomass pyrolysis is an endothermic reaction in which biomass is converted into charcoal, bio-oil and gases at high temperature (~500 °C) in the absence of oxygen. It involves complex simultaneous reactions such as dehydration, depolymerization, fragmentation, re-polymerization, condensation and carbonization. Even though many researchers explored the experimental and modelling aspects of biomass pyrolysis, still there is no ideal kinetic model that can be adopted for design and optimization of pyrolysis reactor. Recently, (Fantozzi et al., 2016) investigated and optimized a kinetic mechanism of glycerol pyrolysis process for the reactor design purposes. Therefore, in order to design a pyrolysis reactor, it is noteworthy to define a reaction kinetics and governing mechanism. In literature, the pyrolysis of biomass is modelled using two stage of kinetic reaction mechanism. In first stage reaction, the biomass is converted into char, bio-oil and gases. Further bio-oil and gases are broken into components of gases and bio-oil during the secondary stage reaction (Babu and Chaurasia, 2003; Sadhukhan et al., 2014).

The quality and yield of the products produced from wood pyrolysis is sensitive with respect to residence time, particle size, moisture in the feedstock, type of biomass, temperature, heating rate, pressure, flow rate of carrier gas and type of reactor, respectively. The charcoal yield is increased, when pyrolysis is performed at low temperature, slow heating rate and longer residence time. However, the quality of the charcoal in terms of heating value is found to be very low. The wood pyrolysis at higher temperature, heating rate and longer residence time leads to completion of carbonization phase, that will produce high gas yield and low solid charcoal and liquid bio-oil yield (Williams and Besler, 1996).

The charcoal, bio-oil yield increases and gaseous product yield decreases with increase in particle size (Suriapparao et al., 2015). This phenomenon is occurring due to the change in mass and heat transfer resistance with respect to particle size. The effect of particle size on gas yield can be explained using following two phenomena: (i) the smaller wood particle provides larger surface area and that will improve the heat and mass transfer phenomenon between wood particle and gas medium. A single smaller wood particle can be assumed as a lumped system. In a lumped system, the temperature distribution in wood particle will be uniform and raises to its pyrolysis temperature much faster than larger particle. In another aspect, the reduced mass transfer resistance improves back diffusion flux of product gases from wood to gas phase. Due to improved mass and heat transfer, the smaller wood particle leads to completion of carbonization phase. The improved carbonization process will be producing more light gases and less char and condensate, (ii) in the case of larger particle size, the particle will be acting as a distributed system, wherein temperature and gas concentration will be varying across the particles. Due to the heat transfer resistance, initially the carbonization reaction will be occurring in the particle outer core then, it will be moving towards the particle interior side. Simultaneously due to the high mass transfer resistance, the back diffusion of product gas will be reduced, that will increase the resident time of product gas in a wood particle, that will be enhancing secondary reaction (thermal cracking) between product gas and volatile matter to produce more liquid tar and less product gas. Similarly, due to high heat transfer resistance, the centre portion of bigger wood particle is not able to carbonize completely and this process leads to increased charcoal yield, but they are not fully carbonized. The maximum energy of both charcoal and bio-oil was recovered from the larger particle size of biomass whereas lowest energy was recovered in the form of non-condensable gases. The gases produced from pyrolysis is expected to have all major light gases such as CO_2, CO, CH_4 and H_2 (Granada et al., 2012).

Considering above arguments, the identification of optimal condition for pyrolysis of PJ wood in a pyrolysis reactor is very important aspect to produce high quality char and bio-oil as a by-product, such that the green energy produced from the process can be maximized. Also another important requirement, i.e. specific to the Indian market is that the pyrolysis unit is expected to have very low capital expenditure, easy operating and maintenance procedure. As reported in literature, the advanced pyrolysis reactors such as, microwave (Suriapparao et al., 2015), fluidized and entrained bed reactors (Sadhukhan et al., 2014) may able to provide better performance than the fixed-bed tubular reactor. However, they are expensive technology and it requires highly skilled resources for operation and maintenance activity. Therefore, due to above said Indian market requirements; the fixed-bed tubular reactor is chosen for this research work. To the best of our knowledge, this is the first study on identification of optimal condition for pyrolysis of PJ wood in a fixed-bed tubular reactor. To achieve same, the pyrolysis of PJ wood is carried out in a fixed-bed tubular reactor by varying the particle size, moisture in the feedstock, heating rate and temperature. Further to enable model-based pyrolysis reactor design and optimization for PJ wood, the kinetic modeling and its validation, using the experimental data is presented in this article.

2. Materials and methods

2.1. Kinetic modeling of PJ wood pyrolysis

The kinetic modeling of two-step parallel reaction mechanism for PJ wood is given in Fig. 1. It can predict the yield of pyrolysis products, which are char, volatiles (liquids) and gases for different operating conditions.

As shown in Fig. 1a, Babu and Chaurasia et al., proposed a kinetic model (Babu and Chaurasia, 2003) for biomass pyrolysis. In that, the primary reaction products such as volatiles and gases (G_1) and Char (C_1) will be reacting as per reaction (3) and lead to secondary products of volatiles and gases (G_2), and char (C_2) whose compositions are different from the primary ones. The reaction rate equation for individual components during the pyrolysis are given below,

$$\frac{dC_B}{dt} = -(k_1 + k_2)(C_B)^{n_1} \tag{1}$$

$$\frac{dC_{G_1}}{dt} = k_1(C_B)^{n_1} - k_3(C_{G_1})^{n_2}(C_{C_1})^{n_3} \tag{2}$$

$$\frac{dC_{C_1}}{dt} = k_2(C_B)^{n_1} - k_3(C_{G_1})^{n_2}(C_{C_1})^{n_3} \tag{3}$$

$$\frac{dC_{G_2}}{dt} = k_3(C_{G_1})^{n_2}(C_{C_1})^{n_3} \tag{4}$$

$$\frac{dC_{C_2}}{dt} = k_3(C_{G_1})^{n_2}(C_{C_1})^{n_3} \tag{5}$$

where C_B, C_{G1}, C_{C1}, C_{G2} and C_{C2} are the concentrations of raw biomass, primary volatiles and gases, primary char, secondary volatile and gases and secondary char, respectively. k_1, k_2 and k_3 are the rate constants for the devolatilization of biomass and n_1, n_2 and n_3 are the order of reaction.

The rate constant equation for primary and secondary reaction are given below,

$$k = k_1 + k_2 = A\exp[-E/RT] \tag{6}$$

$$k_i = A_i \exp[-E_i/RT],\ i = 1, 2, 3 \tag{7}$$

The temperature and time have a linear relationship as per the TGA experimental procedure and the equation can be written as:

$$dT = (\beta)dt + T_0 \tag{8}$$

The initial condition for kinetic equation follows;

$$C_B(0) = 1,\ C_{G1}(0) = 0,\ C_{G2}(0) = 0,\ C_{c1}(0) = 0,\ C_{c2}(0) = 0 \tag{9}$$

As shown in Fig. 1b, the waterloo model assumes that the primary reactions produce the char, gas and oil. The secondary reaction proceed