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Investigation of particle level kinetic modeling for babul wood pyrolysis

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ABSTRACT

To design a large-scale pyrolysis reactor, a complete particle level model was developed using pyrolysis of babul wood. Babul wood, the abundant woody biomass in India, is a highly reactive and promising feedstock for pyrolysis and considered as a case study in the present work. Thermo-balance was used to devolatilize the wood particles at different heating rates from (10 to 20 K min^{-1}), thereby estimate the intrinsic kinetics parameters. Non-condensable gases released from wood pyrolysis were also modeled and derived the kinetic parameters. Large wood single particle dimension of L/D ~3.5 was chosen to investigate the pyrolysis reaction and developed a particle level model which involves both heat transfer and chemical reactions phenomena. Particle model developed was simulated with intrinsic kinetic parameters generated from kinetic models. Two-step consecutive model with different reaction orders (m = 1, n = 2) was found to explain the experimental data very well. Additionally, optimum conditions for maximum product yields and detail characterization of bio-oil was carried out using different analytical techniques.

1. Introduction

Biomass is a renewable energy source, environment friendly as well as abundant in nature. Currently, about 10% (50 EJ) of the world energy was supplied by several biomass-derived fuels [1–4]. In the present work, babul wood biomass was considered as a case study. Babul is a high energy density source and abundant in India (110 M Tonne $year^{-1}$), as compared to other biomass crop residues such as rice husk, groundnut shell, corncob, cotton stalk, etc [5]. Babul trees can tolerate extremes of temperature and moisture which suits for planting on marginal lands, also can survive both drought and flooded conditions. Babul tree grows quickly, coppices readily and a source of fixing nitrogen, improving soil fertility and its leaves and pods are widely used as fodder [6,7]. The babul wood contains 69.14 wt% volatile matter and 18.81 wt% fixed carbon with minimal amount of ash 1 wt%.

As a source of energy, it is known that biomass can be converted into highly efficient fuel through thermochemical conversion processes such as pyrolysis [8–10]. There are several studies reported in literature on kinetics of pyrolysis of biomass. Antal and Varhegayi [11] performed the thermal degradation of biomass under non-isothermal conditions and described the reaction as single-step kinetic model with first order and high activation energy (238 kJ mol^{-1}). It was also found that pyrolysis reaction is endothermic reaction from this kinetic model. Whereas, Milosavljevic and Suuberg [12] describes the biomass thermal degradation by two-stage consecutive reaction, first reaction occurs at low temperature with high activation (218 kJ mol^{-1}) and second reaction occurs at high temperature with low activation energy (150 kJ mol^{-1}). While, Teng and Wei [13] modeled biomass thermal degradation using three independent parallel first-order reactions assuming the composition of biomass as hemicellulose, cellulose and lignin.

Manya et al. [14] investigated the thermal degradation of different lignocellulosic biomass and modeled the reaction by considering degradation of hemicellulose and cellulose as first-order reaction and decomposition of lignin as third order reaction. This formulated model was more flexible to describe the decomposition of pyrolysis and was used by many researchers [15–18].

A mass loss kinetic model explains several reaction steps that occur during pyrolysis but does not predict the rate of release of the condensable/non-condensable gases. Less attention has been paid to predict the total range of products, including stable end-product gases such as H_2, CH_4, CO and CO_2 and tar. The study of release of these gases during pyrolysis with respect to temperature and time are called evolution kinetics. The evolution of non-condensable gases has been studied separately using thermo-balance connected to mass spectrometer [19] or Fourier transformation infrared spectrometer [20,21]. Fixed/

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Nomenclature

CO_2	Carbon dioxide
CO	Carbon monoxide
CH_4	Methane
CHNS	Carbon, hydrogen, nitrogen sulfur
DAEM	Distributed activation energy model
DTG	Differential thermogravimetric
FID	Flame ionisation detector
FTIR	Fourier-transform infrared spectroscopy
GC	Gas chromatography
HPLC	High performance liquid chromatography
H_2	Hydrogen
kJ	Kilo joule
mg	Milligram
mL	Milliliter
MJ	Mega joule
MS	Mass spectrometer
MSE	Mean squared error
NO_x	Nitrous oxide compounds
PID	proportional–integral–derivative
s	seconds
SO_x	Sulfur oxide compounds
TCD	Thermal conductivity detector
TGA	Thermogravimetric analyzer
α	Fractional conversion
β	Heating rate(dT/dt)
C	Mass fractions of biomass
E_i	Activation energy of the ith reaction, kJ mol^{-1}
E_M	Mean activation energy
σ	Standard deviation
k	Rate constant
K	Kelvin
mf	Ultimate yield of char during the reaction
mol	Mole
n	Reaction order
I	Mass fraction of intermediate
R	Universal gas constant (8.3144×10^{-3} kJ mol^{-1} K^{-1})
V_i	Yield of gas component at time t
V_i^*	Ultimate attainable yield for each gas
t	Time, s
T	Temperature, K
µm	Microgram
W	Mass fraction of char
x	Yield of intermediate of solid during the reaction/stoichiometric coefficient

fluidized bed reactors connected to gas chromatography equipped with thermal conductivity detector have also been employed [22,23].

The derived kinetic parameters based on devolatilization of biomass and species evolution are used to predict single particle pyrolysis model, which are useful in reactor design of large scale. Most of the studies are performed based on the shrinkage models. However, single particle pyrolysis can take place with or without shrinkage. Bellais et al. [24] have modeled pyrolysis based on uniform shrinkage, shrinking shell and shrinking cylinders, to validate the experimental data for mass loss versus time. Other parameters that are important are extent of volume loss and the kind of structural modifications the particle undergoes. Guillaume et al. [25] have presented a single biomass particle modeling that involves strong interactions between chemical kinetics, both in the solid, gas phase, and heat/mass transfer phenomena.

Bamford et al. [26] studied mass loss of wooden sheets and modeled it based on conservation equation of mass and heat inside the decomposing wood with chemical reaction. Further advances in the modeling have been made by incorporating internal convection and variable transport properties effects [27,28]. In another study, the conservation equation for momentum to model the motion of the vapors inside the solid has also been incorporated [29].

Biomass as fuel currently under research because there are large varieties of heterogeneous biomass feedstock available in nature whose properties may influence its application as fuel. The de-polymerization of biomass feedstock results in variety of different chemicals depending on its composition. Thus, there need to develop further comprehensive biomass pyrolysis models.

The overall aim of this study was to investigate whether a mathematical model using kinetic parameters from thermogravimetric analysis (TGA) and gas species evolution analysis can adequately predict the essential characteristics of single biomass particle pyrolysis in a fixed bed. To produce biofuels through pyrolysis in a continuous mode, it is necessary to study kinetics of pyrolysis and predict overall performance of a large scale pyrolyzer. Most of the previous studies either provide kinetic data or propose a particle model based on the kinetics available in literature. The present work is a complete study in itself that covers kinetics, gas evolution and particle level model necessary for a reactor design. The approach presented here can be extended to other biomass feedstocks, coal and solid waste.

The article organized as follows: First we provide the characteristics of the biomass of interest i.e. babul wood, followed by the experimental methods and detail physio-chemical characterization, intrinsic kinetics, gas evolution kinetics, and particle level modeling. Various intrinsic kinetic models are then screened to explain the kinetic data. The chosen kinetic model and the gas evolution kinetics are then used to propose a particle level model.

Table 1
Characteristic properties of babul wood and other similar feedstocks (d.b.) (wt%).

	Babul wood	Corn cob	Cotton stalk	Groundnut shell [30]	Rice husk [31]	Pine wood [32]	Platanus wood [33]	Eucalypt wood [34]
Moisture (as received)	10.88	6.3	7.5	8.0	6.63	7.52	9.88	9.7
volatiles matter	77.6	71.41	66.16	64.63	61.53	84.76	84.1	78.9
fixed carbon	21.1	25.75	27.15	29.45	14.26	14.91	15	21.0
ash	1.3	2.84	6.68	5.91	17.5	0.33	0.9	0.7
carbon	50.1	43.8	44.19	42.02	34.87	47.1	41.58	50.4
hydrogen	6.11	6.41	6.3	5.8	5.3	5.9	5.14	6.0
nitrogen	0.5	0.64	0.74	1.88	0.8	0.04	0.24	0.01
sulfur	0.0	0.0	0.0	0.0	0.03	0.06	0.14	0.01
oxygen (by difference)	43.29	49.13	48.74	50.28	59.02	46.4	42.22	43.5
bulk density kg m^{-3}	785	282.38	230.5	331.2	166.2	370–420	N.A	780–1000
higher heating value (MJ kg^{-1})	19.53	15.2	15.24	20.2	13.95	16.91	16.95	17.77