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Non-isothermal pyrolysis of torrefied stump – A comparative kinetic evaluation

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HIGHLIGHTS

- The first pyrolysis kinetic study of torrefied stump.
- Three pseudo-components model with $n \neq 1$ is the most suitable for the kinetics.
- The torrefied stump has higher activation energy than the untreated stump.

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ABSTRACT

The pyrolysis of native and torrefied stump materials was studied in the kinetic regime by means of a thermogravimetric analyzer operated in the non-isothermal fashion. Three different kinetic models applicable to biomass pyrolysis were evaluated for the collected data, which include a single-reaction model, two three pseudo-components models, and a distributed activation energy model (DAEM). It was shown that the single-reaction model was not suitable to simulating stump biomass pyrolysis. The other models including the three pseudo-components model with $n = 1$ and $n \neq 1$, and the DAEM demonstrated very good fits between simulated and experimental curves. However, the three pseudo-components model with $n \neq 1$ is recommended as the most suitable for simulation and prediction of kinetic behaviour of slow pyrolysis for both untreated and torrefied stump, considering that it offers the best fits to the experimental data and that the generated reaction orders are realistic, being slightly higher than unity. It appears that the torrefied stump has higher activation energy than its native material. The activation energy predicted for the native stump pyrolysis is in the range of 105.2–108.9 kJ/mol, 183.5–183.6 kJ/mol, and 40.3–48.01 kJ/mol for hemicelluloses, celluloses, and lignin, respectively. That for pyrolysis of the stump torrefied at 200 °C is 105.13–111.19 kJ/mol, 183.68–185.79 kJ/mol, and 40.49–50.70 kJ/mol, respectively.

1. Introduction

Biomass resources have been used by mankind for a very long time in order to meet its primary energy needs and to power human development. With increasing concerns of human impacts on the environment and climate, biomass is once again considered as an important energy source to meet a significant portion of the increasing energy demand in the modern world. The challenges today in using biomass as fuel are various, but can be best related to scale and density, among which the scale of energy demand by far exceeds all the needs in past [1]. Both the increasing world population and the energy intensity of modern life compound the high demand for energy as never before. Consequently, the extraction of biomass from forest and agriculture for use as fuel has become a common practice in various countries and increased the burden on the soil. In addition to the problems of land-use conflict and increased food price, today people even fear the problem of competing for wood between the paper and energy industries [2].

One way to meet the growing demand of forest biomass for energy application, without increasing the annual harvesting volume of stem wood, is to utilize tree stump, which may be defined as all belowground and aboveground wood and bark mass of a tree beneath the merchantable timber cross-section. It is reported that when tree stumps and small round-wood from thinning are used to replace fossil fuels, the potential CO_2 reduction will be about

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Nomenclature

Abbreviation

DAEM	distributed activation energy model
TG	thermogravimetry
TGA	thermogravimetric analysis
DTG	derivative thermogravimetry

Symbols

A	pre-exponential factor
E_a	activation energy
E_o	mean activation energy
$f(E)$	distribution function of activation energy
T	absolute temperature, K
R	universal gas constant, 8.314 J mol^{-1} K^{-1}
n	reaction order
t	time of conversion
m_0	the initial mass
m_f	the final residual mass
m_t	the mass of the sample at time t
α	degree of conversion
x	mass fraction of released volatiles
V	accumulated volatiles produced
V^*	final accumulated volatiles produced
β	heating rate
σ	standard deviation

Subscript

i	ith component

four times as great as when only logging residues are used with a traditional chip system [3]. However, tree stumps have not yet been recognized as a bioenergy resource. For these reasons, a study on torrefaction of Norway spruce stump wood for energy application has been performed [4]. Torrefaction is a pretreatment process for biomass fuels, in which the biomass is slowly heated to 200–300 °C in the absence or little contact with oxygen [5–7]. Torrefaction alters the chemical structure of biomass hydrocarbon and increases its carbon content while reducing its oxygen [5,6]. In addition, torrefaction increases the heating value and grindability of the biomass and makes the biomass hygroscopic. These attributes thus enhance the market value of biomass fuel for energy supply and transportation.

Due to the aforementioned benefits, torrefaction had been being considered for effective utilization of biomass as a clean and convenient solid fuel [7]. A significant effort has been made to understand better the effects of the torrefaction conditions on the yield and fuel properties of the solid product. However, the behaviour of torrefied biomass during pyrolysis, gasification or combustion has received little attention [8], considering that changes in chemical structure of biomass by torrefaction would cause changes in the reaction mechanisms and kinetics of further thermochemical conversions of biomass, which include pyrolysis, gasification, and combustion [8].

Apart from combustion and gasification, the kinetics of biomass pyrolysis is of great importance in the context of energy recovery [9]. Modelling the processes of pyrolysis, gasification, and combustion of biomass requires the kinetics of mass loss and gas evolving. Kinetic evaluation of the data obtained from isothermal or non-isothermal thermogravimetric analysis (TGA) of biomass fuels is needed for the design of thermochemical conversion system. For these reasons, past research in the field was very active with numerous reports in open literature sources, which can be found in a recent review [10]. However, kinetic studies which take into account the pyrolysis of hemicellulose, cellulose and lignin, already developed for biomass, have not yet been fully applied to torrefied fuels [8]. Only few attempts [8,11,12] can be found in the open literature. Ren et al. [12] described the thermogravimetric (TG) curves in nitrogen of torrefied sawdust. A one-step global kinetic model was employed for extracting the kinetic parameters from the derivative thermogravimetric (DTG) curves. Broström et al.[8] employed a multi pseudo-components kinetic model built on the basis of n-order independent parallel reactions to study the thermal decomposition of torrefied spruce wood chips in nitrogen, as well as in air. Furthermore, Tapasvi et al. [13] established even more detailed and more complex model, mainly based on the distributed activation energy model (DAEM), to describe better the pyrolysis kinetics of biomass, which is claimed suitable for pyrolysis of torrefied biomass as well.

Biomass pyrolysis is a very complex process due to differences in reactivity of biomass constituents. Different chemical reactions associated with the thermal decomposition of each biomass constituent may occur, which lead to very different levels of modelling. A recent review [10] of biomass pyrolysis kinetics indicated that, while some workers tried extreme simplifications, others used elaborate mechanisms to explain several details. In kinetic modelling and simulation, however, Levenspiel [14] argued that it is essential to select a kinetic model which reasonably represents the physical phenomenon under investigation without too many mathematical complexities. It is of little use to select a model which very closely mirrors reality but which is so complicated that we cannot do anything with. Having this argument in mind, perhaps, a study on pyrolysis of biomass with a comparison of different kinetic models was reported by Hu et al. [15]. However, this work was performed for untreated biomass only and the DAEM was not included. This along with the reasons discussed above suggested a need to perform a similar study for torrefied fuels and to include the DAEM for kinetic evaluation. Therefore the study reported in this present paper was carried out for Norway spruce stump chips, untreated and torrefied, using a TG analyzer operated in the non-isothermal fashion. Apart from the model-free Ozawa method, three different kinetic models applicable to biomass pyrolysis were evaluated for the collected data, which were single-reaction model, three-pseudo-component model, and DAEM. The objective of the present study was manifold. The first objective was to confirm the study by Hu et al. [15] (Sections 4.1–4.3). The second was to compare the kinetic behaviour between untreated and torrefied stump chips (Sections 4.3–4.5). The third, being the primary objective of the present study, was to identify among the models based on independent parallel reactions the most suitable one for the kinetic evaluation of torrefied stump fuels, from which the kinetic parameters were extracted (Sections 4.3–4.5).

2. Kinetic modelling

Despite the complexity, the process of biomass pyrolysis may be represented by a simplified kinetic model which involves lumping (pseudo) [16,17] of the complicated multiple reactions together as a single first- or nth-order reaction according to the following global reaction scheme: Solid biomass → Char + Volatiles.