Industrial Crops and Products 92 (2016) 244–254

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

# Influence of torrefaction pretreatment on the pyrolysis of Eucalyptus clone: A study on kinetics, reaction mechanism and heat flow

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ARTICLE INFO

*Article history:*
Received 3 February 2016
Received in revised form 3 August 2016
Accepted 7 August 2016
Available online 11 August 2016

*Keywords:*
Eucalyptus clone torrefaction
Torrefied biomass
Non-isothermal kinetics
Torrefied biomass pyrolysis
Pyrolysis
Reaction mechanism

ABSTRACT

The adverse nature of biomass requires specific pretreatment processes to better utilize it in bioenergy applications, and torrefaction is one of the most recognized thermal pretreatment methods. In this regard, we studied the effect of torrefaction pretreatment on kinetics, reaction mechanism and heat flow during the pyrolysis of biomass by making a comparative analysis between the pyrolysis of dried and torrefied Eucalyptus wood. Torrefied biomass was produced at three temperatures, namely 250, 275 and 300 °C. Pyrolysis was performed at 700 °C. The char yield during pyrolysis increased from 22.39 percent to 36.34 percent when the torrefaction temperature was increased from 250 to 300 °C. Kinetic analysis showed that torrefied biomass has higher activation energy values than dried biomass. The reported activation energy values for dried biomass were within the range of 165–185 kJ/mol, and for the biomass torrefied at 300 °C they were within the range of 180–245 kJ/mol. We used two different approaches, namely master plots and kinetic compensation parameters, to identify the reaction mechanism. The results showed that torrefaction treatment had an effect on the reaction mechanism of the biomass pyrolysis. The reason could be the degradation of hemicellulose during torrefaction, and thereby the formation of smaller molecules during the pyrolysis of torrefied biomass. The heat flow data from differential scanning calorimetry (DSC) showed that pyrolysis started with exothermic reactions for dried samples, and endothermic reactions for torrefied samples. The results presented provide valuable insights into increasing the understanding of the pyrolysis of torrefied biomass.



## 1. Introduction

Some of the most concerning environment-related issues include global warming, and the increasing usage and depletion of fossil fuels. Researchers from around the world are increasingly focusing on these issues, and are trying to resolve them with various approaches, of which biomass usage for energy production is one. At the moment, biomass acts as a primary energy source in rural areas of Asia and Africa, where its use is restricted to domestic applications. Because of its attractive characteristics, such as being carbon dioxide neutral, and being a renewable energy source, the interest in biomass energy is also increasing in the Western world (Senneca, 2007). Biomass fuels include wood, short rotation energy crops, grass, agricultural waste, aquatic plants, sawdust, herbaceous shrubs, and so on. According to Alén et al. (1996), biomass mainly comprises cellulose, hemicellulose, lignin and a small amount of extractives.

Biomass-to-energy conversion processes are grouped into three categories based on the approach used—physical, thermochemical, and biological. Of these, thermochemical conversion is the most commonly employed on the industrial scale. The thermal conversion processes are further subdivided into combustion, pyrolysis, torrefaction, and gasification. Compared with other processes pyrolysis is interesting due to its characteristic of producing multiple products (gaseous, bio-oils and char). Pyrolysis is typically defined as the thermal decomposition and devolatilization of organic materials in an inert environment.

However, because of their heterogeneous structure, and their diverse physical and chemical properties, biomass fuels are associated with several issues during their conversion. Commonly reported issues are: their high moisture content, their low energy density, their fibrous and hydrophilic nature, ash and inorganic

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http://dx.doi.org/10.1016/j.indcrop.2016.08.013
0926-6690/

elements and tars. Because of these issues, the thermal conversion of biomass is often considered to be a complex process. To achieve better conversion efficiency, it is equally important to pretreat biomass, and several technologies have been developed in that regard. Torrefaction is one such pretreatment method, which is considered as a mild form of the pyrolysis process where biomass is heated slowly in an inert environment to a temperature in the range 200–300 °C (Tran et al., 2014). Torrefaction enhances the biomass utilization by altering the physical and chemical properties discussed above.

As pyrolysis occurs simultaneously with biomass combustion and gasification, it is important to understand the decomposition characteristics of the fuels for the better design and optimization of the thermochemical processes (Poletto et al., 2012). Important characteristics that need to be evaluated in order to better understand the pyrolysis process are kinetics, the reaction mechanism, and heat flow data of the devolatilization process.

Eucalyptus, which has a high rate of production with an average yield of 45–60 m3/ha/year, is the most widely planted hardwood in the world. In addition to most commonly planted species such as Eucalyptus grandis (EG), E. urophylla (EU), E. camaldulensis, and E. globulus, several hybrids have also been developed under a project called the Brazilian Genolyptus, with the aim of improving the wood quality and productivity (Gomes et al., 2015). These new biomass materials are used in the paper and pulp industry but another interesting option is bioenergy applications. In this regard, it is essential to have a detailed understanding of the thermal decomposition of Eucalyptus clones.

On the other hand, a considerable amount of research data is available on the effects of torrefaction on the physical and chemical properties of the biomass. Also, there are numerous studies available on the pyrolysis of biomass, but very few studies are available on the pyrolysis of torrefied biomass. To the knowledge of the author, no research data is available on the pyrolysis of torrefied Eucalyptus clones. Tolvanen et al. (2013) studied the fast pyrolysis of torrefied wood using a drop tube reactor. Ren et al. (2013a) studied the pyrolysis of torrefied Douglas fir sawdust using the Friedman method; they observed the trend that activation energy decreased as torrefaction temperature increased. Tran et al. (2014) studied the pyrolysis of torrefied stump materials using the Distributed Activation Energy Model (DAEM) and three pseudo-component models, and observed that torrefied stump has a higher level of activation energy than the original stump. In the study of co-pyrolysis of torrefied wood with coal blends, Lu et al. (2013) reported that biomass torrefied at 300 °C contained more lignin than raw biomass. Worasuwannarak et al. (2011) studied the pyrolysis of torrefied Leucaena biomass using the thermal gravimetric mass spectrometry (TG-MS) technique, and concluded that the product distribution between raw and torrefied biomass pyrolysis was significantly different. These studies focused mainly on kinetic parameters but to better understand torrefied biomass pyrolysis, it is equally important to study the reaction mechanism and heat flow.

The aim of the present works was to identify the effect of torrefaction pretreatment on biomass pyrolysis characteristics—kinetics, reaction mechanism and heat flow. In the present study, we employed thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to investigate the pyrolysis of Eucalyptus biomass. The biomass was torrefied at three different temperatures, that is, 250, 275 and 300 °C. Torrefied biomass pyrolysis is carried out at 700 °C, with heating rates of 5, 8, 12 and 20 °C/min. For the kinetic analysis, we used the methods of Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS), and the Friedman model free method. The model-fitting method, called the Coats-Redfern method, was used to identify the reaction mechanism during the pyrolysis of torrefied biomass. We carried out a preliminary analysis on DSC data to support the findings of the TGA. The presented results provide valuable insights into increasing the understanding of the pyrolysis of torrefied biomass.

## 2. Materials and method

### 2.1. Materials

The biomass sample selected for this study was Eucalyptus clone E. urophylla (Timor) × E. camaldulensis (VM1). The selected material is also known as "urocam". The debarked stems of the selected Eucalyptus biomass samples were supplied by the Department of Forest Engineering, Federal University of Vicosa, Minas Gerais, Brazil. The detailed compositional analysis of the selected biomass was presented by Rocha et al., 2015a and Gomes et al., 2015. Prior to the experimental analysis, the biomass samples used in the experiments were ground using a Retsch ZM 200 centrifugal mill. To avoid the internal heat transfer effects, the ground biomass was sieved to a mesh size of 100–125 μm. Biomass of the same particle size was used for all the experiments.

### 2.2. Experimental plan

#### 2.2.1. Thermogravimetric analysis

Both torrefaction and pyrolysis of the Eucalyptus samples were carried out in a Mettler Toledo TGA850. To create the inert environment around the sample, and also to remove the released volatile gases, we used nitrogen gas at a flow rate of 80 ml/min. For each test, we used a sample size of about 7.5 mg in a 70 μl aluminum oxide crucible. To make sure that an inert environment was achieved in the TGA furnace, we allowed a purging time of 20 min at the beginning of each experiment. For each experiment, we raised the furnace temperature from room temperature to 105 °C at 20 °C/min., and maintained the temperature of 105 °C for an isothermal period of 30 min to ensure the drying was complete. To produce the torrefied biomass, the furnace temperature was increased from 105 °C to the selected torrefaction temperature (250, 275 or 300 °C) at 50 °C/min., and kept at that temperature for 1 h. Later, we used the same crucible with the torrefied biomass for the subsequent pyrolysis process. For pyrolysis, the furnace temperature was increased from 105 °C to 700 °C at selected heating rates, and the samples were kept at 700 °C for 40 min. The selected heating rates (β) were 5, 8, 12 and 20 °C/min. All experiments were conducted twice to check the reproducibility. The sample temperature and the corresponding mass were automatically recorded simultaneously by the TGA equipment. Hereafter, the torrefied biomass is represented by TB250, TB275 and TB300 for a torrefaction temperature of 250, 275 and 300 °C, respectively, and the dried Eucalyptus clone is abbreviated to DEC.

#### 2.2.2. Differential scanning calorimetry

The torrefied biomass for the DSC experiments was produced in a tube furnace, located at the Material Science Department, Tampere University of Technology, Tampere, Finland. Torrefied biomass was produced by increasing the furnace temperature from 105 °C to the selected torrefaction temperature (250 and 300 °C) at 20 °C/min., and kept at that temperature for 1 h. For each test, a sample size of about 10 mg in ceramic crucible was used. The DSC experiments were carried out in a Mettler Toledo DSC821e differential scanning calorimeter. The dried biomass and torrefied biomass samples of 3.5–4 mg were each loaded into 40 μl aluminum crucibles, and later closed with a pierced lid. An empty 40 μl aluminum crucible with a pierced lid was used for the reference. The relative mass difference between the sample and the reference was approximately one percent. At the beginning of each test, a purging time of