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Experiments and modeling of fixed-bed debarking residue pyrolysis: The effect of fuel bed properties on product yields

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HIGHLIGHTS

- We investigate the effect of fuel bed properties on pyrolysis yields with a model.
- The model describes fixed-bed pyrolysis of Norway spruce debarking residue.
- The model is calibrated with experimental data of debarking residue pyrolysis.
- Particle size affects intraparticle tar cracking, but not extraparticle cracking.
- Low porosities increase liquid yield but does not affect solid yield.

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ABSTRACT

This paper presents a study on the fixed-bed pyrolysis of debarking residue obtained from Norway spruce. Analysis is based on the dynamic model of packed bed pyrolysis which was calibrated by determining appropriate reaction rates and enthalpies to match the model predictions with the experimental data. The model comprises mass, energy and momentum equations coupled with a rate equation that describes both the primary and secondary pyrolysis reactions. The experiments used for the model calibration determined the yields of solid, liquid and gaseous pyrolysis products as well as their compositions at three distinct holding temperatures. Subsequently, the dynamic model was used to predict the product yields and to analyze the underlying phenomena controlling the overall pyrolysis reaction in a fixed-bed reactor.

1. Introduction

Anthropogenic climate change is forcing global society to increase the share of renewable sources in energy production. As a consequence, the combustion of lignocellulosic biomass for power generation as well as its conversion to biofuels has undergone a marked increase in recent years as it offers an attractive way to replace fossil fuels and to reduce net CO_2 emissions. However, the use of these bioresidues and their blends poses significant challenges due to variability in several critical factors including, composition, material density, devolatilization enthalpies and kinetics. Without special consideration in process design and operation, these inconsistencies may result in suboptimal conversion conditions for energy or fuel production. Furthermore, these variables can create disturbances to the plant operation resulting in economic losses, increased equipment wear and pollution. Thus, a large number of experimental studies on the thermal conversion of renewable fuels in a fixed-bed reactor, which allow replicating industrial conditions, have been reported in literature (Yang et al., 2007b).

Typically the experimental studies explore the effect of wood constituents on the pyrolysis mass loss dynamics and resultant products. For instance, Di Blasi et al. (2001) experimentally analyzed the weight loss dynamics of wood chips and determined that liquid and gaseous product yields were dependent on the content of holocellulose, while the char yield was specifically dependent on the lignin and extractives content. Burhenne et al. (2013) found that the increased lignin content of a biomass leads to slower decomposition rates, a higher devolatilization temperature and lower gas

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yield. Grønli (1996) also demonstrated that interparticular temperature gradients have a noticeable effect on the pyrolysis product yields. The results by Părpăriță et al. (2014) highlighted differences in the compositions of the bio-oils produced from different feedstocks: forestry biomass tends to produce more carboxylic acids, ketones and furans, but less phenolic compounds when compared to energy grass. The effect of heating rates has have also been examined and studies concerning pine (Williams and Besler, 1996) and pine bark (Şensöz, 2003) have shown that the effects of heating rates are less significant when compared to those of final temperature.

Although, experimental studies provide fundamental information on the pyrolysis of biomass, mathematical modeling allows an even deeper investigation of the underlying phenomena (Peters et al., 2003). However, only a limited number of studies on modeling of fixed bed pyrolysis have so far been reported. Cozzani et al. (1996) modeled the fixed-bed pyrolysis of milled refuse-derived fuel (RDF) with the aim of predicting product yields at different holding temperatures. Their results indicated that physical properties and variations in simulated wood composition had a more significant effect on the model predictions compared to other factors. In order to investigate thermal decomposition of beech wood, Peters et al. (2003) modeled packed bed pyrolysis of the material as an ensemble of separate particles, with each being described by a set of mass and energy conservation equations. The model was later extended by Mahmoudi et al. (2014) to also include effects of granular interactions and both these groups have demonstrated that this approach can adequately describe mass loss rate of a biomass sample. In contrast, Yang et al. (2007b) developed a fixed bed pyrolysis model for predicting product yields from devolatilization of wood, textile and cardboard residues, which assumed the competitive nature of gas, liquid and char formation processes. Results from the simulation indicated that the kinetic parameters determined for milled samples could not directly predict product yields in a packed bed and were optimized to fit experimental data. Anca-Couce et al. (2013) modeled fixed-bed pyrolysis of thick particles with a representative particle model (RPM) and their results suggested that particle diameter has a strong influence on the conversion time: doubling the diameter increases the time required for complete pyrolysis by 30%. In the study by Lamarche et al. (2013), a pyrolysis model of a fixed bed reactor was employed in order to investigate the effect of fuel bed heat transfer resistance on the overall conversion process of the fuel. It was found that for the reactor configuration with a diameter of 10 cm used by researchers, high temperatures and long residence times were required in order to complete the devolatilization of the material. However, thus far no attempt has been made to study the effect of physical factors like fuel bed density and porosity on the pyrolysis yields at low heating rates in a fixed-bed reactor.

As a consequence, the aim of this study is to investigate the effect of fuel bed density and porosity as well as various combinations of particle size and sweep gas flow on the pyrolysis product yields and their influence on tar cracking. For these purposes, we develop a detailed dynamic model of fixed-bed pyrolysis which is calibrated against the experimental data obtained in this study. The paper is structured as follows: Section 2 presents the material and the set-up for fixed-bed pyrolysis experiments. This is subsequently followed by the experimental results and analyzes (Section 3). In Section 4 the model and the determination of reaction rates for primary and secondary reactions as well as reaction enthalpies and the validation of the model with the determined reaction rates and enthalpies are all outlined. Section 5 presents the discussion and analysis before finally, in Section 6, the results are summarized and the conclusions presented.

Table 1
Particle size distribution of the debarking residue.

Size class (mm)	Probability (%)	Cumulative probability (%)
0–3.15	20.1	20.1
3.15–8	22.6	42.7
8–16	26.4	69.1
16–45	29.9	99.1
45–63	0.9	100
63–100	0	100
100	0	100

2. Materials and methods

2.1. Material

The material for the experiments was collected from the Metsä Wood Sawmill in Vilppula, Finland. The debarking residue is composed of thin, irregularly shaped shavings of stem wood chips and spruce bark (3:7). The particle size distribution of the material is presented in Table 1.

2.2. Methods

2.2.1. Fixed-bed experiments

Prior to the fixed-bed experiments, the material was dried for two weeks at room temperature. In each experiment approximately 100 g of material was used and the sample was loaded into a sample basket which was then inserted into the reactor that comprised of a metal cylinder surrounded by a temperature controlled furnace. Temperature measurements were obtained from inside the fuel bed with three M-type thermocouples, at 11, 15 and 20 cm from the top of the reactor and data from these was logged every 4–5 s.

In the first two experiments, the samples were heated to a target temperature of 500 °C, in the third and fourth to 700 °C and in the final one 600 °C. All samples were heated at a pre-programmed wall heating rate of 6 °C/min and the material was held for one hour at the specified temperature with the exception of the first sample, which was held at the final temperature for three hours prior to switching off the furnace. In order to collect the condensable gases, the products from the pyrolysis reaction were directed into a water-cooled condenser with an exit that was connected to a glass flask immersed in icy water. This set-up allowed liquid phase samples to be collected into a glass bottle throughout the experiment. The hose from the bottle outlet was connected to a diverter T valve, and its two other outlets were connected to an extraction hood and to a gas collection bottle. The gas sample was collected only after the pyrolysing material reached the target temperature and nitrogen was used to purge the pyrolytic gas from the reactor at a rate of 2 l/min.

On completion of the experiment, the solid residue and the collected liquid samples were all weighed. The liquid product composition was analyzed with Perkin-Elmer GC–MS, 5% phenyl column (30 m × 0.25 mm × 0.25 μm), where helium was the carrier gas (1 l/min). The oven temperature was programmed to rise from 60 to 260 °C at a rate of 10 K/min and then held at 260 °C for 10 min. The gaseous product composition was analyzed using a Varian CP 3800 gas chromatograph featuring a capillary column (CP sil 5, 5 μm, 60 m × 0.32 mm) and helium carrier gas for hydrocarbon analysis. H_2, O_2, N_2, CO and CO_2 concentrations were quantified with a molecular sieve (packed bed columns, 1.5 m × 3.2 mm) and the carrier gas utilized was argon. The reactor set-up used in the experiments is presented in Fig. 1.