Flash co-pyrolysis of biomass with polylactic acid. Part 1: Influence on bio-oil yield and heating value

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Abstract

High amounts of water present in bio-oil are one of the major drawbacks for its utilisation as a fuel. One technology that shows the potential to satisfy the demand for bio-oil with a reduced water content is the flash co-pyrolysis of biomass with polylactic acid, PLA. The influence of PLA on the pyrolysis of willow is investigated with a semi-continuous home-built pyrolysis reactor. Flash co-pyrolysis of willow/PLA blends (10:1, 3:1, 1:1 and 1:2) show synergetic interaction. A higher bio-oil yield and a lower water content as a function of the willow/PLA ratios are obtained. Among the tested blends, the 1:2 willow/PLA blend shows the most pronounced synergy: a reduction in the production of pyrolytic water of almost 28%, accompanied by an increase of more than 37% in the production of water-free bio-oil. Additionally, PLA shows to have a positive influence on the energetic value of the bio-oil produced and on the resulting energy recuperation.

1. Introduction

Global Warming, the Kyoto Protocol, the emission of greenhouse gases and the depletion of fossil fuels are the topics of environmental pleadings worldwide. The development of new and renewable energy sources (including bio-fuels) is the key to change [1]. The flash pyrolysis of biomass is a promising route with regard to the production of solid (char), liquid (bio-oil) and gaseous materials as possible alternate energy sources [2–4]. In order to maximise the bio-oil yield, process conditions should be: low temperature, high heating rate and short gas residence time [5,6]. Today, bio-oil can substitute fuel oil or diesel in many static applications including boilers, furnaces, engines and turbines used for electricity generation. Additionally, it can be upgraded to transportation fuels [7] and even to chemicals with added value.

The flash pyrolysis of biomass inherently results in the production of pyrolytic water, which is one of the major drawbacks of the bio-oil produced. Nevertheless, the presence of water has both positive and negative effects on the bio-oil properties [5,8]. It improves bio-oil flow characteristics, which is beneficial for combustion. Moreover, it leads to a more uniform temperature profile in the cylinder of a diesel engine and to lower NO_x emissions. On the other hand, it lowers the heating value and flame temperature of the bio-oil. It also contributes to the increase in ignition delay and in some cases to the decrease of combustion rate as compared to diesel fuels. The reduction of the water content is one of the few required but essential upgrading steps in order to increase the applicability of bio-oil and to make the production of bio-oil competitive. Oasmaa summarised the requirements of bio-oil set by Ensyn (a liquid producer), Wärtsilä (an engine manufacturer) and Birka (a

potential bio-oil user). Here, the maximum water content was defined as 25–26 wt.% [9], while the literature reports a water content between 15–30% and even more [6,8].

To our knowledge, the flash pyrolysis of willow has not been investigated extensively yet. Ingemarsson studied the slow pyrolysis of willow and analysed the compounds produced using gas chromatographic methods [10]. Meszaros et al. performed TG/MS analysis of willow and other young wood samples in order to obtain information on their thermal behaviour [11]. Prins et al. specifically addressed the decomposition of hemicellulose of willow in the relatively low temperature range of 498–573 K, a process also known as torrefaction [12,13].

The use of co-pyrolytic techniques on biomass/plastic ratios has already been investigated [14–17]. One of the most important parameters for liquid production is the ratio in the feedstock.

Polylactic acid, PLA, is a biologically degradable polymer and is produced principally via microbial fermentation of sugar feedstock [18]. PLA is possibly the most commonly applied biopolymer and has the most potential for widespread use, but does not have the best biodegradability properties amongst biopolymers. Therefore, co-pyrolysis of PLA and biomass (willow) offers an alternative waste treatment option and may act as an upgrading step during the pyrolysis of willow. The thermal decomposition of PLA has already been studied in detail [19–22].

The goal of the present research is to reduce the amount of pyrolytic water by flash co-pyrolysis of willow and PLA. Therefore, the co-pyrolytic behaviour of the willow/PLA blends is investigated with a semi-continuous home-built pyrolysis reactor. In this paper, the influence of PLA and willow on the bio-oil yield, its water content and heating value during flash co-pyrolysis will be discussed.

2. Experimental

2.1. Materials

The experiments are performed on willow – Salix, PLA and willow/PLA blends. The willow branches (the leaves are not taken into account in this study) are cut and dried at room temperature before being shredded into small particles ($\sim$2 mm). A particle size of <2 mm guarantees a fast inner-heating rate during pyrolysis and thus ensures a flash pyrolysis of the entire particle.

The experiments on willow/PLA blends with a w/w ratio of 10:1, 3:1, 1:1 and 1:2 are investigated and compared with the results obtained for 100% willow and 100% PLA (reference samples 1 and 2, respectively) to evaluate the effects on the bio-oil yield, its water content and its calorific value.

2.2. Explorative analysis of pure biomass and PLA

2.2.1. Ultimate analysis

The CHNS- and O-content of the input materials are determined via two distinct experiments, using a FlashEA 1112 Elemental Analyser of Thermo Electron Corporation. Approximately 2–4 mg of sample is introduced into a container, which is injected by an autosampler. In case of CHNS-determinations, 5–10 mg vanadiumpentoxide is added to the sample as a combustion catalyst. 2,5-Bis(5-*tert*-butyl-benzoxazol-2-yl)thiophene (BBOT) and L-cystine are used as standards for the CHNS- and O-determinations, respectively.

2.2.2. Thermogravimetric analysis – TGA

About 30 mg of sample is pyrolysed under approximately 35 ml/min N_2 flow at a heating rate of 10 K/min from room temperature (RT) to 973 K with a DuPont Instruments 951 Thermogravimetric Analyzer.

2.2.3. Thermogravimetric/mass spectrometric analysis – TG/ MS

A Hi-Res TGA 2950 Thermogravimetric Analyzer of TA Instruments is connected with a Pfeiffer Vacuum ThermoStar mass spectrometer. Approximately 1–2 mg of sample is pyrolysed under a Helium flow of 100 ml/min at a heating rate of 20 K/min from RT to 873 K. The mass spectrometer is set at the standard ionising voltage of 70 eV with a mass range m/z of 5–255 and a scan rate of 5 scans/min.

2.2.4. Thermogravimetric/Fourier transform infrared analysis – TG/FT-IR

A DuPont Instruments 951 Thermogravimetric Analyzer, interfaced (at 473 K) with a gas cell, and coupled with a Bruker Vertex 70 FT-IR spectrometer (resolution: 4 cm^{-1}) is applied. Approximately 20 mg of sample is pyrolysed at a heating rate of 20 K/min from RT to 873 K under a constant Helium flow of 100 ml/min.

2.3. Flash pyrolysis

2.3.1. Experimental flash pyrolysis set-up

The semi-continuous home-built pyrolysis reactor (360 mm high with a diameter of 88 mm), Fig. 1 (part a), is manufactured in stainless steel (AISI 304). Within the reactor, a heat transfer medium (white sand, $\pm$700 g or 450 ml) is inserted. Before use, this sand is dried at 383 K to ensure that all water is removed. Preliminary, the sand is pre-treated in batch at 873 K to remove all impurities. During the entire process, the sand is in constant motion with the aid of an Archimedical screw, ensuring a homogeneous temperature sand bed operating system. This Archimedical screw also serves as a gas inlet system. The reactor (and the sand) is heated by a tailored heating jacket (Horst GmbH, Lorsch, Germany).

The injection system, Fig. 1 (part b), is manufactured in stainless steel (AISI 304) as well. It consists of a reservoir with a volume of 600 ml and an injector. The injector is a hollow tube linking the reservoir, which contains the biomass, with the reactor. Via this tube, the biomass is transported into the reactor by means of a second Archimedical