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Valorization of raspberry seed cake by flash and slow pyrolysis: Product yield and characterization of the liquid and solid fraction

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ABSTRACT

The valorization of raspberry seed cake by flash and slow pyrolysis is investigated in this study. During flash pyrolysis, temperature significantly affects the yield and properties of the products. The highest liquid yield (53.6 wt%) is found at 450 °C. This liquid has a water content (26.2 wt%), a HHV (18.6 MJ/kg) and a pH-value (3.2) that are comparable to those of pyrolysis liquids produced by flash pyrolysis of lignocellulosic biomass. In terms of added-value chemicals, levoglucosan and phenols are interesting compounds because of their high economic value. The solid residue has potential as solid energy carrier at industrial scale because of its high energy content (24.5 MJ/kg). Pyrolysis liquid from slow pyrolysis of raspberry seed cake is collected in three fractions as a function of pyrolysis temperature. Fraction 1 (220–320 °C) and fraction 2 (320–350 °C) are single-phased and have a high water content. In contrast, fraction 3 (350–450 °C) spontaneously separates in two fractions. The organic fraction (12.1 wt%), mainly composed of phenols, is promising as renewable fuel because of its relatively high calorific value (27.0 MJ/kg) and its relatively low water content (9.3 wt%). The aqueous fraction (10.2 wt%) has a high water content (67.4 wt%), but also contains a high amount of levoglucosan. The solid residue can be valorized as solid energy carrier because of its high calorific value (30.9 MJ/kg) or as precursor in the production of activated carbon.

1. Introduction

The demand for energy and its sources is increasing every day due to the rapid growth of world's population and developing technologies [1]. Nowadays, the largest part of world's energy demand is still fulfilled by fossil fuels, although their use has led to serious environmental problems such as atmospheric pollution, global warming, acid rain, etc. Additionally, fossil fuels also serve as raw materials for a wide range of industrial organic chemicals. However, growing environmental concern, predictions of scarcity, supply oscillations and rising prices of fossil fuels strongly stimulate the search for sustainable and renewable sources of energy and chemicals [2].

Renewable energy includes solar, water, tidal, wind and geothermal power as well as biomass [3]. The latter, including biomass waste, is considered as the renewable energy source with the highest potential to contribute to the energy needs of modern society [4]. Moreover, biomass energy is reported to play an important role in the future energy systems of the world [5]. However, conversion of (solid) biomass into a more useful and valuable form is usually required. In general, a liquid or solid energy carrier that is easily transportable and storable is preferred [6]. Depending on the biomass characteristics and the desired energy form, a suitable conversion process has to be selected. Among several thermochemical conversion techniques, pyrolysis is very promising since it is the only technique that converts biomass into three fractions: solid, liquid and gas. Pyrolysis can be defined as the thermochemical decomposition of material, including biomass waste, at moderate temperatures (350–700 °C) and in an oxygen deficient atmosphere [7,8]. The yield of each fraction depends on the applied pyrolysis conditions (temperature, heating rate, vapor residence time, presence of a catalyst, etc.) and the features of the biomass feedstock [9]. In general, high liquid yields require moderate temperatures and very short vapor residence times (i.e. flash pyrolysis), while the production of solid residue is favored by relatively low pyrolysis temperatures and long vapor residence times (i.e. slow pyrolysis) [1,10]. The pyrolysis liquid has potential as renewable fuel or as source of added-value chemicals. Since pyrolysis liquids are usually viscous, acidic and thermally unstable liquids that contain high amounts of oxygenated compounds and water, both

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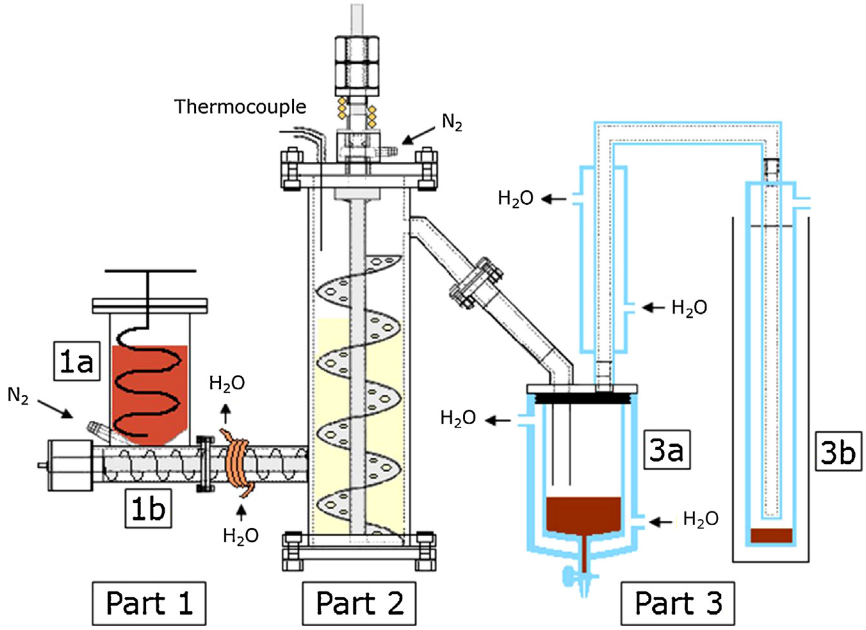

Fig. 1. Home-built lab-scale pyrolysis reactor setup.

leading to low calorific values, upgrading is frequently necessary before valorization as renewable fuel or as fuel additive [3,10,11]. Besides energy, pyrolysis liquid can also be a source of added-value chemicals. Levoglucosan (1,6-anhydro-β-D-glucopyranose), for instance, is a promising added-value chemical that is frequently found in relatively high amounts in pyrolysis liquids produced from (demineralized) cellulose or lignocellulosic biomass. Typically, this chemical has potential for manufacturing of pharmaceuticals, pesticides, surfactants and biodegradable polymers [11–13]. Phenolic compounds, degradation products of lignin components, are also commonly present in pyrolysis liquids and can be valorized as phenol replacement in phenol-formaldehyde resins. These phenolic resins, in turn, can be used as adhesives in plywood and particleboard manufacturing [3,7,11] or as construction materials in the automotive industry [14]. Additionally, several monomeric lignin derived products are of significant economic value as synthetic raw materials, flavor chemicals (e.g. vanillin), plant growth inhibitors, plant pathogen control agents and pharmaceutical precursors [12]. The solid residue (or char) has opportunities as precursor in the production of activated carbon, as fertilizer or as improved solid energy carrier [1,15]. Frequently, the gaseous fraction still has a moderate energy content that can be used to provide process heat by combustion [1,6].

In this study, the valorization of raspberry seed cake by pyrolysis is investigated. The examined raspberry seed cake is the solid biomass waste delivered by a Belgian company after commercially processing of raspberry seeds. Hence, these seeds (about 10 wt% of fresh berries) are a source of polyphenolic compounds that are effective antioxidants and of high quality oil (10–23 wt%) that can be valorized in food, cosmetic and pharmaceutical industries [16,17]. The raspberry seeds, in turn, are obtained as by-product in the production of raspberry juice. Globally, the total annual production of raspberries (*Rubus Idaeus* L.) in 2011 was estimated at 0.54 Mt [18]. Since, to the knowledge of the authors, no suitable valorization pathway has been published yet for raspberry seed cake, the opportunities of pyrolysis are investigated in this study. Therefore, the raspberry seed cake is firstly characterized into detail. Then, the effect of the pyrolysis temperature on the product yield and the properties of the pyrolysis liquids in flash pyrolysis is studied by complementary analytical techniques. Finally, the pyrolysis liquid is collected in separate fractions as a function of pyrolysis temperature during slow pyrolysis up to 450 °C in order to gain a better understanding of the pyrolytic behavior of raspberry seed cake.

2. Materials and methods

2.1. Raspberry seed cake

The raspberry seed cake, delivered by Eco Treasures (Lokeren, Belgium), was obtained as solid waste after supercritical CO_2-extraction of raspberry seeds (*Rubus Idaeus* L.) in the production of high value chemicals (i.e. antioxidants and high quality oil). The raspberry seeds were separated from the fruit flesh during the production of raspberry juice. Prior to analysis and pyrolysis, the raspberry seed cake has been ground to a particle size smaller than 2 mm and oven-dried at 110 °C.

2.2. Flash and slow pyrolysis experiments

Flash and slow pyrolysis experiments were performed in a home-built lab-scale reactor in view of fundamental research. Compared to the setup described in previous work [19], the reactor setup used in this study contained a condensation vessel equipped with a valve at the bottom, allowing fractionated collection of the pyrolysis liquid as a function of temperature during slow pyrolysis. Pyrolysis atmosphere was ensured by a double N_2 inlet system (2 × 70 mL/min). A schematic overview of the reactor setup is shown in Fig. 1.

Prior to flash pyrolysis, the reactor (part 2) was filled with white sand (about 700 g) that was used as heat transfer medium. This sand (particle size: 125–500 μm) was pre-treated in an oven at 600 °C (6 h) to remove all organic contamination. The sand in the reactor was heated by an electric heating jacket until the desired pyrolysis temperature (350, 450 or 550 °C) was reached. A perforated Archimedes' screw ensured a homogenous temperature of the sand and created a fluidized bed effect, allowing maximal mixing of the biomass sample and the sand. Once pyrolysis temperature was reached, the raspberry seed cake (about 100 g) was injected from the storage vessel (part 1a) into the hot reactor by the screw