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Quantitative analysis of the aqueous fraction from the Fe-assisted hydrothermal liquefaction of oil palm empty fruit bunches

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ABSTRACT

Hydrothermal liquefaction is a promising candidate method for the conversion of biomass resources. To improve economic efficiency, the development of processes that utilize the water-soluble (WS) hydrothermal-liquefaction fraction is critical; consequently, a fundamental method for the analysis of the WS fraction is required. In this study, the quantitative analysis of the WS fraction obtained from the Fe-assisted hydrothermal liquefaction of oil palm empty fruit bunches was comprehensively investigated by combining various separation and analysis methods The volatile components of the WS fraction were analyzed by gas chromatography–mass spectrometry (GC–MS) and gas chromatography–flame ionization detection (GC–FID), and they were quantified using the relative response factors estimated by the effective carbon number method. Heavy components not detectable by GC were isolated by freeze-drying, and their elemental compositions, functional groups, and molecular-weight distributions were analyzed. The results reveal that the addition of Fe during hydrothermal liquefaction alters the types of compounds present in the WS fraction by a large extent, and increases the proportion of volatile compounds. The reactivity of the WS fraction in the zeolite-catalyzed cracking reaction was also investigated, which revealed that the volatile components of the WS fraction are efficiently converted into olefins.

1. Introduction

The effective utilization of biomass resources, such as agricultural residues, algae, and sewage sludge, is an urgent and important issue that will help society prepare for the depletion of fossil-based resources in the future. Fast pyrolysis and hydrothermal liquefaction reactions have been extensively studied as methods for the liquefaction of biomass resources and their subsequent use as fuels and chemical feedstocks [1,2]. The hydrothermal liquefaction reaction is a promising method for the liquefaction of biomass, and operates at moderate temperatures (280–370 °C) and high pressures (10–25 MPa) [3–6]. During this process, ubiquitous water is used as the solvent, which is advantageous since wet biomass can be used without any pre-drying. The product of the hydrothermal liquefaction reaction is separated into four fractions, namely water-soluble (WS) and water-insoluble (WI) fractions, as well as solid residues (SRs), and gases (Fig. 1) [7]. Increasing the levels of the WS and WI fractions, which can be used as fuels and chemical feedstocks, is important in order to improve biomass-utilization efficiency. Until now, the WI fractions (biocrudes) have largely been regarded as useful resources and the focus of analytical research has almost exclusively been directed toward these fractions; however, the use of the WS fraction also needs to be considered as a possible strategy in this regard [8–13].

Recently, we demonstrated the hydrothermal liquefaction of palm empty fruit bunches (EFBs) and demonstrated that the use of Fe-metal powder, as an additive, considerably increased the yield of the WS fraction [14]. In addition, catalytic cracking of the WS fraction over a solid acid catalyst (HZSM-5 zeolite) afforded hydrocarbons, such as olefinic and aromatic compounds, that can be used as basic chemical raw materials. During the cracking reaction, the WS fraction obtained from the Fe-assisted hydrothermal system contained higher levels of hydrocarbon products than that obtained from a conventional hydrothermal system, revealing that Fe not only accelerates decomposition, but also affords more upgraded products. Preliminary analysis of the WS fraction revealed that the product composition had changed significantly following addition of Fe. However, further analysis of the WS fraction was difficult due to its complex composition; consequently, only a qualitative discussion on the effect of Fe was provided. In order to clarify the role of Fe, optimize the hydrothermal decomposition process, and develop methods that use the WS fraction, a rapid and accurate method for the evaluation of the WS fraction is a key technological objective.

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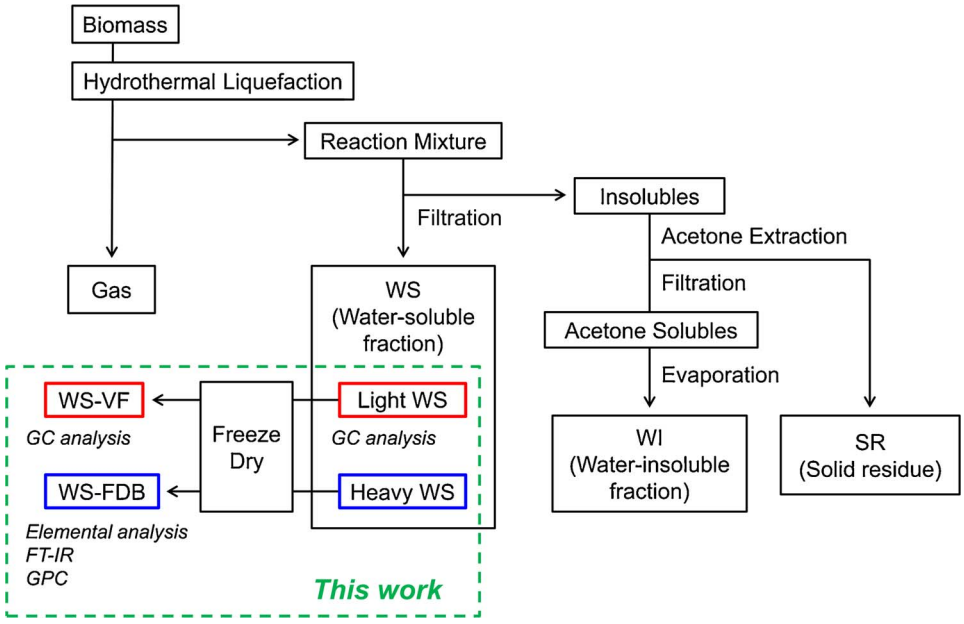

Fig. 1. Products from the hydrothermal liquefaction of biomass and an overview of our analysis strategy.

Reports on the analysis of the aqueous fractions from the hydrothermal liquefaction of biomass have been published; however, quantitative analyses are limited to only a few cases [15–19]. As analytical methods, gas chromatography–mass spectrometry (GC–MS) and gas chromatography–flame ionization detection (GC–FID) are often used; these methods are powerful because they can rapidly analyze multicomponent mixtures. For quantitative analysis by GC, the preparation of calibration curves using authentic samples is necessary. The analysis of complex mixtures, such as those from the thermochemical decomposition of biomass, is labor-intensive and costly. In particular, when no standard reagents are on hand, and when they cannot be easily purchased, it becomes necessary to synthesize authentic samples, which is not a realistic approach for trace amounts of product.

Even when standards are not available, relative response factors (RRFs) of analytes for FID analysis can be estimated from the chemical structures of the analytes; consequently, calibration curves can still be prepared. Sternberg et al. proposed a method for predicting the RRF of a compound bearing heteroatoms by introducing the concept of effective carbon number (ECN) [20]. They showed that the effect of heteroatoms on the ECN of a molecule depended on the nature of the functional groups and empirically quantified the contribution of each functional group to the ECN. A number of studies on predicting RRF have been reported [21–24], and the predicted RRFs have been shown to be useful for the analysis of scent [25] and taste [26], and in other areas [27]. Biomass-derived components produced by thermochemical conversion were also analyzed using predicted RRFs [28–31]. For example, Undri et al. successfully quantified the composition of the biocrude obtained by rapid pyrolysis using an independently developed RRF prediction method [32].

In this study, we developed a modified technique for predicting ECN based on the above-mentioned method, quantitatively analyzed the crude WS fraction from the hydrothermal liquefaction of biomass, and clarified the composition of the volatile components. In addition, we introduce a freeze-drying method [33,34] and succeeded in isolating non-volatile WS components that cannot be detected by GC. The compositions and properties of the isolated heavy components were determined by elemental analysis, Fourier-transform infrared spectroscopy (FT-IR) and gel-permeation chromatography (GPC). Combining these methods has enabled the comprehensive analysis of the WS fraction and a detailed discussion of the effect of the Fe additive. In addition, by examining the cracking characteristics of the volatile and heavy components of the WS fraction, guidelines for the optimization of the hydrothermal liquefaction process are proposed.

2. Materials and methods

2.1. Materials

Oil palm empty fruit bunches (EFBs) from Indonesia were supplied by the Nippon Shokubai Co., Ltd. (Japan), and were used as the lignocellulosic-biomass feedstock. The EFBs were dried at 25 °C and crushed into particles less than 300 μm in size. Fe powder (99.9%, NM-0029-UP) was purchased from Ionic Liquids Technologies GmbH (Germany). HZSM-5 zeolite with a Si/Al ratio of 24:1 was supplied by the Nippon Shokubai Co., Ltd. (Japan). Internal standards and authentic samples for GC analyses were obtained commercially. 2-Methoxyethanol, cyclopentanone, 1-hydroxy-2-propanone, propanol, acetic acid, propanoic acid, cyclopentanol, cyclohexanol, propyleneglycol, 1,2-ethanediol, 1,2-butanediol, 1,4-butanediol, 1,2-pentanediol, 1,2-hexanediol, 1,2-cyclohexanediol, 4-oxopentanoic acid, furfural, phenol, methyl *p*-hydroxybenzoate, cinnamaldehyde, and 3-phenyl-2-propen-1-ol from purchased from Wako Pure Chemical Industries, Ltd., while cyclohexanone, 3-hydroxy-2-butanone, methyl DL-2-hydroxy-3-butenoate, 2-butanone, 2,3-butanediol, *tert*-butyl alcohol, *tert*-amyl alcohol, 5-hydroxymethyl-2-furaldehyde, guaiacol, syringol, syringaldehyde, and vanillin were purchased from Tokyo Chemical Industry Co., Ltd.

2.2. Preparation of the WS fraction

EFB liquefaction and separation experiments were conducted following a previously published method [14]. Briefly, EFB (4.0 g), Fe powder (0 or 6.256 g), and H_2O (40 g) were introduced into a Hastelloy C high-pressure reactor, which was purged four times with nitrogen. The initial pressure was set to 1.0 MPa with nitrogen, and the stirring rate was adjusted to 700 rpm. The reactor was then heated to 300 °C and maintained at this temperature for 10 min. The reactor was then rapidly cooled to 25 °C using ice-water. The reaction mixture was filtered and the filtrate was collected as the WS fraction. The total organic carbon (TOC) content of the WS fraction was determined using a total organic carbon analyzer (Shimadzu, TOC-LCSH/CSN). The pH of the WS fraction was measured with a LAQUAtwin B–711 pH analyzer