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Mineralogical characterization of chemically isolated ingredients from biomass

H. Haykiri-Acma [a], S. Yaman [a,*], M. Alkan [b], S. Kucukbayrak [a]

[a] Istanbul Technical University, Chemical and Metallurgical Engineering Faculty, Department of Chemical Engineering, 34469 Maslak, Istanbul, Turkey
[b] Istanbul Technical University, Chemical and Metallurgical Engineering Faculty, Department of Metallurgical and Materials Engineering, 34469 Maslak, Istanbul, Turkey

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ABSTRACT

The complex structure of biomass materials can be studied by means of a number of different techniques. Of which, chemical isolation of macromolecular biomass ingredients such as lignin, hemicellulose, and cellulose, and then characterization of each isolated ingredient has been a common practice. However, the isolated individual ingredients have always been regarded as pure materials, and so far potential inorganic impurities resulting from the parent biomass have not been considered. Accordingly, this paper focuses on the determination of inorganics, if any, in the isolated parts of biomass. For this, two different biomass species such as hybrid poplar wood and apricot stones have been subjected to sequential isolation procedures of ASTM D1105, Wise's Chlorite Method, and van Soest's Method. The isolated holocellulose (hemicellulose + cellulose), lignin, and extractives-free bulk were then characterized mineralogically by X-ray Diffraction (XRD) and X-ray Fluorescence (XRF) techniques, and the results were compared with those for the parent biomass species. It was found that the isolated holocelluloses and lignins are not just ash-free and they have ash contents up to 2.2% and 4.0%, respectively. Also, various minerals including potassium chloride, several phosphate minerals, and alumina silicates were found to survive after chemical treatments applied during isolation. In addition, several heavy metals were also detected. These results reveal that minerals cannot be eliminated entirely because of the natures of the chemicals used, and they unavoidably remain in the isolated macromolecules.

1. Introduction

Characterization of biomass structure mostly relies on distribution of the macromolecular ingredients in biomass such as hemicellulose, cellulose, and lignin. Indeed, these ingredients usually account for the major part of the organic fragment although they are often accompanied by some other organics such as starch, proteins, triglycerides, lipids. Hence, the term of "lignocellulosic" is frequently used for many types of biomass species. Besides, all of hemicellulose, cellulose, and lignin are comprised of C, H, and O in different ratios and consequently, configurations of their molecules are highly different from each other.

Several forms of celluloses $(C_6H_{10}O_5)_n$ are the primary structural component in the cell wall of biomasses, and they are long chain polymers with high degree of polymerization [1]. Cellulose is insoluble in water [2]. Hemicelluloses are complex polysaccharides with the generic formula $(C_5H_8O_4)_n$ that occur in association with cellulose in the cell walls, and xylan is the most abundant form of hemicelluloses [2]. These compounds are soluble in weak alkaline solutions and are easily hydrolyzed by dilute acid or base. Lignin is the second most abundant natural raw material after cellulose and nature's most abundant aromatic (phenolic) polymer [3]. The lignocellulosic structure can be broken and the lignin fraction is separated by treatment with concentrated sulfuric acid, in which lignin is insoluble.

Kumar et al. [4] investigated the distribution of these ingredients in seventeen different types of biomasses including hardwoods, softwoods, nut shells, grasses, straw, wastes, manure, etc. and found that the highest cellulose content is in paper (up to 99%), the highest hemicellulose content is in leaves (up to 88%), and the highest lignin content is in nut shells (up to 40%), while Daud and Ali reported even higher lignin content of 53.4% in palm shell [5].

Thus, a number of projects have been carried out to specify the individual effects of these macromolecular ingredients during specific processes. For this, mostly model compounds purchased from commercial market have been used instead of using isolated real ingredients from the targeted biomass [6–10]. Namely, xylan has mainly been used as the model compound of hemicellulose [6,7]. In some cases, usage of specific commercial xylan types that are produced from particular biomass sources such as birch wood, beech wood, oat spelt have also been reported [7,8,10]. Alternatively, glucomannan was also used to represent hemicellulose

* Corresponding author. Tel.: +90 212 2853351; fax: +90 212 2852925.
E-mail address: yamans@itu.edu.tr (S. Yaman).

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[8]. On the other hand, different commercial celluloses such as microcrystalline celluloses and Sigmacell microcrystalline celluloses have been addressed in literature [7]. Besides, organosolve lignin (THF soluble) has been used in some studies [11], while gunpowder lignin [12], commercial kraft pine lignin [10], and alkali polymeric kraft lignin [13] were also used. In this way, synthetic mixtures prepared by simply mixing of these compounds have been used to simulate the composition of typical biomass species, and to monitor the effects of each ingredient in miscellaneous applications [6]. Meanwhile, very limited number of investigations directly focused on isolation of the macromolecular ingredients from alternative biomass species, and usage of these real ingredients in various applications [14–16]. However, isolation of lignin from cellulosic materials is generally difficult because of condensation and oxidation reactions that take place during isolation [3].

The striking feature for these studies is that such model compounds are not fully organic, and some inorganics are also involved [6,8,17]. So far, the existing literature on this topic only deals with the ash contents in these commercial compounds. For instance, Gani and Naruse [17] reported that microcrystalline cellulose and organic-solved lignin chemicals have ash contents of 0.51% and 1.71%, respectively. Whereas, Cagnon and the co-workers [6] determined that commercially provided hemicellulose, cellulose, and lignin have the ash contents of 6.7%, <0.3%, and 3.9%, respectively. Collard et al. [18] reported that the ash content in the microcrystalline cellulose (Merck 102330) is only 0.04%, while xylan (from beech wood, Sigma X4252) contains 13.15 wt.% ash.

Besides, it is possible to find elemental compositions of ashes in some studies. Sharma and Hajaligol [19] reported that lignin obtained from Aldrich was alkali and it had 5.7 wt.% ash, consisting mainly as oxides of Na, K, Si, and Al. Watanabe et al. [20] investigated ash contents of commercially available cellulose powder (C6413, microgranular, Sigma–Aldrich Corp.) and lignin powder (471003, alkali, low sulfonate, typical MW: 60,000, Sigma–Aldrich). They reported that cellulose does not contain ash, while lignin has an ash content of 18.2 wt.%. Inductivity Couple Plasma/Absorption Emission Spectroscopy (ICP/AES) results also revealed that there were eight elements in lignin, Na, Al, K, Fe, Mg, Si, P, Ca.

These inorganics should not be only regarded as impurity but also their complex effects including catalytic activities must be taken into account. It is known that certain elements (such as Ca, K, Na, Mg, and Fe) exert a significant catalytic effect, and even a small amount of them is capable of altering pyrolysis behavior to a large extent [21]. Effect of the addition of switchgrass ash as little as 0.5 wt.% into cellulose was studied by Patwardhan et al. [22], and they concluded that even such a low presence of ash leads to striking variations in the product distribution from fast pyrolysis of cellulose. That is, formic acid was tripled and glycolaldehyde was quadrupled due to ash, while levoglucosan was reduced to less than half.

Inorganic compounds decrease both the temperature of onset of decomposition and maximum weight loss. Minerals also catalyze the depolymerization reaction producing macromolecules, and accelerate the secondary degradation of these macromolecules to produce smaller molecules through lowering the activation energy [22]. Minerals present in polysaccharides display a catalytic activity that favors char formation and inhibits depolymerization reactions, leading to lower tar yields [18]. Besides, bio-oil obtained in the presence of ash was reported to have aqueous nature [23].

Heavy metals also have been reported to show catalytic effects to upgrade the pyrolysis liquids from biomass [24]. Not only heavy metals but also alkali metals have catalytic effects during thermal conversion processes. Seaweed's ashes that are composed of alkali metals such as potassium and sodium affect the pyrolysis process. That is, the more alkali metals mean the more acids production at the expense of pyrolytic oil [25]. Shi et al. [26] investigated effects of the removal of alkali and alkali earth metals from rice straw, and concluded that pyrolytic characteristics are highly affected from the catalytic activity of these metals.

As to the composition of ash in these model compounds, there is a lack of information in literature. Namely, the mineralogical phases were not given, and only the elemental analysis results have been presented.

Since, quantitative/qualitative investigations of the inorganic phases on these compounds have not been properly investigated so far, this paper deals with the characterization of the inorganic structure of these macromolecular ingredients isolated from biomasses such as hybrid poplar and apricot stone by analytical methods.

2. Materials and methods

2.1. Characterization of biomasses

Hybrid poplar and apricot stones are the biomass species used in this study, and they were provided from forestry/agricultural industries in Turkey. The reason for the choice of these biomasses is that hybrid poplar is a holocellulose-rich biomass while apricot stone is poor in holocellulose and very rich in extractives, being so different in terms of the fuel characteristics. At the sample preparation stage, the biomasses were not dried in an oven to avoid any modification in their original structure due to thermal treatment; instead they were allowed to stay in open containers at laboratory for two weeks to obtain air-dried samples. Then, air-dried samples were milled to reduce the particle size to lower than 0.25 mm using a grinder that has been specially designed for leafy materials. Proximate analyses of the samples were carried out according to ASTM standards, and the gross calorific value measurements were conducted using IKA 2000 model calorimeter. All analysis was conducted in triplicates, and the mean values were used provided that the deviations were within 5%.

2.2. Isolation of the ingredients

Macromolecular ingredients in biomass such as holocellulose, and lignin as well as the extractives-free bulk (extracted sample) were isolated chemically from the parent biomass samples using the following analytical procedures. First, the standard test method of ASTM D1105 was applied to the parent biomass materials to obtain the extractives-free bulk. That is, extractable – organics and – some inorganics were removed through extraction with solutions of benzene and ethyl alcohol. For this purpose, 10 g of biomass (<0.250 mm) was leached using benzene-ethyl alcohol of 1:2 (v/v of biomass to the solvent) in a soxhlet extractor for 5–6 h according to TAPPI, T264 om-97 method [27], and then benzene was separated and the bulk was filtered and washed with ethyl alcohol and subsequently with hot water. The yield of extractives was calculated from the loss in the mass of the biomass. This method enables to monitor the miscellaneous effects of the extractive matter on any process by comparing the results on treated and untreated biomass.

On the other hand, isolation of either holocellulose or lignin is carried out on this extracted bulk in the subsequent experiments in which it is further treated with other chemicals. Namely, the mixtures of $NaClO_2$, acetic acid, and water were employed to isolate the holocellulose content according to "Wise's Chlorite Method" [28]. Besides, the lignin content was determined by "van Soest's Method" [29] by which extracted bulk was treated with 72 vol% sulfuric acid to hydrolyze the cellulosics and to isolate the lignin. Neutralized bulk was then subjected to drying in an oven at 100 °C and then ashing at 400 °C in a muffle furnace. This