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Solvent Fractionation Method with Brix for Rapid Characterization of Wood Fast Pyrolysis Liquids

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The solvent fractionation method based on water extraction has been proven to be an effective tool for characterization of pyrolysis liquids and for studying their storage stability. However, for quality follow-up in pilot/demonstration plants, a simpler and faster fractionation scheme is needed. There is also a need for a rapid method for analyzing the carbohydrate content of pyrolysis liquid. Carbohydrates of pyrolysis liquid cause problems in fuel oil use due to their reactivity and sticking tendency. The new method includes much faster separation of water extract using centrifuge and characterization of carbohydrates by the Brix method. The determination of water content, water-insolubles, and carbohydrates by Brix accounts for 80−85 wt % of pyrolysis liquid composition. The main changes in aging happen between these groups; hence, these changes give information on the quality of pyrolysis liquids.

Introduction

Pyrolysis liquids consist of 20−30 wt % water, which can be determined by the Karl Fischer titration.[1,2] The amount of lignin-derived material in the pyrolysis liquid can be measured by water extraction as water-insoluble material.[2−6] However, determination of the total chemical composition of pyrolysis liquids is very challenging because pyrolysis liquids are, due to their thermal instability, not distillable, and only about 40 wt % of the organic matter of the liquid can be quantified by the conventional GC/MSD method.[7,8] Carbohydrates (mainly anhydropolysaccharides) are especially demanding to characterize.[9,16]

The solvent fractionation scheme was developed[6,10] in order to have a method for comparison and for following the main chemical changes in whole pyrolysis liquids. The method has been successfully used in studying the storage stability and quality improvement of pyrolysis liquids.[11−13]

Carbohydrates are the ether-insoluble material of the water-soluble fraction of the product liquid. They are a syrup-like fraction containing monosaccharides, anhydrosugars (levoglucosan, cellobiosan), and anhydropolysaccharides. Aliphatic hydroxy carboxylic acids (C < 10) are also found in this fraction. The amount of GC-eluted compounds of the fraction is low, and this fraction cannot be thoroughly identified using present analytical tools. One problem is lack of calibration standards. The fraction was identified to be mainly carbohydrates based on elemental analysis, solubility, behavior (syrup-like), thermogravimetric analysis (TGA), and C^{13}−NMR.[6,10] The fraction was also pyrolyzed by pyroprobe at higher temperatures (500 − 800 °C). All formed GC-eluted compounds were degradation products of carbohydrates, with the main compounds being water and levoglucosan.[10] In this publication this fraction is called "sugars".

Sugars of pyrolysis liquid cause problems in fuel oil use because of their reactivity and sticking tendency.[14] The material causing stickyness, for example, in diesel engines has been analyzed at VTT and reported only in internal reports. The change in sugars is an important quality factor. In the solvent fractionation scheme, sugars[6] are determined from the water-soluble phase as material insoluble in diethylether. By GC-MSD only 5−10 wt % (monomers and dimers) of the fraction can be identified. There is a need for a rapid method for analyzing the sugar content of pyrolysis liquid. This paper focuses on

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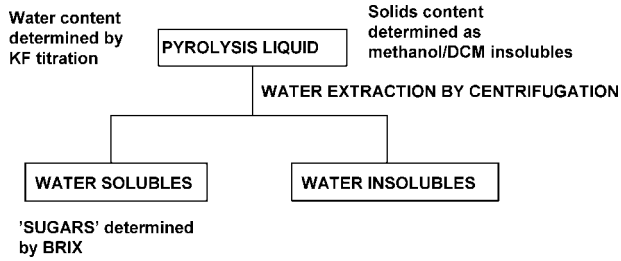

Figure 1. Solvent fractionation method with Brix for rapid characterization of wood fast pyrolysis liquids.

description of a so-called Brix method in sugar analysis. In addition, a simplified solvent fractionation scheme is represented.

Experimental Section

Pyrolysis Liquids. Pyrolysis liquids tested were produced at VTT in the Process Development Unit (PDU), which is based on the use of a transport bed reactor. Pyrolysis feedstock used was pine saw dust. Pine saw dust (*Pinus sylvestris*) was received from Pihlava saw mill, situated on the western coast of Finland (Pori), and was stored after drying to below 10 wt % moisture content. The ground, sieved (main fraction below 3 mm), and dried (moisture content 4−6 wt %) feedstock was fed to the reactor by a screw feeder. Pyrolysis temperature was about 520 °C. The residence time for pyrolysis vapors was about 1−2 s. The main part of the char particles as well as the circulation sand was removed by cyclones from a hot stream of product gases and vapors, before entering to liquid scrubbers. The product vapors were condensed in liquid scrubbers, where the product oil ("seed oil") was used as a cooling agent. The amount of raw material and the amount of product oil was measured by weighing. Typical product yields from pine were 64 wt % organic liquids, 12 wt % product water (chemically dissolved in organic liquids), 12 wt % char, and 12 wt % noncondensable gases.

Solvent Fractionation Scheme. The original solvent fractionation scheme is presented in detail elsewhere.[6,10] In the method, pyrolysis liquid is divided into water-soluble (WS) and water-insoluble (WIS) fractions. The WIS fraction of fresh pyrolysis liquid consists mainly of lignin-derived material,[4−6] extractives, and solids.[6] The WIS fraction is further separated by dichloromethane (DCM) extraction into two fractions having different molecular size distributions. The DCM-soluble fraction of fresh pyrolysis liquid consists of low-molecular-mass (LMM) lignin material (MM 400 Da) and extractives.[6,10] If needed, solids and extractives are analyzed separately from the original pyrolysis liquid and volatile acids[6,8,10] and alcohols[6,10] from the aqueous phase extract. The DCM-insoluble fraction is referred to as high molecular mass (HMM) lignin. In aged liquids, polymerization and condensation products are included in both of these WIS fractions. The WS fraction is extracted with diethyl ether, yielding an ether-soluble (ES) fraction containing mainly aldehydes and ketones but also lignin monomers. The ES fraction contains most of the GC-eluted compounds.[6] The ether-insoluble (EIS) fraction contains mainly sugars, with a minor part of it being identified by GC-MSD.[6,10]

Brix. The Brix method is commercially used to quantify the sugar content of grapes and wine. The Anton Paar DMA 4500 equipment contains the method for determining Brix at 20 °C. The sugar content is determined by a hydrometer, which indicates a liquid's specific gravity (the density of a liquid in relation to that of pure water). Each degree of Brix (°Br) is equivalent to 1 g of sugar per 100 g of grape juice. In this scheme, the saccharose concentration (% weight) according to the NBS (National Bureau of Standards) based on the true density at 20 °C was determined.

Stability Test. In the test[2,12] pyrolysis liquid sample is mixed properly and left to stand until the air bubbles are removed. Then, 90 mL of the sample is poured into a 100 mL tightly sealed glass bottle. A duplicate is included. The bottles are firmly closed, weighed, and placed in a heating oven at 80 °C for 24 h. After the test, the sample bottles are cooled rapidly in cold water, weighed, and analyzed. The possible difference in the weights before and after the test is an indication of leakage, and the test should be repeated if the net weight loss is above 0.1 wt % of original weight. The viscosity of the liquid at 40 °C is measured before and after the test as kinematic viscosity according to ASTM D 445. The water content is analyzed by Karl Fischer titration according to ASTM D 1744.[1,2] The changes in viscosity and water are also measured.

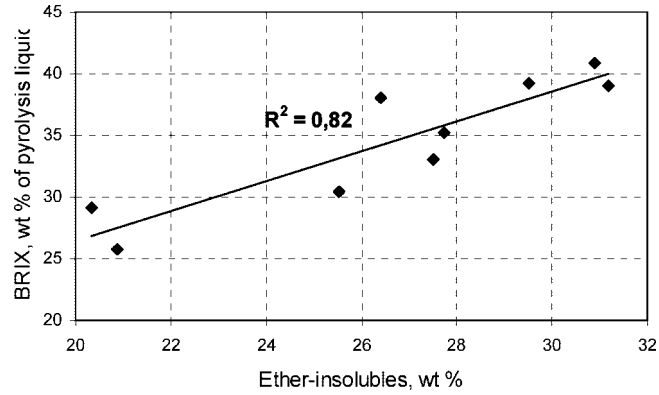

Figure 2. Correlation of the sugars measured as ether-insoluble (EIS) and by the Brix method.

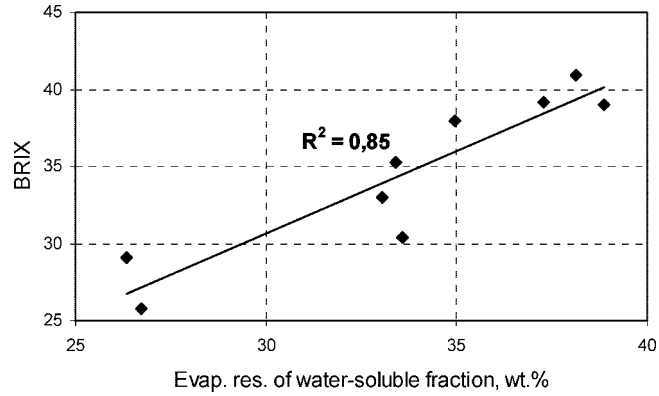

Figure 3. Correlation of the sugars measured as evaporation residue[6,10] of the WS fraction and by the Brix method.

Results and Discussion

New Solvent Fractionation Scheme. This method is based on water extraction (Figure 1). Pyrolysis liquid is divided into WS and WIS fractions. The water content of the pyrolysis liquid is analyzed by Karl Fischer titration. The WIS material consists mainly of lignin-derived material, extractives, and solids. In aged liquids this fraction also includes HMM reaction products. There is a clear correlation of the WIS fraction with its HMM fraction.[6] Hence, the change in WIS gives similar information than the change in HMM fraction of WIS. The different fractions of the solubility scheme are calculated as percent by weight of the original liquid. Results are presented graphically, in the form of a chart.

Development of Brix Method for Characterization of Sugars in Pyrolysis Liquids. The method has been developed for single-phase biomass pyrolysis liquids. In the method, the sample is first homogenized by mixing. Immediately after mixing, 3 g of the sample is weighed into a 45 mL centrifuge tube. The sample should be spread over a wide area on the bottom of the tube, so that water will have a maximum contact surface with the sample. The centrifuge tube is filled with water (liquid/water = 1:10) to the mark (30 mL). The water/sample ratio must not exceed 1:11 or fall below 1:9. The centrifuge

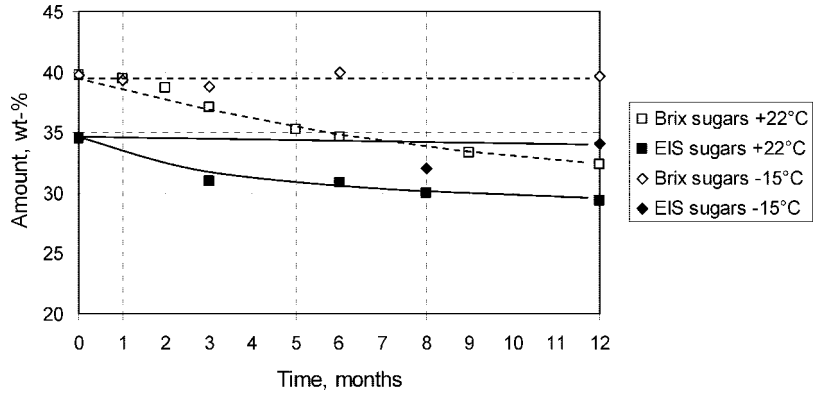

Figure 4. Change in sugars measured by solvent extraction (EIS sugars) and by Brix method (Brix sugars) during storage at various temperatures.

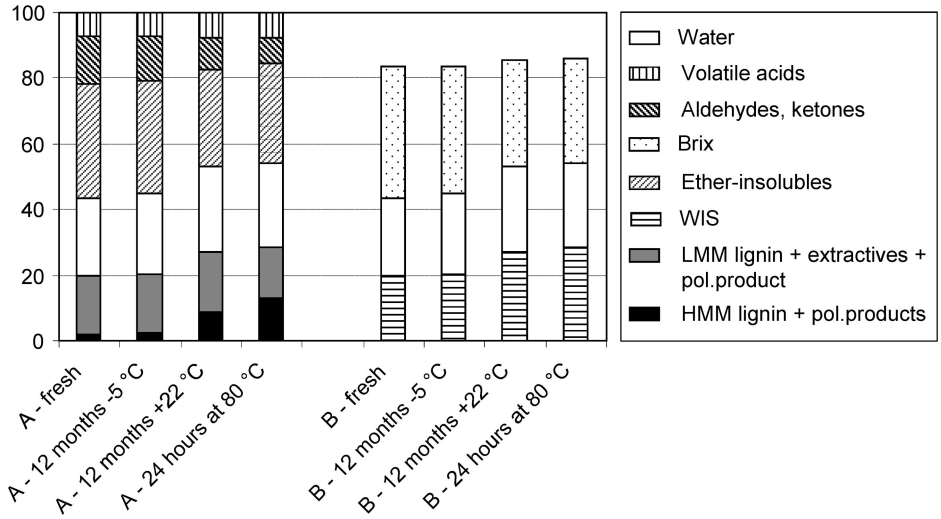

Figure 5. Composition of pyrolysis liquid based on solvent extraction scheme. Chemical characterization by measuring sugars by solvent extraction as EISs (A) and by Brix method (B).

tube is placed in an ultrasonic bath for approximately 30 min (to ensure complete solubility of the WS matter). The temperature of the ultrasonic bath will increase during the treatment, but the temperature must not exceed 40 °C. This temperature is based on long experience for preventing acid hydrolysis and other reactions from taking place.[15,16] For pyrolysis liquids, the extract is often strongly emulsified and also contains WIS matter. When kept standing, the majority of the insoluble matter falls to the bottom or sticks to the walls of the tube. The tube is centrifuged if required (4500 rpm, 30 min). A sample for Brix analysis is taken using a 5 mL syringe. If the extract remains opaque, the sample (5 mL) can be filtered through a disposable filter (Millipore Millex-LCR Hydrophilic PTFE 0.45 μm) for analysis. Aqueous solutions remain unchanged in a refrigerator for at least a week. The result is the Brix concentration in the solution (30 mL). Using the Brix method, the amount of sugar-like material in the WS fraction of the pyrolysis liquid was measured. The model compounds used were cellobiosan and levoglucosan. A standard laboratory solution from these model compounds was prepared and Brix was measured. The Brix method gave exactly the same results as the calculated values. For the aqueous phase of the pyrolysis liquid, the standard deviation of Brix was <0.7 (eight determinations). The mean result for parallel samples is indicated with one decimal place. Reproducibility for parallel samples is ±3%. The main source of error is the homogeneity of the weighed sample. A viscous sample may be difficult to mix. The sample can be heated to below 40 °C. The method does not appear to be suitable for surface phases in which the amount of sugar is small. Surface phases are also too viscous and contain a large amount of solid matter.

$$\text{Brix \% by weight in the initial product} = (\text{reading} \times 0.03(\text{l})/\text{amount of sample(g)}) \times 1000 \quad (1)$$

WIS. The water portion is pourred out of the centrifuge tube, and the centrifuge tube and precipitate (WIS) is flushed using a small amount of water. The centrifuge tube and its precipitate are dried in the heating oven in 50 °C overnight and weighed. the amount of water-insolubles is calculated.

Comparison of Sugars from Solvent Fractionation and by Brix Method. The amount of EIS sugar fraction (Figure 2) obtained from solvent fractionation correlated well with the Brix determinations. However, it has to be pointed out that the Brix method systematically gives 20 wt % higher values for fresh liquids. The Brix values were similar to those for the evaporation residue[6,10] of WS fractions (Figure 3), which includes the EIS sugar fraction and larger nonvolatile aldehydes and ketones in the ES fraction. The Brix method has been used in the sugar industry for samples that do not contain hydroxyaldehydes. Carbohydrates are polyhy-

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droxy aldehydes and ketones,[17] much of the chemistry of which is the familiar chemistry of the alcohol and carbonyl functional groups. The carbonyl group can be reduced to yield alditol or oxidized to yield aldonic acid. When applying the Brix method to the analysis of the aqueous phase of pyrolysis liquids, it is suggested, based on all presented analytical results, to give the total amount of sugars (aldoses and ketoses) and that part of the hydroxyl aldehydes/ketones fraction, the structure of which is similar to those of aldoses/ketoses.

The developed Brix method was used for following the change in sugar fraction of pyrolysis liquid during storage (Figures 4 and 5). The sugars were characterized as EIS using the solvent fractionation scheme and by Brix from the aqueous extract of pyrolysis liquid. The degree of change was very similar.

Conclusions

The solvent fractionation method based on water extraction has been proven to be an effective tool for characterization of pyrolysis liquids and studying their storage stability. However, for quality follow-up in pilot/demonstration plants, a simpler and faster fractionation scheme is needed. There is also a need for a rapid method for analyzing the carbohydrate content of pyrolysis liquid. Carbohydrates of pyrolysis liquid cause problems in fuel oil use due to their reactivity and sticking tendency. The new method includes much faster separation of water extract using centrifuge and characterization of carbohydrates by the Brix method. The determination of water content, water-insolubles, and carbohydrates by Brix accounts for 80−85 wt % of pyrolysis liquid composition. The main changes in aging happen between these groups; hence, these changes give information on the quality of pyrolysis liquids.

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