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Centrifugal partition chromatography a first dimension for biomass fast pyrolysis oil analysis

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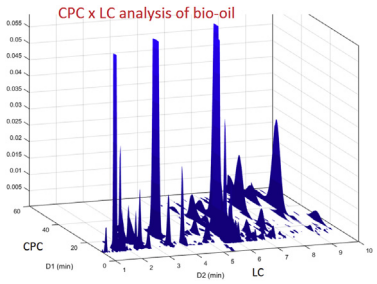
HIGHLIGHTS

- 280 fractions collected by CPC from a biomass fast pyrolysis oil.
- Separation according to partition coefficient in a solvent system.
- Satisfactory mass balance for semi-preparative fractionation of a bio-oil.
- Comprehensive off-line CPC × LC analysis of a bio-oil.

GRAPHICAL ABSTRACT



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ABSTRACT

Biomass fast pyrolysis oils contain molecules having a large variety of chemical functions and a wide range of molecular weights (from several tens to several thousand grams per mole). The good knowledge of their complex composition is essential for optimizing the conversion of bio-oils to biofuels, thereby requiring powerful separation techniques. In this work, we investigate the interest of centrifugal partition chromatography (CPC) as a first dimension for the analysis of a bio-oil. A CPC method is proposed to separate oxygen containing compounds according to their partition coefficients in the solvent system. This approach is a powerful and easy-to-use technique that enables fractionation of a bio-oil at a semi-preparative scale, without any sample loss related to adsorption on the stationary phase. Collected fractions are then injected in liquid chromatography as a second dimension of separation. Contour plot representations of the CPC × LC separation are established to discuss the potential of this approach. These representations can be used as a veritable fingerprint in the comparison of different samples or samples at different steps of a conversion process but also as a powerful tool to identify new compounds and describe the entire composition of the bio-oil.

1. Introduction

Diversification of energy sources has become a major issue we have to face up today in order to meet the growing demand for mobility. Thermochemical transformation of lignocellulosic materials is an intensively investigated route for production of second generation biofuels [1]. Liquids derived from fast pyrolysis of lignocellulosic biomass, also called 'bio-oils', are constituted of a large number of oxygenated compounds (carboxylic acids, alcohols, aldehydes, ketones, sugars, phenols,…) and need a further upgrading to be used as biofuels [2–6]. To get a molecular description of such liquids, a suitable analytical approach is required taking into account features that are specific to bio-oils:

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compounds having a wide range of functional groups and molecular weights as well as thermosensitive molecules. Recently Crepier et al. demonstrate that supercritical fluid chromatography (SFC) may be a promising approach to analyze bio-oils [7]. On-line comprehensive two-dimensional liquid chromatography (LC × LC) [8] was also successfully applied to the aqueous fraction of a bio-oil and compared more recently to on-line LC × SFC [9]. However such hyphenated techniques require quite sophisticated instruments and still under development today. So alternative approaches have been proposed in literature to fractionate bio-based samples prior to a detailed analysis. For instance liquid extraction (LLE) is often implemented for biomass products as a first dimension. In the case of bio-oils, aqueous phase is often generated in a first step in separatory funnel to isolate polar water soluble compounds on one hand and high molecular weight phenolic compounds on the other hand [2,10]. In view of the large scale of polarity and also of solubility of biomass compounds, LLE seems to be an interesting approach to fractionate biomass samples in a first step because no solid packing material is used (so no irreversible adsorption of compounds is expected on the stationary phase) and it seems to be well-adapted to thermosensitive molecules. However, because of the complexity of such samples, LLE remains limited in term of efficiency and the chain of different extractions becomes essentials [3]. Also, the use of centrifugal partition chromatography as a first dimension of separation may be considered as a preferred alternative technique. Indeed in CPC the sample injected is subject to multiple extractions thanks to the cells placed in series and linked together in the column. CPC is a liquid/liquid chromatography technique based on the separation of solutes from a mixture according to their specific partitioning coefficient between the mobile and stationary phases which are both liquid [11]. Main applications for CPC technique are focused on purification of natural or biological products [12,13] and sometimes used for other products (*i.e*). separation of monosaccharides from hydrolyzed sugar beet pulp [14], separation and purification of xylose oligomers from birch wood xylan [15,16]. As described by Faure et al. [17] little publications were found involving the hyphenation of the CPC technique with LC in on-line and off-line modes essentially in the objective to isolate and purify compounds from highly complex samples. More recently Faure et al. propose to consider a 2D plot CPC × LC at the first stage of method development in order to select the fraction for the purification and isolation of two antioxidants from Edelweiss plant extract [18]. To the best of your knowledge 2D plot CPC × LC is not used to describe the composition of complex samples whose all compounds are relevant and CPC has not been applied yet to biomass fast pyrolysis oils.

This paper proposes a relevant methodology to enhance the molecular characterization of a bio-oil. We choose to investigate the interest of centrifugal partition chromatography as a first dimension of separation for the analysis of wood fast pyrolysis oil. A CPC method is proposed to fractionate a bio-oil at a semi-preparative scale to collect fractions of various solubility, without any sample loss related to adsorption on the stationary phase. All collected fractions being analyzed by reversed phase liquid chromatography, comprehensive off-line two dimensional CPC × LC is performed and contour plot representation is established with UV detection. Preliminary results obtained in hyphenation to mass spectrometry detection are presented in order to point out the potential of this approach for bio-oil analysis.

2. Materials and methods

2.1. Chemicals and reagents

The investigated sample is a fast pyrolysis oil produced from softwood sawdust, supplied by IFP Energies nouvelles. Solvents are analytical grade: heptane, ethyl acetate, methanol, tetrahydrofuran (THF), acetonitrile, butanol, toluene, cyclohexane from VWR (Fontenay sous Bois, France), methyltertiobutylether (MTBE) from Acros Organics (Fisher Scientific, Illkirch, France). Formic acid is provided from Sigma-Aldrich (Saint-Quentin Fallavier, France). Water is purified by de-ionization and reverse osmosis. Model compounds are purchased from Sigma-Aldrich.

2.2. CPC instrument

The experiments are carried out with a SCPC100 + 1000 Instrument from Armen Instrument, France (now Gilson Purification, USA). This apparatus is equipped with two columns: the first one with an exact volume of 131 mL adapted for method development and the second one with an exact volume of 988 mL adapted to scale up. A built-in manual valve is used to switch to the column of choice. The columns are coupled with a Spot Prep II integrated system from Armen Instrument that combines: a quaternary pump, an automatic sample injection valve with a 5 and 10 mL sample loop respectively used for the 100 and 1000 mL column volume, a diode array detector which allows absorbance recording over a range of wavelengths comprised between 200 and 400 nm and a fraction collector. Chromatographic data were acquired by using the Armen Glider CPC Control Software.

2.3. Selection of CPC solvent systems

All solvent systems are tested using the shake-flask methodology used as a first easy and fast screening. A suitable amount of bio-oil is added to a test tube and 2 mL of each of the equilibrated two-phase solvents are added. The tube was shaken vigorously to equilibrate the compounds between the two phases. The appropriate system is selected based on the partition coefficient ratio of the sample between the lower and upper phases. Bio-oil being colored, the quality of the partition is visually assessed for a first screening. The distribution of the compounds will be confirmed with mass balance on the collected fractions after CPC separation only for the solvent system adopted resulting from the screening step.

2.4. Preparation of solvent systems

For the selection of the solvent systems, the biphasic systems are prepared by mixing the corresponding volume portions of the solvents. The different proportions of the solvents are listed in Table 1. For the CPC separation of the bio-oil, the solvent system ARIZONA K is directly generated by the quaternary pump.

2.5. CPC methods

The conditions of elution for the two columns are presented in Table 2 for the bio-oil separation. Under these conditions 63% and 79% of stationary phase retentions are observed for solvent system ARIZONA K respectively with the 100 and 1000 mL column.

Bio-oil is diluted in a mixture of stationary and mobile phases (1/1, v/v) before injection: 4 mL for the 100 mL column and 10 mL for 1000 mL column. The signals were monitored at 210, 254 and 280 nm.

2.6. Evaluation of compounds partition

Five fractions (CPC1 to CPC5) are recovered during the separation of bio-oil with ARIZONA K in descending mode. Start and end times of the different fractions are defined according to the peaks

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