Separation and Purification Technology 152 (2015) 238–245

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Separation of phenols and ketones from bio-oil produced from ethanolysis of wheat stalk

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ARTICLE INFO

Article history:
Received 21 November 2014
Received in revised form 28 February 2015
Accepted 7 March 2015
Available online 25 March 2015

Keywords:
Bio-oil
Extraction
Column chromatography
Phenols
Acetophenone
Cyclopentenones

ABSTRACT

To realize an efficient utilization of bio-oil, extraction-column chromatography was employed to separate bio-oil produced by ethanolysis of wheat stalk. The bio-oil was roughly separated by extraction with acid and alkaline solutions as well as organic solvents. Some species in the extracts was enriched by column chromatography with petroleum ether or mixture of acetone/carbon disulfide as the elution solvent. The bio-oil and all the sub-fractions were analyzed by gas chromatography/mass spectrometry. C_8–C_{30} alkanes were enriched into petroleum ether-eluted sub-fractions in a concentration of 97.6%. Phenols and acetophenone were isolated in concentrations of near 100% and 71.2%, respectively, by elution with acetone/carbon disulfide. In addition, ketones were also significantly concentrated.

1. Introduction

Biomass has been walking into our life and industries as an interesting renewable resources used to provide second generation of biofuels or chemicals [1,2]. Abundant amount and CO_2 neutrality with low sulfur and nitrogen contents make biomass a sustainable and eco-friendly energy source [3]. Bio-oil, a liquid product from thermal conversion of biomass, has been paid attention to provide fuels and chemicals [4–6]. It is a complicated liquid mixture consisting of hundreds of compounds (especially oxygen-containing organic compounds), and contains high contents of water and oxygen with low heating value and high acidity [4,7–9]. The poor fuel quality of bio-oil makes it unsuitable to be used directly as vehicle fuel, and the compositional complexity makes it difficult to be upgraded [7]. Recently, increasing attention has been paid to the recovery of chemicals from bio-oil. Providing chemicals compared to fuels could make recovery of even small concentrations viable [5]. As we all know, most of oxygen-containing organic compounds, such as phenols, ketones, and alcohols, are value-added chemicals used in industry and life. Until now, most of oxygen-containing chemicals are mainly produced from fossil fuels via oxidation or hydration of olefins to introduce oxygen-containing functional groups. Fortunately, these functional groups have already existed in bio-oil. Hence, providing value-added chemicals from bio-oil is a potential approach for efficiently utilizing biomass.

Distillation, extraction, and column chromatography are three common methods for separation. Distillation separates the bio-oil into different fractions by the boiling-point. The thermal and chemical instability of bio-oil leads to a low distillation yield and coke formation during distillation [7,10]. Recently, molecular distillation was introduced to separate bio-oil, which can increase the distillate yields and lower the formation of coke [11–13]. Bio-oil was mainly separated into light fraction (main compounds: acetic acid and 1-hydroxy-2-propanone), middle fraction (main

Abbreviations: SEB, bio-oil produced from supercritical ethanol; DEE, diethyl ether; PE, petroleum ether; BRCKs, benzene ring-containing ketones; CPs, cyclopentenones; HCPs, hydroxycyclopentenones; DHF, dihydrofuranone; PHBs, polyhydroxybenzenes; MHBs, monohydroxybenzenes; SG, silica gel; GC/MS, gas chromatograph/mass spectrometer; FTIR, Fourier transform infrared; IEP, inextractable portion; WP_1, water phase 1; BP_1, benzene phase 1; IES_1, inextractable solution 1; E_I, extract I; BP_2, benzene phase 2; E_{II}, extract II; IES_2, inextractable solution 2; E_{III}, extract III; ES_{an}, effluent solution a1 or a2; ES_{bn}, effluent solution b1 or b2; $ES_{bn\text{-}w}$, milk-white solids obtained from effluent solution b1 or b2; ES_{cn}, effluent solution c1, c2, c3, or C4; ASP, acetone-soluble phase; AISP, acetone-insoluble phase.

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http://dx.doi.org/10.1016/j.seppur.2015.03.032
1383-5866/

Table 1
Summary of bio-oil separation by extraction and column chromatography.

Bio-oil precursor	Solvent	Species isolated	Ref.
Extraction			
Forest residues	Trioctylamine and 2-ethyl-hexanol	Acetic acid	[16]
Model compounds	Trioctylamine and 2-ethyl-1-hexanol	Glycolaldehyde and acetic acid	[17]
Scots pine	Water	Levoglucosan	[18]
Lauan sawdust	CH_2Cl_2, water, NaOH and HCl aqueous solutions	Phenols	[7]
Eucalyptus wood	Ethyl acetate, NaOH and HCl aqueous solutions	Phenols	[10]
Corn stalk	NaOH and HCl aqueous solutions	Phenol, cresols, guaiacol, 4-methylguaiacol and syringol	[19]
Wood and forest residues	Ethyl acetate, water, $NaHSO_3$ and alkali aqueous solutions	Phenols	[20]
A biomass	Hexane, PE, chloroform and water	Phenols and guaiacols	[21]
Column chromatography			
Cashew nut shell	Hexane, ethyl acetate, chloroform and methanol	Cardanol, cardol, dioctyl phthalate, bis(2-ethylhexyl) phthalate and didecyl phthalate	[22]
Linseed	Pentane, toluene and methanol	Alkanes, arenes and polar species	[23]
Rapseed, linseed and hazelnut shell	Hexane, toluene, dichloromethane and methanol	Alkanes, arenes and polar species	[24]
Rice husk	Ethyl acetate, PE, ethanol, NaOH and HCl aqueous solutions	Dialkyl phthalates	[2]
Soybean cake	Pentane, toluene, ether and methanol	Alkanes, alkenes, arenes, esters and polar species	[25]
Rice straw	Pentane, toluene, ether and methanol	Alkanes, alkenes, arenes, esters and polar species	[26]

compounds: phenols, aldehyde, and ketones), and heavy fraction (main compounds: levoglucosan) by molecular distillation [11,14,15]. Considering the mild condition, extraction and column chromatography has been employed to separate bio-oil. As listed in Table 1 [2,7,8,16–26], extraction is always used as bench-scale separation technique of bio-oil and has been widely investigated to isolate phenols and sugars (such as levoglucosan and glycolaldehyde) from bio-oil. Acid and alkaline solutions are always employed to separate phenols from bio-oil. Wang et al. [7] obtained a phenolic fraction in a concentration of 94.35% through liquid–liquid extraction with acid and alkaline solutions and carbon dichloride. Zilnik and Jazbinsek [20] tried to recover phenolic fractions from various bio-oils by two methods and found that 4-methylpentan-2-one combined with alkali solution is effective for extracting phenolic compounds. Recently, liquid–liquid extraction with organic solvents was investigated by Wei et al. [21] and a fraction with 85% of phenols was obtained. As Table 1 shows, separation of bio-oil by single column chromatography always gives aliphatic, aromatic, and polar fractions [23–26]. The aliphatic fraction is determined as a mixture of alkane and alkene [25], while aromatic and polar sub-fractions are paid less attention. By multi-steps column chromatography, Das et al. [22] separated cardanol, cardol, di-n-octyl phthalate, bis (2-ethylhexyl) phthalate, and di-n-decyl phthalate from a pyrolysis oil, and Zeng et al. [2] obtained five fractions, mainly containing phthalates.

The objective of this study is to isolate possible chemicals such as phenols and ketones from a bio-oil at a laboratory scale. Extraction and column chromatography were combined to separate the bio-oil, and provide possible chemicals. The bio-oil was produced by ethanolysis of wheat stalk. Liquid–liquid extraction was employed to separate the bio-oil into different fractions. Column chromatography was used to isolate each fraction into some sub-fractions. C_8–C_{30} alkanes, phenols, acetophenone, and cyclopentenones were enriched successfully. Different from the separation of phenols from bio-oil, publications on separation of ketones from bio-oil are very limited. Acetophenone and cyclopentenones were also enriched in high concentrations from the bio-oil in this study.

2. Experimental

2.1. Wheat stalk and reagents

The wheat stalk used in this study was collected from Xuzhou, Jiangsu Province, China. It was pulverized and passed through an

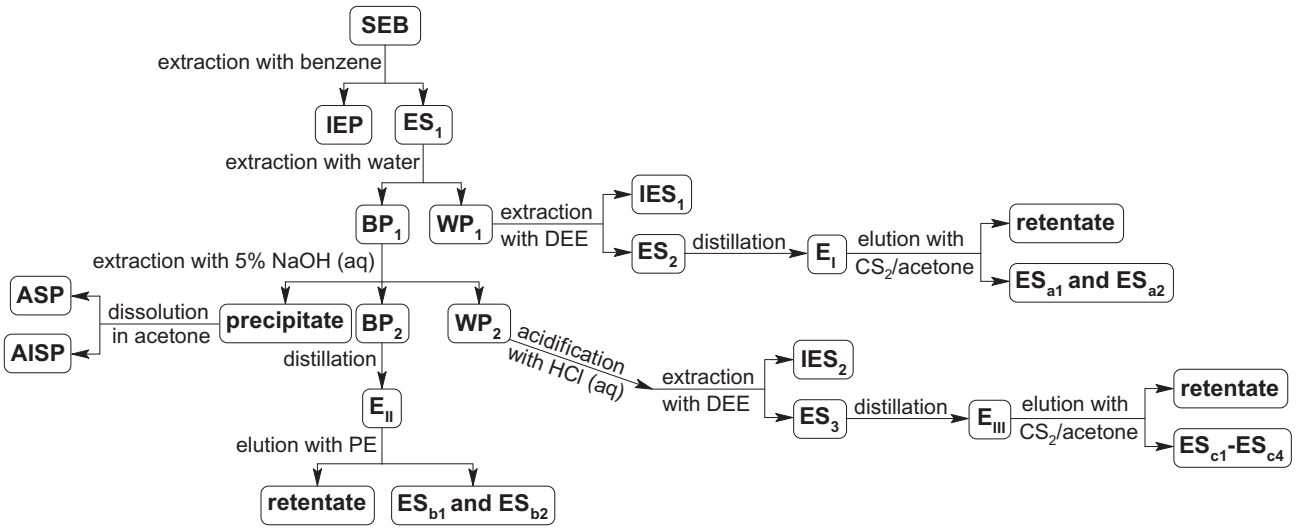

Fig. 1. Schematic diagram for the separation of SEB.