

Fractionation of Pyroligneous Acid: The First Step for the Recovery of Levoglucosan

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Levoglucosan (LG) obtained from lignocellulosic biomass exhibits great potential as a specific tracer for biomass burning aerosols and as a raw material for synthesizing stereoregular polysaccharides. One potentially viable source of LG is pyroligneous acid (PA). This study investigated the effects of heating temperature on the extraction capability and the chemical composition of distillate and residual fractions. The results demonstrated that vacuum distillation extracted the acids, alcohols, ketones, aldehydes, and other organic matter. When the heating temperature was above 80 °C, the moisture content of the residual fraction was unchanged. The chemical composition of residual fraction was analyzed by gas chromatography-mass spectrometry (GC-MS). The analysis showed that the relative content of the LG, as obtained from the 90 °C distillation temperature, was 75.6%. Thus, it can be used as raw material for subsequent purification.

Keywords: Pyroligneous acid; Levoglucosan; Vacuum distillation; Distillate; Residual fraction

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INTRODUCTION

Pyroligneous acid (PA) is a brownish-yellow acidic liquid derived from the slow pyrolysis of biomass in an oxygen-free environment (Loo *et al.* 2008). PA is obtained by the condensation of pyrolysis vapor, which is a by-product of making charcoal (Mathew and Zakaria 2015). The composition of PA is very complicated, including complex mixtures of acids, phenols, sugars, furan and pyran derivatives, ketones, aldehydes, and other carboxylic acids (Mathew and Zakaria 2015). These components mainly originate from the decomposition of cellulose (40 to 50%), hemicellulose (20 to 30%), and lignin (10 to 25%) (Vitasari *et al.* 2011).

Organic bonds such as C-C, H-O, C-H, and C-O bonds in lignocellulosic biomass are decomposed by various reactions including dehydration, hydrolysis, oxidation, decarboxylation, and depolymerization to produce pyrolysis vapors, tar, gaseous products, and water vapor (Mansur *et al.* 2013).

Levoglucosan (LG) is a primary product arising from the pyrolysis of cellulose, either as an intermediate or product (Zhang *et al.* 2013); however, the pyrolysis mechanism has not been demonstrated. The three LG formation mechanisms are glucose intermediate, free-radical mechanism, and ionic mechanism (Hosoya *et al.* 2007). Cellulose decomposition consists of two competitive reaction channels: the formation of tars (mainly LG) and char, and the formation of light gases (Capart *et al.* 2004). In an investigation of the mechanism of the cellulose pyrolysis and the formation of the main products, Wang *et al.* (2012) found that LG and other anhydrohexoses are formed directly from cellulose, and

that these anhydrosugars can further decompose into furfural and acids. The pyrolysis of cellulose is divided into three stages: 150 to 300 °C, 300 to 390 °C, and 380 to 800 °C. Different reactions occur, and the active cellulose, or anhydrocellulose, is formed in the first stage. Many reactions occur simultaneously because the glycosidic bond becomes very reactive, leading to the rapid depolymerization of cellulose in the second stage. In the last stage, CO, H₂, and CH₄ are released *via* the depolymerization of cellulose (Collard and Blin 2014).

Levoglucofan is generated at temperatures higher than 300 °C. A variety of factors affect the LG yield, and of these, the pyrolysis temperature and the inorganic impurities are the most important (Kawamoto *et al.* 2009). A small amount of inorganic impurities has a noticeable impact on the yield of LG (Shimada *et al.* 2008).

LG, which can be regarded as a rare sugar, is not commercially available. Accordingly, there are limitations to obtain a sufficient supply for basic research. LG is mainly used as a chiral raw material to synthesize stereoregular polysaccharides (especially chiral chemicals) (Bailliez *et al.* 2004; Bennett *et al.* 2009) or as a chemical tracer of the atmospheric pollutant from combustion of biomass (Jordan *et al.* 2006; Zangrando *et al.* 2016). Some researchers have produced or extracted LG from bio-oil (Bennett *et al.* 2009; Tessini *et al.* 2011; Lu *et al.* 2014).

Conventional separation or purification technologies such as centrifugation, liquid chromatography, extraction, and distillation have been exploited to isolate pyrolysis liquid. Centrifugation is a simple pretreatment technique, but there are some limitations on the separation of the homogeneous PA (Lian *et al.* 2010). Liquid chromatography effectively separates aromatic and saturated hydrocarbons, but there is the problem of high solvent consumption and cost (Chi *et al.* 2013). Extraction is used for phenol recovery, which leads to a large amount of flocculation (Elkasabi *et al.* 2015). Conventional distillation includes atmospheric distillation, vacuum distillation, flash distillation, and steam distillation. Flash and steam distillation have the advantage of short residence time, which can avoid secondary reactions, but they are only suitable for pre-separation. Atmospheric and vacuum distillation have the disadvantages of long residence time, high temperature, and low efficiency. Because they are relatively inexpensive and simple, and this experiment is the first step for the recovery of LG, high-purity products were not the prime objective of this experiment. More importantly, PA is a complex mixture of many compounds with a wide range of boiling points. It is heat-sensitive and easily undergoes decomposition, polymerization, and oxygenation. Vacuum distillation is mainly used for compounds that are degraded or transformed by high temperature. Based on previous studies, distillation can separate valuable chemicals.

This study investigated the optimum temperature of distilling the PA to obtain the residual fraction with less impurities. Removing the water and the light weight liquid from PA is the main purpose under the structure of LG not being destroyed. As temperature increases, the polymerization reaction occurs to small molecules, which may produce macromolecules that are hard to separate from LG (Chen *et al.* 2014). Vacuum distillation is a physical separation of chemical components based on the relative volatility of chemicals at various temperatures to purify PA. The purpose of vacuum distillation was to isolate more components. To accomplish this target, the specific aims were to: (1) distill evaporate the water of PA at different temperatures and analyze the components and (2) compare the components of residual fraction of the distillation flask at different distillation temperatures.

EXPERIMENTAL

Raw Materials

Forest residue-derived and pine-derived PA were provided by Shandong Tairan Biotechnology Co. Ltd. (Dongying, China). The crushed raw materials were fed into the charcoal kiln, and vapors originating from the biomass was cooled through multistage condensers. The pH of PA was measured by a PHS-3C pH meter (Shengci, Shanghai, China).

The moisture contents of PA, distillate, and residual fraction were measured by Karl Fisher titrator (870 Titrino Plus, Herisau, Switzerland) in accordance with ASTM E203 (2008). The moisture content of PA and distillate were directly measured after the residual fraction was diluted with ethanol to reduce its high viscosity. The rotary evaporation contained a 250 mL collecting bottle and a 500 mL rotary bottle. The temperature accuracy was ± 2 °C.

Experimental Procedure of Distillation

The volume and speed of the rotating bottle were 500 mL and 75 rpm, respectively. Two hundred mL of PA was injected into the rotary bottle and distilled at 50 to 100 °C, and 0.1 MPa vacuum for 1 h.

After fractionation, the volumes of the distillate and residual fraction were measured in the 200 mL cylinder, and their components were analyzed by gas chromatography-mass spectrometry (GC-MS). The degree of separation of each chemical group was evaluated using a separation factor based on the relative peak concentrations from GC-MS (Guo *et al.* 2010)

Analytical Methods

Chemical composition analysis by GC-MS

GC/MS analysis of the PA, distillate, and residual fraction was performed using an Agilent 6980-5973N instrument (Palo Alto, America). For MS detection, the electron ionization mode with an ionization energy of 70 eV was used. A DB-1701 capillary column (60.0 m, 250 μ m, film thickness 0.25 μ m) was used for GC/MS. The column temperature was programmed from 45 to 220 °C at the heating rate of 5 °C/min with the hold time for 5 min. GC was performed in the splitless mode. Helium was used as a carrier gas at a flow rate of 1.0 mL/min.

An injection volume of 1 μ L was used for each sample. Essential compounds were identified by retention times and mass fragmentation patterns using data of standards at the NIST05 library. The PA, distillate, and residual fraction were filtered with PTFE 0.22 μ m before injection.

Moisture content determination using Karl Fisher titration method

At a water-bath temperature of 50 to 60 °C, the residual fraction had better fluidity, so its moisture content was measured directly by a Karl Fisher titrator. It was diluted with ethanol because of poor fluidity when the water-bath temperature > 70 °C. The accuracy of the measurement was within 5%. The sample was measured three times to obtain the optimal measurement results.

RESULTS AND DISCUSSION

Pyroligneous Acid Composition

Pyroligneous acid is an acidic reddish-brown aqueous liquid. It is obtained by clarifying the liquid from the pyrolysis of wood residue or tree branches. Forest residue-derived and pine-derived PA have complicated chemical compositions that were elucidated in this study.

Nearly 50 compounds were discovered by GC-MS. Acids, sugars, and phenols were the major components, and ketones, alcohols, furan and pyran derivatives, aldehydes, esters, were identified as minor components. Acetic acid and LG were the most abundant components in PA. LG is the primary product of the thermal degradation of cellulose, formed by depolymerisation through transglycosylation. It further transforms to the small amount of furans and acids through fission and disproportionation (Zhang *et al.* 2013). A high yield of LG was obtained at 550 °C, demonstrating its high thermal stability (Lian *et al.* 2010). The relative contents of the compounds identified were measured from their peak areas and expressed as percentages (Table 1).

The proportion of the macromolecular components varies in different biomass (Vassilev *et al.* 2012). The cellulose component is a polysaccharide consisting of D-glucose units connected to each other by glucosidic bonds, which has a strong tendency to form intermolecular hydrogen bonds and creates a highly crystalline structure (Patwardhan *et al.* 2011; Wang *et al.* 2013).

Hemicellulose is a complex polysaccharide mainly composed of pentose sugars and hexose sugars. Lignin is a randomly linked, amorphous, high-molecular weight phenolic compound composed of p-coumaryl, coniferyl, and sinapyl alcohol units (Anca-Couce 2016). Some polysaccharides are easily cleaved during pyrolysis to form acetic acid, which is the principal component of PA.

The chemical compounds identified in PA are shown in Table 1. PA was found to be a complex mixture of organic compounds consisting of a wide range of organic chemicals. The detected compounds were classified into several categories: acids, sugars, ketones, alcohols, aldehydes, phenols, and others containing a small amounts of oxides, furan derivatives.

The acid compounds consisted of acetic acid, propanoic acid, butanoic acid, 4-hydroxy, dl-2,3-diaminopropionic acid, and the pH of PA was within the range of 2.2 to 2.4. The acid concentration in PA were was 25.16% (area), which was the most abundant organic compound in PA. The relative contents (RC, area%) decreased in order: acids (25.16%) > sugars (23.85%) > ketones (9.51%) > alcohols (4.2%) > phenols (3.97%) > aldehydes (0.83%).

The sugars were mainly composed of LG, d-allose, and vanillin lactoside in PA. Levoglucosan and d-allose are rare monosaccharides that exist in nature in very small quantities; they exhibit similar physicochemical properties, as shown in Table 2. Research on the separation of LG and d-allose have not been found in literature. Therefore, the target product was expected to contain only a component between LG and d-allose for subsequent processing.

Table 1. Major Chemical Components of Pyroligneous Acid Present in GC-MS and their Relative Contents in Percentage

Retention Time (min)	Name of Compound	Formula	Relative Content (%)
4.12	Carbon dioxide	CO ₂	1.32
4.377	Water	H ₂ O	20.09
5.895	2-Propen-1-ol	C ₃ H ₆ O	0.37
6.146	2,3-Butanedione	C ₄ H ₆ O ₂	1.04
7.639	Acetic acid	C ₄ H ₈ O ₂	21.21
8.117	3(2H)-Furanone, dihydro-2-methyl-	C ₅ H ₈ O ₂	0.25
8.717	2-Propanone, 1-hydroxy-	C ₃ H ₆ O ₂	5.75
9.696	2-Butanone, 3-hydroxy-	C ₄ H ₈ O ₂	1.32
10.131	Propanoic acid	C ₃ H ₆ O ₂	2.86
11.122	1,2-Ethandiol	C ₂ H ₆ O ₂	2.30
11.422	1-Hydroxy-2-butanone	C ₄ H ₈ O ₂	0.73
12.714	Butanoic acid	C ₄ H ₈ O ₂	0.66
13.313	Furfural	C ₅ H ₄ O ₂	0.55
15.027	1,2-Ethandiol, monoacetate	C ₄ H ₈ O ₃	0.23
15.554	Ethanone, 1-(2-furanyl)-	C ₆ H ₆ O ₂	0.42
18.302	Butanoic acid, 4-hydroxy-	C ₄ H ₈ O ₃	0.46
19.795	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	C ₆ H ₈ O ₂	0.64
19.93	2(5H)-Furanone, 3-methyl-	C ₅ H ₆ O ₂	0.31
20.64	Phenol	C ₆ H ₆ O	0.51
21.295	Phenol, 2-methoxy-	C ₇ H ₈ O ₂	0.78
22.593	Butanedial	C ₄ H ₆ O ₂	1.20
23.089	Phenol, 3-methyl-	C ₇ H ₈ O	0.35
23.315	2(5H)-Furanone, 3-methyl-	C ₆ H ₆ O ₂	0.38
24.258	1,3-Benzenediol, 4-ethyl-	C ₈ H ₁₀ O ₂	0.27
24.46	Cyclopentanol	C ₅ H ₁₀ O	0.98
24.582	2,2-Dimethyl-4-octenal	C ₁₀ H ₁₈ O	0.32
26.718	2-Vinyl-9- [3-deoxy-d- ribofuranosyl] hypoxanthine	C ₁₂ H ₁₄ O ₄	0.25
29.063	2-Furancarboxaldehyde, 5- (hydroxymethyl	C ₆ H ₆ O ₃	0.23
29.228	1,2-Benzenediol	C ₄ H ₆ O ₂	2.06
29.503	5-Hydroxymethyl-dihydrofuran-2-one	C ₅ H ₈ O ₃	0.96
31.998	Hydroquinone	C ₂ H ₆ O ₂	0.31
32.111	Vanillin lactoside	C ₂₀ H ₂₈ O ₇	0.27
34.076	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)	C ₉ H ₁₀ O ₃	0.28
34.143	D-Allose	C ₆ H ₁₂ O ₆	0.95
35.802	levoglucosan	C ₆ H ₁₆ O ₅	2.97
37.43	levoglucosan	C ₆ H ₁₀ O ₅	19.66
39.848	Naphthalene, 1-nitro-	C ₁₀ H ₇ NO ₂	0.99

Table 2. Physicochemical Characteristics of LG and D-allose

	LG	D-allose
Chemical family	1,6-anhydro--D-glucose	Carbohydrate monosaccharide, C-3 epimer of D-glucose
Molecular formula	C ₆ H ₁₀ O ₅	C ₆ H ₁₂ O ₆
Molecular weight	162.1406 gmol ⁻¹	180.16 gmol ⁻¹
CAS number	498-07-7	2595-97-3
Density	1.688 g/cm ³	1.732 g/cm ³
Melting point	182-184 °C	141-146 °C
Boiling point	383.8 °C at 760 mmHg	410.8 °C at 760 mmHg
Flash point	185.9 °C	202.2 °C

Moisture Content of Residual Fraction

The main purposes of distillation were to remove water and dissolved organic matter while not forming new compounds. Water (72.4 wt.%) initially present in PA is miscible with the oligomeric lignin-derived compounds because of the solubilizing effect of other polar hydrophilic compounds (Hu *et al.* 2015; Anca-Couce 2016; Ochiai *et al.* 2016).

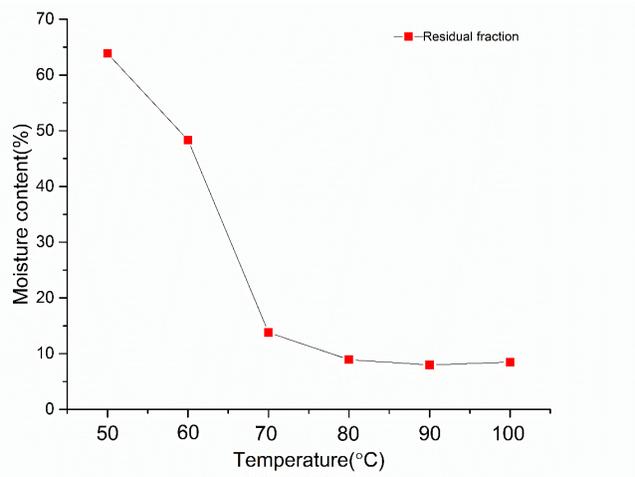


Fig. 1. The moisture content of residual fraction

Figure 1 shows that moisture content was dependent on temperature in the residual fraction. The moisture content of residual fractions fraction decreased sharply from 63.86% to 13.81% as the temperature rose from 50 to 70 °C, decreased slightly with further temperature increase to 80 °C, and thereafter did not change to an important extent. Apparently, the moisture content of the residual fraction is related to temperature. However, temperature had little impact on the moisture content when the temperature exceeded 80 °C. Because of the solubilizing effect of other polar hydrophilic compounds (low-molecular-weight acids, alcohols, aldehydes, and ketones), mostly originating from the decomposition of carbohydrates and a weak hydrogen bond interaction between LG and water, it is impossible to completely remove the moisture by distillation (Vitasari *et al.* 2011).

Effect of Temperature on the Chemical Compositions of Distillate and Residual Fraction

The distillate was analyzed to determine the change of chemical compositions along with temperature by GC-MS. Water is the most abundant component in distillate, but it is not counted in the quantitative analysis of the distillate. Figures 2 and 3 show the changes of relative contents of organic components of distillate and residual fraction at 50, 60, 70, 80, 90, and 100 °C. Most polar compounds were distilled in PA, but it was not selective due to the relatively pronounced co-extraction of non-polar compounds and the competition among polar compounds (Ochiai *et al.* 2016). Regarding the distillate, Fig. 2 shows that the composition changed at different temperatures. The relative content of acids reached 33.17% at 50 °C and decreased slightly to 33.03% at 100 °C. However, it first increased then decreased during the process. The relative content of ketones fluctuated between 10.23% and 14.88% but showed no obvious variation in this period. The relative content of alcohols dropped rapidly from 19.42% to 1.29% when the temperature increased from 50 °C to 60 °C, which was similar to changes in aldehydes and phenols.

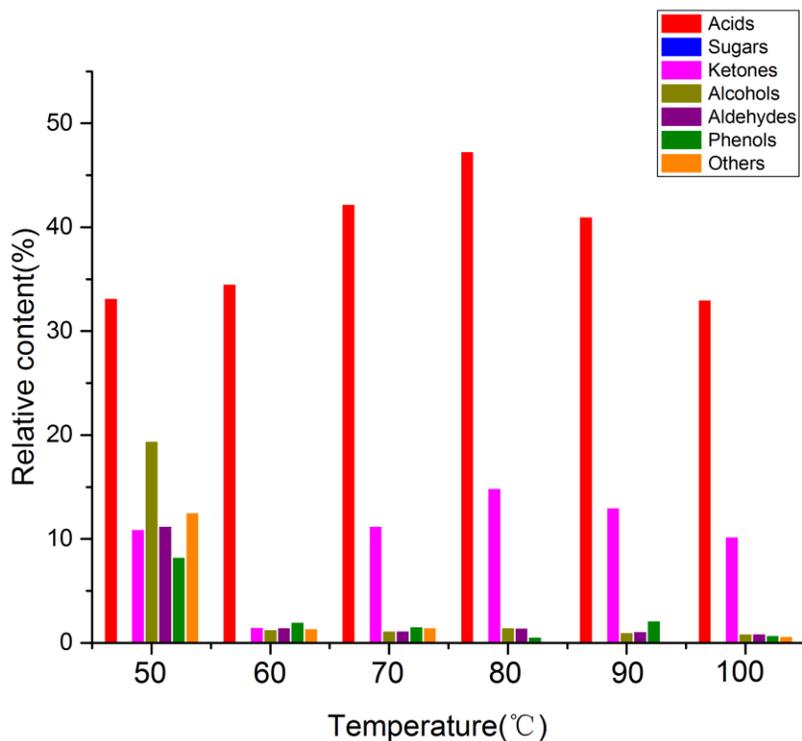


Fig. 2. The chemical composition groups of distillate at different temperatures

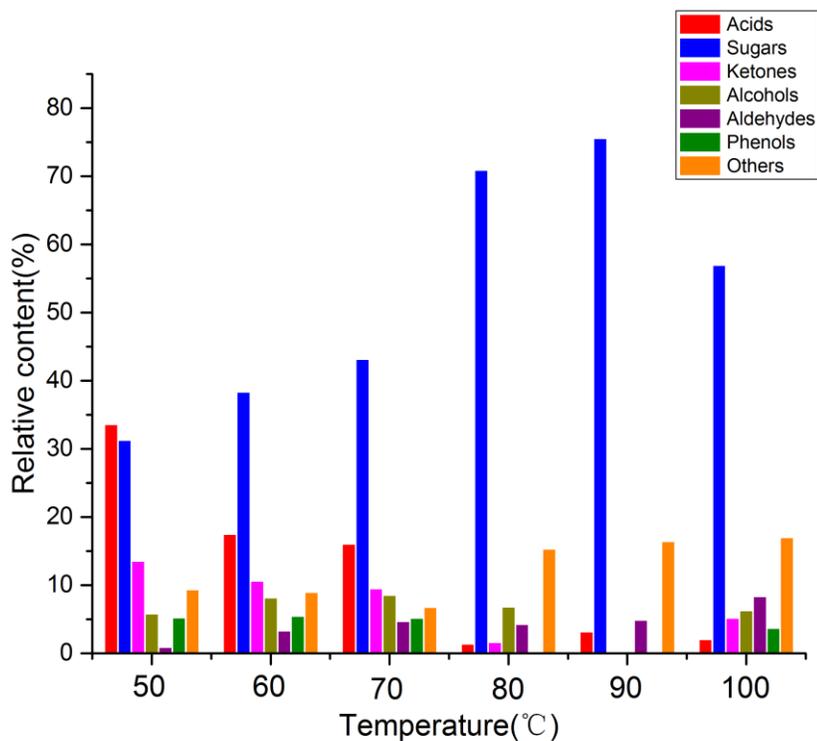


Fig. 3. The chemical composition groups of residual fraction at different temperature

As for the residual fraction, the trend of the change of the relative contents should be opposite to that of distillate under the circumstances of not forming the new compounds. However, GC-MS analysis showed that new compounds were formed during vacuum distillation. The relative content of acids decreased sharply above 70 °C. In contrast, the relative content of sugars greatly increased above 70 °C but declined slightly over 90 °C. Phenols were not observed between 80 to 90 °C. Although the separation of sugars and aromatics had been widely studied and solvent extraction or activated carbon adsorption have served as effective methods to separate them, there was no need to separate sugars and aromatics (Chi *et al.* 2013; Elkasabi *et al.* 2015).

Sugars were undetectable in the distillate. Thus, they were not extracted in the process of distillation of water and other organic compounds. The experimental pressure had an important influence on the boiling point of the sugars, ranging from 383.8 °C at 100 kPa (room pressure) to 280 °C at 10 kPa (maximum vacuum of the experimental equipment). It had the same effect on the boiling point of D-allose, which also ranged from 410.8 °C at 100 kPa (room pressure) to 300 °C at 10 kPa.

Figure 3 shows the effect of temperature on chemical composition of residual fraction temperature between 50 and 100 °C. An optimum LG yield of 75.56% of the residual fraction was achieved using 90 °C. The effects of temperature on the extraction of LG were empirically evaluated by yield and impurities contained in residual liquid. High yields of LG were obtained at 80 and 90 °C. The detailed comparison of the relative chemical composition of residual fractions between 80 and 90 °C are shown in Table 3.

Table 3. Comparison of Chemical Composition Groups between 80 and 90 °C of Residual Fraction

Compounds	Relative Content	
	80 °C	90 °C
Acetic acid ethenyl ester	3.02	--
1,2-Ethandiol, monoacetate	3.76	3.76
Acetaldehyde, hydroxy	4.25	4.87
Acetic acid, anhydride	1.37	--
Acetic acid, methyl ester	3.75	--
Ethanethioic acid	--	3.18
Acetic acid, hydrazide	0.78	--
Propanamide, 2-hydroxy	--	1.18
Piperazine, 1-(aminoacetyl)	0.65	--
2-Cyclopenten-1-one, 2-hydroxy-3-methyl	0.70	--
o-Methylisourea hydrogen sulfate	--	2.53
Cyclopentanol	4.31	--
2(5H)-Furanone, 3-methyl	0.91	--
Oxirane, (2-methylbutyl)	2.45	1.76
Tetrahydropyran Z-10-dodecenoate	--	1.26
Acetic acid, [(aminocarbonyl)amino] oxo	0.72	--
Carbon monoxide	--	0.91
2-Acetoxyindan	--	1.19
2-Methyl-2-(4-methoxyphenyl)-1,3-dithiane	--	0.98
1,6-Anhydro--D-glucopyranose (levoglucosan)	65.33	75.46
D-Allose	5.59	--
3-(3-Hydroxy-4-methylphenyl)-1,1,3,5-tetramethylindan-4-ol	2.52	--
1,2-Dihydro-2,4-diphenyl-quinazoline	--	2.00

The enormous differences existed in chemical composition between 80 and 90 °C, which may be explained by the fact that PA is heating-sensitive and undergoes chemical reactions such as decomposition, polymerization, and oxygenation during fractionation. The D-allose of main components of PA was not present in residual fraction obtained under the 90 °C heating temperature. The physicochemical properties of D-allose, based on above-mentioned analysis, is similar to LG. The residual fraction obtained under the condition of 90 °C was suitable for the subsequent isolation and purification.

The results indicated that the heating temperature has an important effect on the relative content of acids, but it had a marginal effect on the relative content of alcohols, aldehydes, and phenols above 60 °C. The majority of alcohols, aldehydes, and phenols can be distilled at temperatures higher than 60 °C.

In general, the results give a clear picture of the extraction of LG from PA in vacuum distillation. The yield profiles for LG provide useful data to design the LG extraction process and subsequent purification steps in a biorefinery system.

CONCLUSIONS

1. A novel method of primary separation, vacuum distillation, was presented based on the properties of PA.
2. This study showed that heating rate determines the moisture content and the distribution of chemical group of distillate and residual fraction. The distillate was mainly composed of water and other polar organic compounds. However, the sugars were not found in the distillate.
3. When the heating temperature was 90 °C, the phenols and D-allose were difficult to separate from LG and were not present in the residual fraction. The highest relative concentration of LG was 75.56%. Overall, vacuum distillation is not a selective method, but it is very useful to remove the majority of polar compounds and to reduce the complexity of PA prior to further isolation steps.

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