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Analysis of Organic Compounds in Residual from Wheat Stalk Depolymerized in Supercritical Methanol

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Abstract: Liquefaction of biomass is a practical source of clean liquid fuel and possible source of value-added chemicals. But if solid residual formed during liqufaction can't be properly handled, it will be a new environmental problem. In this study, we use n-hexane and carbon disulfide to extract (under ultrasonic) the biomass residual from wheat stalk depolymerized in supercritical methanol. In the fraction extracted by n-hexane, Oxy-compounds and compounds containing benzene ring are present in high concentration. The fraction extracted by carbon disulfide is separated by column chromatography. The first sub-fraction eluted by n-hexane only detected three compounds, benzenethiol, diphenylmethane and diphenyldisulfide. The second sub-fraction eluted by n-hexane is mainly alkyl-benzenes and alkyl-cyclohexanes. Nine saturated fatty hydrocarbons from C21 to C29 are eluted in the sub-fraction eluted by mixture of n-hexane and benzene.

Keywords: Residual from Wheat Stalk Depolymerized; Supercritical Methanol; Ultrasonic Extraction.

1. Introduction

Biomass is a renewable and clean energy, and receives attention from scientific institution. Ways of utilization of biomass are varied, such as gasification, liquefaction and solidification [1-5]. And Liquefaction of biomass is a practical source of clean liquid fuel and possible source of value-added chemicals [2, 6-8]. Rapid pyrolysis and high-pressure direct liquefaction (HPDL) are two mainly well-used methods for converting biomass into liquid fuel [9-14]. However no matter what kind of liquefied method is used, solid residual (SR) is inevitable. When liquefaction of biomass widely puts into production and use, if solid residual can't be properly handled, it will be a new environmental problem, which can impact the economy and application value of biomass. Understanding the structure and compounds in SR is important to deal with or make use of SR. Solvent extract is an efficient method to study organic compounds in solid, such as coal and plant resources for Chinese medicine [15-19]. Column chromatography is common and high-efficiency to separate mixture. Wei et.al [15-18] found organonitrogen and organosulfur compounds, successfully isolated a series of pure compounds, when they extracted different coal with different solvent, and used column chromatography to separate the extract. In this study, to understanding SR well, we used n-hexane and carbon disulfide to extract SR, which obtained during wheat stalk depolymerized in supercritical methanol. And we future separated the extract using column chromatography.

2. Experimental

2.1. Biomass sample and solvents

Wheat stalk was collected from Xuzhou, Jiangsu Province, China, and pulverized to pass through a 80-mesh sieve and then dried in a vacuum oven at 105°C for 3.5 h. Solvents, including n-hexane (H), carbon disulfide (CDS) and benzene (B), used in the experiments are analytical-pure reagents and were distilled prior to use. Adsorbent, silica gel (SG, 100-200 mesh, Wako Pure Chemical Industries, Ltd.), was activated in a vacuum oven at 145°C for 6 h.

2.2. Biomass residual preparation

Wheat stalk (15 g) was depolymerized with 450 ml methanol in a vacuum autoclave. The temperature stepped up gradually, and at 300°C for half an hour. The SR was separated from liquid by filtration through a membrane filter with 0.8 m of pore size. The filter cake (residual) was repeatedly washed with methanol to remove the methanol soluble fraction as completely as possible, and then dried in a vacuum oven at 105°C for 1h after drying overnight in the room temperature.

2.3. Solvent extraction

SR (5 g) was extracted with n-hexane (H) in a modified extractor under the action of ultrasonic. Then the slurry was filtrated through a polytetrafluoroethylene membrane filter with pore size of 0.8 m. The residue was extracted with H and the extraction was repeated several times until filtrate was colourless. Then the filtrates were incorporated and concentrated with a Büchi R-134 rotary evaporator, affording this fraction F_H. The process of extraction was repeated with carbon disulfide (CDS) as extractant, and this fraction was named F_{CDS}. The extract yield Y was calculated according to the formula: $Y = (W_{SR,daf}-W_{SRR,daf})/W_{SR,daf}$, where $W_{SR,daf}$ and $W_{SRR,daf}$ denote weights of original SR and SR after extraction, respectively.

2.4. Column chromatography

1.5 g F_{CDS} was mixed with 50 ml of CDS (as solvent) and 8 g of SG, and then removed CS_2. The mixture was transferred into a 2 cm i.d., SG-packed column (height of SG-packed about 50 cm). F_{CDS} was sequentially eluted with H, B and isometric H/B mixed solvent. The sub-fractions afforded F_{CDS-1} ($F_{CDS-1-1}$ to $F_{CDS-1-n}$) to F_{CDS-3} ($F_{CDS-3-1}$ to $F_{CDS-3-n}$), respectively.

2.5. GC/MS Analysis

All the fractions and sub-fractions were concentrated and then analyzed with a Hewlett-Packard 6890/5973 GC/MS equipped with a capillary column coated with HP-5MS (cross-link 5% PH ME siloxane, 30 m × 0.25 mm i.d., 0.25

μm film thickness) and a quadrupole analyze in electron impact mode at 70 eV.. The column temperature was held at 50 °C for 2min, raised to 300°C at a rate of 15°C min^{-1}, and held at that temperature for 2 min. The mass spectrometer was scanned from 30 to 500 amu. Data were acquired and processed using Chemstation software, by comparing mass spectra with library NIST05.L data.

3. Results and Discussion

3.1. Yields of the extract FH and FCDS

The yield of F_H and F_{CDS} are 4.12% and 32.56%, respectively. It indicates that SR contains much amount of CDS-soluble components, while H-soluble components are low. Using the same method to analyse coal, the yield of extract is much lower than that of SR [15, 16]. One possible reason is the bonds in coal are so strong that few compounds could be extracted out, while during the process of wheat stalk depolymerized in supercritical methanol, some bonds in the biomass are weakened, but it is still not enough to be liquefied or dissolved in methanol. So when SR is extracted by CDS, compounds with weakened bonds dissolved in CDS.

SR is black solid granular before extracted, but brown flocculated sludge after extract. Compounds detected in F_H are similar with bio-oil from wheat stalk depolymerized in supercritical methanol [7, 8]. The compounds extracted by H maybe some compounds in bio-oil adsorbed by SR. When SR extracts by H, compounds adsorbed are desorbed.

3.2. Identification of organic compounds in F_H

As Table 1 list, 67 compounds are detected in F_H. Oxy-compounds are present in high concentration, 77.82% (area %). Esters are the most abundance, and they are mainly fatty acid methyl esters and methyl benzoates as shown in Table 1. Methyl palmitate (peak 51) is dominated in this fraction. Ketones in F_H include 4 cyclopentenones (peak 8, 13, 17 and 22), 2 cyclohexenones (peak 29 and 39) and heptadecan-2-one (peak 50), while 6 phenols are detected in F_H, among which only 1 phenol (peak 26) is without methoxyl, and other phenols are methoxy-phenol. Moreover, compounds containing benzene ring, such as alkyl-benzenes, methoxy-benzenes, phenols and benzoic ethers, are plentiful in F_H, 45.37% (area%), while the area% of methoxy-benzenes and phenols are 10.68% and 7.28%, respectively. Compounds containing benzene ring may form from the depolymerization of lignine [20].

Table 1. Compounds detected in F_H

Peak	Compound	Peak	Compound	Peak	Compound
1	methylcyclohexane	22	2,3,4,5-tetramethylcyclopent-2-enone	43	1,2,3-trimethoxy-5-methylbenzene
2	toluene	23	(4-isopropylphenyl)methanol	44	methyl 3-methoxy-4-methylbenzoate
3	octane	24	2-methoxy-4-methylphenol	45	(E)-3-(2,5-dimethoxyphenyl)acrylic acid
4	1-ethylbenzene	25	2-methoxy-4-methylphenol	46	(E)-methyl 3-(4-methoxyphenyl)acrylate
5	o-xylene	26	2,4,6-trimethylphenol	47	methyl tetradecanoate
6	styrene	27	methyl 4-methylbenzoate	48	methyl pentadecanoate
7	p-xylene	28	methyl 3-methylbenzoate	49	isobutyl octyl phthalate
8	3,4-dimethylcyclopent-2-enone	29	4-ethyl-3,4-dimethylcyclohexa-2,5-dienone	50	heptadecan-2-one
9	methyl 4-methylpent-3-enoate	30	1,2-dimethoxy-4-methylbenzene	51	methyl palmitate
10	1-ethyl-3-methylbenzene	31	1-ethoxy-4-methoxybenzene	52	(E)-methyl octadec-7-enoate
11	1,2,4-trimethylbenzene	32	4-ethyl-2-methoxyphenol	53	(E)-methyl octadec-8-enoate
12	(tetrahydrofuran-2-yl)methanol	33	methyl 2,3-dimethylbenzoate	54	methyl stearate
13	3,4,4-trimethylcyclopent-2-enone	34	methyl 3,5-dimethylbenzoate	55	tricosance
14	2-methoxyphenol	35	methyl 4-ethylbenzoate	56	methyl icosanoate
15	methyl benzoate	36	1,2,3-Trimethoxybenzene	57	methyl docosanoate
16	3-methoxybenzene-1,2-diol	37	methyl 3,4-dimethylbenzoate	58	bis(6-methylheptyl) phthalate
17	2,3,4,5-tetramethylcyclopent-2-enone	38	4-ethyl-1,2-dimethoxybenzene	59	methyl tricosanoate
18	1-ethyl-4-methoxybenzene	39	2,3,5,6-tetramethylcyclohexa-2,5-diene-1,4-dione	60	methyl tetracosanoate
19	1,2,3,4-tetramethylbenzene	40	methyl 4-formylbenzoate	61	dotriacontane
20	dimethyl glutarate	41	5,6-dimethyl-1,2,3,4-tetrahydronaphthalene	62	methyl hexacosanoate
21	1,2-dimethoxybenzene	42	4-allyl-1,2-dimethoxybenzene		

3.3. Identification of organic compounds in F_{CDS} and sub-fractions

Fraction F_{CDS} is deep black. But there are no compounds detected in F_{CDS}. The possible reason is that there is some interaction-force between the compounds in F_{CDS}. In the study, we use column chromatography to separate F_{CDS}, and after the sub-fraction being analysed by GC/MS, there are three sub-fractions, $F_{CDS-1-1}$, $F_{CDS-1-2}$ and $F_{CDS-2-1}$.

In $F_{CDS-1-1}$, only three compounds are detected. Figure 1 shows the mass spectrum of peaks 25, 42 and 46. Compared with library NIST05a.L, compatibilities of the three compounds are all above 95%, and they are benzenethiol (BT, peak 25), diphenylmethane (DPM, peak 42) and diphenyldisulfide (DPDS, peak 46). The possible ion formed from BT, DPM and DPDS are shown in table 3. The three compounds are important intermediates in organic synthesis, applied in various areas of the fine chemical industry, such as

herb antibacterial, pharmaceutical, pesticide, dye. To our knowledge, reports about heteroatomic compounds, especially sulfur, detected in biomass or SR are few. It will add great value of biomass and SR to separate BT, DPM and DPDS from SR in the long run.

Table 2. Compounds detected in $F_{CDS-1-1}$, $F_{CDS-1-2}$ and $F_{CDS-2-1}$

Peak	Compound	Peak	Compound	Peak	Compound
1	heptane	19	propylcyclohexane	36	4,7-Methano-1H-indene, octahydro-
2	methylcyclohexane	20	6-methylundecane	37	1,2,3,4-tetramethylbenzene
3	2-methylheptane	21	2,6-dimethylundecane	38	1,2,3,5-tetramethylbenzene
4	toluene	22	1-propylbenzene	39	Tricyclo[5.2.1.0(2,6)]dec-4-ene, 4-methyl-
5	1,3-dimethylcyclohexane	23	1-ethyl-3-methylbenzene	40	4-methyl-2,3-dihydro-1H-indene
6	octane	24	1,2,3-trimethylbenzene	41	henicosane
7	1,2-dimethylcyclohexane	25	benzenethiol	42	diphenylmethane
8	1,4-dimethylcyclohexane	26	1-ethyl-2-methylbenzene	43	docosane
9	2,6-dimethylheptane	27	1,2,4-trimethylbenzene	44	tricosane
10	propylcyclopentane	28	1-ethyl-3-methylbenzene	45	tetracosane
11	ethylcyclohexane	29	2,3-dihydro-1H-indene	46	diphenyl disulfide
12	4-methyloctane	30	1,3-diethylbenzene	47	pentacosane
13	1-ethylbenzene	31	2-ethyl-1,4-dimethylbenzene	48	2-((2-ethylhexyloxy)carbonyl)benzoic acid
14	m-xylene	32	1,2-diethylbenzene	49	hexacosane
15	nonane	33	1-methyl-4-propylbenzene	50	octacosane
16	cyclohexanone	34	3a,4,5,6,7,7a-Hexahydro-4,7-methanoindene	51	heptacosane
17	4-ethylcyclohexanone	35	o-cymene	52	nonacosane
18	cumene				

In $F_{CDS-1-2}$, compounds are mainly alkyl-benzenes and alkyl-cyclohexanes, while substituent groups of those compounds are mainly methyl and ethyl as shown in Table 2. As Figure 2 and Table 2 lists, ten compounds are detected in $F_{CDS-2-1}$, including nine long chain saturated fatty hydrocarbons from C_{21} to C_{29} (peak 41, 43-45, 47, 49-52) and 2-((2-ethylhexyloxy)carbonyl)benzoic acid (ECBA, peak 48). ECBA (peak 48) is the most abundant. Comparing the two fractions, it is obvious that retention time of compounds in $F_{CDS-1-2}$ is between 5min and 11min, while that in $F_{CDS-2-1}$ is after 13min.

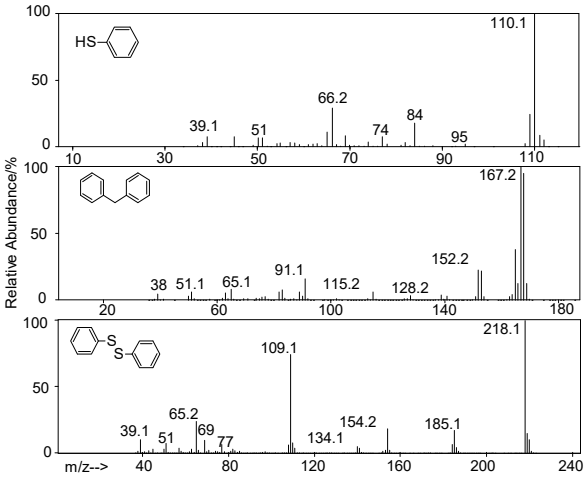


Fig 1. Mass spectrum of peaks 25, 42 and 46

Compounds detected in F_{CDS} are simple, while compounds detected in F_H are manifold. But the yield of F_{CDS} is higher than that of F_H. The possible season is that F_{CDS} contains other compounds, such as strongly polar and/or less volatile compounds that can't be detected and analysed by GC/MS. Our further investigation will be future to analyse the compounds in F_{CDS} by HPLC/MS analysis.

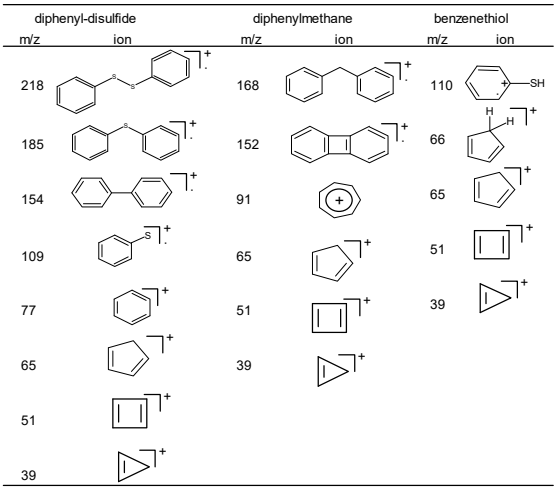


Fig 2. Compounds detected in F_{CDS}

4. Conclusion

In this study, we use n-hexane and carbon disulfide to extract (under ultrasonic) the biomass residual from wheat stalk depolymerized in supercritical methanol. In F_H, Oxy-compounds and compounds containing benzene ring are present in high concentration. After F_{CDS} separated by column chromatography, $F_{CDS-1-1}$ eluted by n-hexane only detected three compounds, benzenethiol, diphenylmethane and diphenyldisulfide, $F_{CDS-1-2}$ eluted by n-hexane is mainly alkyl-benzenes and alkyl-cyclohexanes. Nine saturated fatty hydrocarbons from C_{21} to C_{29} are eluted in the sub-fraction ($F_{CDS-2-1}$) eluted by mixture of n-hexane and benzene. Our future work will focus on the study of quantity relation and new method to detecte the strongly polar and/or less volatile compounds.

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