FTIR Analysis of Liquefaction Product of Long Flame Coal by White-rot Fungi

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Keywords: long flame coal, liquefaction product, FTIR spectra, white-rot fungi.

Abstract. Liquefaction of low rank coal such as long flame coal by microorganisms is one of the most potential ways in coal clean utilization. To promote industrialized application, this paper focuses on structure of liquefaction product by infrared spectrometer. After that, software Peakfit v4.12 was used to peak separation fit the FTIR spectrum of liquefaction product and two structural parameters was calculated subsequently. Results show that liquefaction product is rich in acid amides N-H (3173, 3345, 3436 cm^{-1}) and C=O in aldehyde/ester. Aromatic hydrogen ratio of liquefaction product is 0.686, and the side chain length is 0.791. In comparison Fushun long flame coal before microorganisms liquefaction, a conclusion can be obtained that coal macromolecule was broken up by enzymes excreted by white-rot fungi.

Introduction

Coal bio-liquefaction is a degradation process of coal macromolecule to low molecules or solution process of small molecules in coal by microorganisms excretion products such as enzymes [1]. Because of benefits such as mild reaction, no secondary pollution, etc, it is one of the most important part of coal clean efficient utilization, which has received extensive attention in worldwide since the first reported in early 1980s[2-3]. However, over the past 30 years, coal bio-liquefaction is still at the stage of laboratory research, and fails to get the application in industry. One of the most important facts is the complex composition in liquefaction products, thus it is unable to gain high purity products.

Various modern analysis and testing technologies were used to analyzed bio-liquefaction product, while Fourier transform infrared spectroscopy is one of the most efficient ways in organic substance analysis[4]. Basaran[5] analyzed raw coal and liquefaction product by FTIR and reported that raw coal is rich in groups of CH, C=C, CH_2, CH_3, C-OH and COOH, and the FTIR spectrum of liquefaction product is similar with that of raw coal, except for absorbance of carbonyl group in 1701 cm^{-1} and that of symmetric methyl in tert-butyl in 1391 cm^{-1}. Wang[6] took lignite as research object, results show that FTIR spectra of raw coal and liquefaction product are similar except for OH absorption enhancement in 3424 cm^{-1}, and additional aromatic ketone or conjugated carbonyl in 1385 cm^{-1}, 1096 cm^{-1}. However, there is little report about long flame coal so far. This paper uses white-rot fungi selected by own laboratory to liquefy Fushun long flame coal, FTIR spectra of liquefaction was peakfited subsequently, and structural parameters were calculated at the end, which lays the foundation for bio-liquefaction mechanism.

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Materials and methods

Coal sample

Coal used in this paper was from Fushun (northeast China) western open mine. According to elemental analysis, it belongs to long flame coal. After crushing under 0.25mm, range between 0.25mm and 0.15mm was chosen as coal sample. In order to enhancing coal bio-liquefaction ratio, nitric acid was used to pretreated coal before microorganism liquefaction.

Microorganism liquefaction

Microorganism used in liquefaction was selected by own laboratory, according to identification report, it belongs to *Deuteromycotina Moniliales Hypocrea* and named *Hypocrea lixii* AH. Culture media in liquefaction is SMA media, with component as 40g maltose, 10g peptone, 20g agar and 1000mL water. White-rot fungi *Hypocrea lixii* AH was inoculated onto SMA media in 9 cm petri dish, after mycelium covering the media, Fushun nitric acid oxidized long flame coal was sprinkled evenly over the surface of mycelium, and then cultivated at 28℃ incubator. After black drop formation on coal, it was extracted by pipette in clean bench for next step analysis.

FTIR spectra analysis of liquefaction product

Liquefaction black drop was analyzed by the Nicolet 380 IR absorption spectrum analyzer (Nicolet Company, USA). After drying, KBr was ground into powder and then pressed into sheets in tableting machine, liquefaction drop was added into pressed sheet. On the other way, liquefaction drop was dried in room temperature, and then fully mixed with KBr, and been pressed into sheets in tableting machine. Finally the pressed sheets were scanned for 32 times with the scan range of 4000-450 cm^{-1} and a resolution of 4 cm^{-1}.

Peak Fitting of Spectrum

As the coal liquefaction product's composition is very complex, superposition is easy to caused in spectrum, this is very unfavorable for spectral interpretation. Therefore, in this study, software Peakfit v4.12 was used in the peak separation processing of the spectrum of superposition. According to the second derivative diagram of the spectrum to determine the approximate location and number of the initial solution stack fitting peak, and by adjusting the peak height, peak width, peak shape to optimize the fitting peak. The more of the correlation coefficient R^2 between the fitting line and the original line, the smaller of the variance, represented the better of the fitting effect.

Results and discussion

FTIR spectra of liquefaction product

FTIR spectra of liquefaction drop and dried liquefaction product were shown as Figure 1. In view of influence of water in liquefaction drop, a big absorbance peak representing OH (ranging from 3600 cm^{-1} to 3000 cm^{-1}) appears in liquefaction drop FTIR spectrum. Besides, two big peak in 1750-1500 cm^{-1} (absorbance of C=C in aromatic ring, and C=O in carboxylic acid and/or ether) and around 700 cm^{-1} (absorbance of aromatic hydrocarbon). The existence of water overlaps characteristic absorption peaks of liquefaction product, while been dried, these functional groups show up, as shown in Figure 1.

Software peakfit was used to peak FTIR spectrum of dried liquefaction product. After adjusting and revising height and width each small peak, 40 small peaks were obtained, with square of correlation coefficient is 0.987, and the functional groups belonging as show in Table 1. Liquefaction product is rich in N-H in amide (3173 cm^{-1}, 3345 cm^{-1} and 3436 cm^{-1}), which accounts for 56.75% of total peak area, secondly is intermolecular hydrogen bond (3496 cm^{-1}, 3560 cm^{-1}, 3582 cm^{-1} and 3600 cm^{-1}), which accounts for that of 8.75%, and then is carboxylate ion (1398 cm^{-1}), accounting that of 6.76%. Besides

that,unsaturated bond C=O in aldehydes, ketones, esters, amides, and C=C in aromatic hydrocarbon are also been detected also. According to Table 1, functional groups of Ar-N (1320 cm^{-1}), NO_2(1558 cm^{-1}) , enol ether and/or aromatic ether (1044 cm^{-1}) exist in liquefaction product. However, no absorbance of aliphatic methoxy(2830-2815 cm^{-1}) and aromatic methoxy (2850 cm^{-1}) are no been detected.

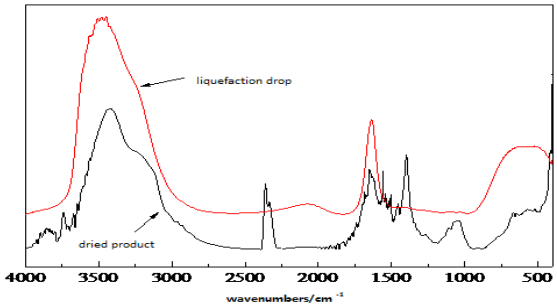

Figure 1 FTIR spectra of black drops and dried liquefaction product

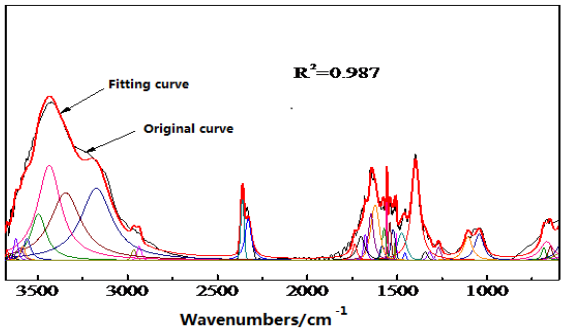

Figure 2 FTIR spectra peakfit of dried liquefaction product

Table 1 Belonging of FTIR spectrum peakfit of dried solubilized coal

area/cm^{-1}	area	Relative area/%	Belonging	Peak shape
648	0.83	0.53	N-H	L
668	3.35	2.15	Single substituted aromatic	L
684	0.74	0.48	Meta substituted aromatic	L
714	0.89	0.57	Meta substituted aromatic	M
744	0.53	0.34	Ortho substituted aromatic	M
767	0.46	0.30	Ortho substituted aromatic	M
1044	3.00	1.93	=C-O-C	M
1107	2.64	1.70	C=C connected with C-C=O	L
1269	0.62	0.40	C-N in amide	M
1320	0.41	0.26	Ar-N in Ar-N-H（R）	M
1345	0.41	0.26	NO_2 in aromatic	M
1398	10.51	6.76	$-COO^-$	L
1458	0.22	0.14	CH_2 in ring aromatic	M
1475	2.50	1.61	CH_3 in side chain	M
1505	0.34	0.22	C=C in aromatic	L
1514	0.20	0.13	C=C in aromatic	L
1523	1.23	0.79	C=C in aromatic	G
1541	1.15	0.74	C=C in aromatic	M
1573	1.33	0.86	C=C in aromatic	M
1583	0.73	0.47	C=C in aromatic or $-COO^-$	M
1623	5.12	3.29	N-H	M
1646	3.21	2.06	C=O in amide or substituted benzoquinone	L
1678	0.99	0.64	C=O in substituted benzoquinone	M
1701	2.47	1.59	C=O in ketone	L
1736	0.96	0.62	C=O in ether	L
2330	3.48	2.24	CO_2	L
2361	1.87	1.20	CO_2	G
2936	0.67	0.43	CH_2	M

2965	0.53	0.34	CH_3	M
3173	30.23	19.43	N-H in secondary amide	L
3345	28.00	18.00	O-H or N-H in secondary amide	L
3436	30.04	19.31	O-H or N-H in secondary amide	L
3496	9.68	6.22	intermolecular hydrogen bond	L
3560	2.11	1.36	intermolecular hydrogen bond	L
3582	0.83	0.53	intermolecular hydrogen bond	L
3600	1.00	0.64	intermolecular hydrogen bond	M
3621	1.04	0.67	intermolecular hydrogen bond	M
3646	0.38	0.24	intermolecular hydrogen bond	L
3671	0.26	0.17	H_2O	M

Note: L-Lorentz peak, G-Gaussian peak, M-Mixed peak

Calculation of structural parameters of liquefaction

According to FTIR analysis data, structural parameters such as aromatic hydrogen ratio, and side chain length can be calculated as follows:

(1) Aromatic hydrogen ratio (f_{ar}^{H}) refers to ratio of aromatic hydrogen to total hydrogen, which assuming hydrogen molecular in liquefaction product exist only in two forms, aromatic hydrogen and fat hydrogen. The absorbance of fat hydrogen is the absorbance area of 2970-2800 cm^{-1}, while that of aromatic hydrogen is the absorbance area of 900-690 cm^{-1}, as shown in formula 1. Thus, aromatic hydrogen ratio of Fushun long flame coal liquefaction product is 0.686.

$$f_{ar}^{H} = \frac{H_{ar}}{H} = \frac{I(900\text{-}690\ cm^{-1})}{I(2970\text{-}2800\ cm^{-1}) + I(900\text{-}690\ cm^{-1})} \quad (1)$$

(2) Side chain length is one of the most important parameters in low rank coal, which can be calculated by comparing of CH_3 and CH_2, as shown in formula 2.

$$\frac{CH_3}{CH_2} = \frac{I(2960\ cm^{-1}) + I(2870\ cm^{-1})}{I(2930\ cm^{-1}) + I(2850\ cm^{-1})} \quad (2)$$

Thus, the side chain length of liquefaction product is 0.791.

Primary analysis of Bio-liquefaction mechanism

According to analysis above, aromatic hydrogen ratio of liquefaction product of Fushun long flame coal is 0.686, while before liquefaction, that of Fushun long flame coal is only 0.086[7]. It is obvious that hydrogen in aromatic compounds is almost 8 times compared with before and after liquefaction, which may attribute that coal macromolecule is opened and hydrogen-added reaction occur when attached by microorganisms. On the other way, side chain of liquefaction product is 0.791, while that of Fushun long flame coal is 0.567, and it increases after bio-liquefaction, which may attribute to oxidation reaction on aromatic ring of Fushun coal by oxidation enzymes such as LiP and MnP excreted by white rot fungi. Except for CH_3 and CH_2, side chain contains other functional groups such as C=O in ketone and ether, and N-H in amides, as shown in FTIR analysis.

Acknowledgement

The authors would like to thank financial support from National Natural Science Foundation of China (No. 51504134) , Guizhou "125 plan" key project of science and technology project (No.Qian jiao he zhong da zhuang xiang zi [2013] 026), Guizhou province science and technology fund project(No. Qianke he J zi [2012]2306), Key Laboratory of Coal Processing and Efficient Utilization of Ministry of Education (No. CPEUKF1405), Liupanshui normal university creative team (LPSSYKJTD201401), Liupanshui normal university high level talent opening foundation(LPSSYKYJJ201402).

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