The Mechanism Study of Degradative Solvent Extraction of Biomass by Liquid Membrane-Fourier Transform Infrared Spectroscopy

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Abstract— Degradative solvent extraction is the method developed for biomass upgrading by dewatering and fractionation of biomass under the mild condition. However, the conversion mechanism of the degradative solvent extraction method has not been fully understood so far. The rice straw was treated in 1-methylnaphthalene (1-MN) at a different solvent-treatment temperature varied from 250 to 350 °C with the residence time for 60 min. The liquid membrane-Fourier Transform Infrared Spectroscopy (FTIR) technique is applied to study the processing mechanism in-depth without separation of the solvent. It has been found that the strength of the oxygen-hydrogen stretching (3600-3100 cm⁻¹) decreased slightly with increasing temperature in the range of 300-350 °C. The decrease of the hydroxyl group in the solvent soluble suggested dehydration reaction taking place between 300 and 350 °C. FTIR spectra in the carbonyl stretching region (1800-1600 cm⁻¹) revealed the presence of esters groups, carboxylic acid and ketonic groups in the solvent-soluble of biomass. The carboxylic acid increased in the range of 200 to 250 °C and then decreased. The prevailing of aromatic groups showed that the aromatization took place during extraction at above 250 °C. From 300 to 350 °C, the carboxyl functional groups in the solvent-soluble noticeably decreased. The removal of the carboxylic acid and the decrease of esters into the form of carbon dioxide indicated that the decarboxylation reaction occurred during the extraction process.

Keywords—Biomass upgrading, liquid membrane-Fourier transform infrared spectroscopy, FTIR, degradative solvent extraction, mechanism.

I. INTRODUCTION

The increase of energy consumption impacts on high demands of fossil fuels and environmental problems. To come up with a solution, the new energy resources and technologies are needed to meet the requirement [1]. Biomass as the precursor of fossil feedstock appears to be an attractive alternative with numerous applications in energy production [2]. Biomass materials have low sulfur and low nitrogen content (relative to coal) thus resulting in lower toxic emissions and nearly zero net carbon dioxide emission [3]. Compared to the other renewable energy resources, biomass has been extensively used as a new energy source with the potential to substitute fossil fuels [3]-[5]. thermochemical conversion appears to be an alternative mean for biomass in energy applications. The most current thermochemical processes of biomass conversion to energy are combustion, pyrolysis, gasification and liquefaction [4]. Noteworthy references of low energy and high moisture content using biomass combustion have resulted in low calorific value as well as inconveniences in the terms of transportation and storage. These are challenges for the direct use of biomass directly in traditional thermochemical processes [4], [6], such as the necessity to dewater and upgrade biomass before utilization and subsequent introduction into the conversion processes.

Degradative solvent extraction, a recently developed method, successfully upgrades and fractionates biomasses [7], [11]-[14]. It was used for dewatering and upgrading of low rank coals and biomass waste at mild conditions (around 350 °C). The raw material was treated in a batch autoclave using a non-polar solvent below 350 °C. Two extracted fractions in the reservoir were obtained at room temperature; the deposit as a solid fraction was obtained after precipitation and the solvent soluble was obtained in the dissolved fraction. The carbon content of soluble was as high as 81.0 to 83.3 wt.% and its oxygen content was as low as 7.3 to 11 wt.% [7]. The effective treatment temperature of biomass by using this method was around 350 °C [7]. Extensive studies have been conducted such as [12] and [14] to investigate the mechanism of the degradative solvent extraction method. The researchers studied molecular components and structure of products by analyzing the solid state of the initial reactant (coal, biomass) and final products [14]. The main reactions involved in the degradative solvent extraction method of biomass are thermal degradation, deoxygenation, and aromatization. However, the mechanisms of the degradative solvent extraction method are not yet fully understood so far.

FTIR spectroscopy is the spectroscopic technique commonly used to obtain infrared spectrum, identify and study molecular structures. Several methods were proposed in order to obtain IR spectrum of carbonaceous materials and coal. As of the 1980s, FTIR has been used in several studies in order to investigate coal [15]-[19] and the band assignment of functional groups of coals [17], [20]. When applied to coal analysis, the lack of reproducibility due to factors that affect
the IR spectrum such as the physical states of the sample and measuring conditions prove to be particularly inconvenient [21]-[24]. Quantitative analysis using IR is preferable without modification of the analyte, physically or chemically. The liquid membrane-FTIR technique was proposed to characterize biomass structure in the liquid state. It was successful in quantitative analysis of solvent-soluble fraction obtained from the degradative solvent extraction [25]. The measurement can be performed with the soluble without removing solvent thus avoiding the contaminations during the sample preparation.

One of the main reactions of degradative solvent extraction method is the deoxygenation [12], [14], as such the present study was conducted to investigate the main oxygen-containing groups in solvent-soluble; hydroxyl and carbonyl groups were involved. To study the mechanism of the degradative solvent extraction process mechanism in-depth, the liquid membrane-FTIR technique was applied. The rice straw sample was treated in 1-MN at different solvent-treatment temperatures from 200-350 °C with a 60 min residence time. The oxygen functional groups investigated in the FTIR spectrum of the solvent-soluble are the oxygen-hydrogen stretching region (3700-3100 cm⁻¹) and the carbonyl stretching region (1800-1500 cm⁻¹). The obtained IR spectrum was deconvoluted into a series of bands in each region and the peak areas for each band are obtained.

II. EXPERIMENTAL SECTION

A. Degradative Solvent Extraction

A raw sample used for the degradative solvent extraction was approximately 6 grams-wet basis of rice straw. 1-Methylnaphthalene (1-MN) of 80 mL was used as non-hydrogen donor solvent for all treatment temperatures.

Based on the result of TG curve of rice straw, the degradative solvent extraction was performed at four different treatment temperatures from 200, 250, 300 and 350 °C. In addition, the study of the thermal decomposition behaviors of soluble showed that the sample weight decrease mainly occurred at 200 to 400 °C and the effective treatment temperature for degradative solvent extraction of biomass was at 350 °C [7], [9], [13]-[14]. The sample was treated in a stainless steel reactor (autoclave, 150 mL of volume). After sufficiently purging the autoclave reactor with helium gas, the autoclave was heated up to the desired treatment temperatures at a rate of ca. 4 °C/min with holding time of 60 min. The extracted products were separated from the residue through the opening valve to the stainless steel reservoir. The extracted fractions collected in the reservoir were cooled by water at room temperature. The extract precipitated at room temperature was filtrated using a PTFE membrane filter, as the solid extracted product (called deposit) and the extracted product dissolved in the solvent is called solvent-soluble. The solvent-soluble of each treatment temperatures was used as the sample in this study.

B. Liquid Membrane-FTIR

The infrared spectra of each treatment temperatures were measured with FTIR spectrometer (JEOL, JIR-WINSPEC50), with a spectral range 4000-1000 cm⁻¹. The FTIR spectra were obtained at 4 cm⁻¹ of resolution and 64 scans. 1.5 liters per minute of nitrogen gas were continuously purging for all measurements in order to eliminate moisture in the sample compartment and to improve the stability of the measurement. The liquid cell windows used 1-mm thick calcium fluoride (CaF₂) flat windows with the transmission range 50000-1025 cm⁻¹. The procedure of measurement was similar to the study of Watcharakorn et al. [25]. The spectra of all samples were performed at room temperature.

C. Analysis of Spectra

The IR spectra of all samples were subtracted with 1-MN spectrum. Background spectra of the air were collected for every sample immediately before collecting the single-beam spectrum of the sample. The measurement spectrum was divided into two regions; oxygen-hydrogen stretching (3700-3100 cm⁻¹) and the carbonyl stretching (1800-1500 cm⁻¹) regions as shown in Fig. 2. Since the baseline of spectra changed with the treatment temperature due to the change in the reflectance of the samples, a baseline correction was performed as follows: A straight line was drawn through two points, which passed two minima of absorption at around 3650 and 3150 cm⁻¹ for the OH stretching region, and around 1800 and 1550 cm⁻¹ for the carbonyl stretching region. After baseline variation was corrected, the IR spectrum was deconvoluted. A spectrum was processed by a multi-peak fit function via the software IGOR Pro 6.31 using the least squares fitting algorithm. A Gaussian function was used for peak shapes [26], [27], [29]-[32]. The number, sub-peak position, width and their variation ranges were assigned in Table I [26]-[32]. Comparing the obtained spectral to the FTIR analysis of coal and to characteristic group frequencies [26]-[32], the band deconvolution was assigned. The band assignment in the hydroxyl region [26], [27] and the six bands in carbonyl region (carboxylic acids, ester, ketone, etc.) were assigned to resolve [28]-[32]. The peaks were derived from the fitted spectrum and the peak areas were obtained. The relative amount of functional groups was measured using the integrated area of the peaks as obtained by the peak-fitting process. Each functional group can be quantified using integral area of relevant absorption peaks. Each sample was prepared and analyzed in triplicate to ensure the reliability and reproducibility of the method employed. The standard deviations of the functional groups at different temperatures were in the range of 0.13-0.23 of the OH stretching region and in the range of 0.11-0.89 of the carbonyl stretching region.

III. RESULTS AND DISCUSSION

Liquid membrane-FTIR was performed to investigate the variation of chemical structure in the main oxygen-containing groups in solvent-soluble which are the hydroxyl and carbonyl groups [30].
TABLE I
PEAK ASSIGNMENTS OF THE MAIN FUNCTIONAL GROUPS

<table>
<thead>
<tr>
<th>Number</th>
<th>Peak Position (cm⁻¹)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3530</td>
<td>OH-π hydrogen bonds(^{a,b})</td>
</tr>
<tr>
<td>2</td>
<td>3400</td>
<td>self-associated n-mers ((n&gt;3)^{a,b})</td>
</tr>
<tr>
<td>3</td>
<td>3280-335</td>
<td>OH-ether O hydrogen bonds(^{a,b})</td>
</tr>
<tr>
<td>4</td>
<td>3150-320</td>
<td>tightly bound cyclic OH tetrarners(^{a,b})</td>
</tr>
<tr>
<td>5</td>
<td>1770-182</td>
<td>phenolic ester of aliphatic acids ((RCOO))(^{c,d,e,g})</td>
</tr>
<tr>
<td>6</td>
<td>1740-1760</td>
<td>alkyl ester of aliphatic acids ((RCOOR'))(^{e,f,g})</td>
</tr>
<tr>
<td>7</td>
<td>1710-1740</td>
<td>carboxylic acids ((COOH))(^{d,e,f,g})</td>
</tr>
<tr>
<td>8</td>
<td>1670-1680</td>
<td>conjugated aromatic ketone (\pi-π)</td>
</tr>
<tr>
<td>9</td>
<td>1650-1670</td>
<td>highly conjugated aromatic ketone (\pi-π)</td>
</tr>
<tr>
<td>10</td>
<td>1607-1620</td>
<td>Aromatics (\pi-π)</td>
</tr>
</tbody>
</table>

\(^{a}\) [26], \(^{b}\) [27], \(^{c}\) [28], \(^{d}\) [29], \(^{e}\) [30], \(^{f}\) [31], and \(^{g}\) [32]

A. The Oxygen-Hydrogen Stretching Region

The IR spectrum in the OH stretching vibration region (3650-3100 cm⁻¹) is shown in Fig. 2 (a). The wide band of the region is centered at around 3400 cm⁻¹ which was attributed to the self-associated n-mers. Fig. 3 shows the profiles of the associated OH bonds at different treatment temperatures. The peak at 3400 cm⁻¹ decreased more rapidly than the peak of 3530 cm⁻¹ in the temperature region 200-300 °C. On the other hand, the peak at 3530 cm⁻¹ decreased markedly at 300-350 °C. In this study, tightly bound cyclic OH tetramers are not found in the OH stretching region at 200 °C. The decrease of the peak area for hydrogen bonds in hydroxyl group obviously occurs at 300-350 °C, suggesting the removal of hydroxyl or carboxyl due to dehydration and decarboxylation reactions [7], [14].

Fig. 1 TG curve of rice straw

Fig. 2 The curve-fitting results for solvent-soluble of 350 °C-treatment temperature: (a) IR spectra between 3650 and 3100 cm⁻¹, (b) IR spectra between 1800 and 1550 cm⁻¹; the band assignments are given in Table I

Fig. 3 Variation of hydrogen bond in the OH stretching region
B. The Carbonyl Region

The obtained IR spectra in the carbonyl stretching region (1800-1550 cm⁻¹) of solvent-soluble of rice straw showed two prominent peaks that centered around 1710 and 1607 cm⁻¹. Six bands were resolved for the region as shown in Fig. 2 (b). Five bands at approximately 1770, 1740, 1710, 1670 and 1650 cm⁻¹ can be ascribed to carbonyl functional groups while the band at 1607 cm⁻¹ is associated with the aromatic ring [28]-[32]. The strongest absorption band at 1710 cm⁻¹ is attributed to carboxylic acid while a shoulder with the bands at 1770 and 1740 cm⁻¹ are assigned to ester groups; phenolic ester of aliphatic acids (RCOOAr) and alkyl ester of aliphatic acids (RCOOR'), respectively.

Relatively weak bands to carboxylic acid at 1670 and 1650 cm⁻¹ are attributed to ketonic structure groups [28]-[32]. A functional group associates in the carbonyl region in Fig. 4, (a) illustrates the deconvoluted peak area relative to that obtained at 200 °C. The peak of carboxylic acid and ester groups gradually decreased with increasing treatment temperature from 250°C. On the contrary, carboxylic acid increased in the range of 200-250 °C and then decreased. The decrease was usually attributed to the decomposition of oxygen-containing functional groups or the formation of small molecules with oxygen-containing functional groups during the extraction reaction. The carbonyl groups in biomass gradually decreased with increasing temperature (300-350 °C) as shown in Fig. 4 (b). These carbonyl groups could have been removed by the decarboxylation into producing carbon dioxide (CO₂) or through the decomposition of ketones by producing carbon monoxide (CO). These suggestions corroborate with the studies of Janewit et al. [7], in which more than 80% of the oxygen was observed to be removed as CO₂, CO, and water. In this study, ester groups were discovered to be one of the functional groups, contributing to the carbonyl group, esters could be the other sources of CO₂ during the extraction process.

The prevailing of aromatic group at 1607 cm⁻¹ in Fig. 4 (a) clearly demonstrates that the aromatization reaction took place during degradative extraction from treatment temperature at 250 °C [7], [12]-[14]. From the results and discussion, the dehydration, decarboxylation and the aromatization reactions occurred from 250 to 350°C which is consistent with the previous publications [7], [12]-[14]. This suggests that liquid membrane-FTIR as a technique was successful in resolving the overlapping IR bands and also helpful in the interpretation of the mechanisms for the degradative solvent extraction of biomass.

IV. CONCLUSIONS

It this paper, we have demonstrated that with the spectra obtained from liquid membrane-FTIR technique, ester and ketone groups resolved in the IR spectra, which was not remarkable in the FTIR spectra of solid-soluble. The dehydration, the decarboxylation and the aromatization reactions can be assured quantitatively by deconvolution of the IR spectra from liquid membrane-FTIR technique, which suggests that this technique can be used to interpret the mechanism of the degradative solvent extraction of biomass.

REFERENCES


