CHARACTERIZING WOOD LIQUEFACTION BY FRACTAL GEOMETRY APPROACH

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(Received April 2012)

Abstract. This study characterized wood liquefaction by the fractal geometry method. Chinese fir (*Cunninghamia lanceolata* Hook.) fine powder was liquefied under various conditions of phenol-to-wood ratio (3:1, 4:1, and 5:1), catalyst content (4, 6, and 8%), and temperature (130, 150, and 170°C). The surface fractal dimension of liquefied wood residues was determined at different liquefaction time levels (30, 60, 90, 120, 150, and 180 min) by software based on the cubic covering method. The relationship between fractal dimension and residue content was examined quantitatively. Results indicated that 1) surface fractal dimensions of liquefied wood residues were between 2.27 and 2.30 under all liquefaction conditions; 2) surface fractal dimension was inversely related to liquefaction time, and it decreased faster at early liquefaction stages; 3) surface fractal dimension was inversely related to phenol-to-wood ratio, catalyst content, and liquefaction temperature; and 4) the relationship between surface fractal dimension and residue content with high R^2 values. This study provides a new alternative to the arsenal of wood liquefaction characterization methods and also sheds light on some fundamental aspects of wood liquefaction research.

Keywords: Chinese fir (*Cunninghamia lanceolata* Hook.), liquefied wood residues, residue content, surface fractal dimension, wood liquefaction.

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Wood and Fiber Science, 44(4), 2012, pp. 440-447 © 2012 by the Society of Wood Science and Technology

Wood is a naturally occurring, sustainable, and environmentally friendly biomaterial with numerous favorable properties. However, its intrinsic insolubility and nonplasticity largely limit its applications. The primary causes are the high degree of polymerization (DP) and hierarchical structure of its major chemical components, ie cellulose, hemicellulose, and lignin (Li and Renneckar 2011). Liquefaction of wood provides an avenue of decreasing DP as well as increasing the reactivity of these chemical components (Hon and Shiraishi 1990), which extends the realm of the applications of wood to adhesives, moldings, foams, and carbon fibers (Shiraishi and Kajita 1993; Ma 2007). Liquefaction hence has become a new area of interest in the research of wood science.

The residue content of liquefaction has been used as an index to measure the degree of liquefaction. However, as some research has indicated, the condensation reaction may occur only at the latter stage of the wood liquefaction process (Yamada et al 2001; Kobayashi et al 2004; Zhang et al 2006; Niu 2011); hence residue content may not be the ideal way to measure liquefaction degree. However, although many research efforts have been devoted to wood liquefaction during the past few decades, eg water effects, solvent types, catalyst types and concentration, liquefaction time and temperature, etc (Alma et al 1995, 1998; Zhang and Zhao 2003; Zhang et al 2004; Lee and Wang 2005; Jun et al 2006; Xie and Shi 2006), very few of them touched on this characterization issue, which is essential for a better understanding of the wood liquefaction mechanism.

The concept of fractal geometry was proposed by Mandelbort (1982) to describe complex geometrical objects that possess nontrivial structures on arbitrary scales with shapes made of parts similar to the whole in some way (selfsimilarity). Fractal dimension, as an index for the complex degree, can be used to describe fractal objects. Porous materials such as wood often have fractal surfaces (Ma et al 2006). In the late 1990s, the fractal theory began to find its applications in wood science (Fei et al 2007) in studies of water adsorption (Hatzikiriakos and Avramidis 1994; Jose and Paulo 1997; Fan et al 1999; Cao and Kamdem 2004), anatomical structure (Konas et al 2009; Xi and Zhao 2011), and wood macroscopic texture (Ren et al 2007; Wang et al 2007), which demonstrated that fractal dimension was an effective tool to characterize wood surface roughness.

The objective of this study was to apply the fractal theory to characterize wood liquefaction process under different liquefaction conditions, focusing on 1) using the cubic covering method (CCM) to determine the real fractal dimension for the surface of liquefied wood residues; and 2) quantitatively describing the correlation between surface fractal dimension and residue content of liquefied wood. This study could provide a new alternative to the arsenal of wood liquefaction characterization methods and also shed light on some fundamental aspects of wood liquefaction research.

MATERIALS AND METHODS

Materials

Chinese fir (*Cunninghamia lanceolata* Hook.) was peeled and processed by a plant grinder to a fine powder of 20-80 mesh. The wood powder was then oven-dried at $103 \pm 2^{\circ}$ C for 12 + h to achieve 0% MC before liquefaction treatment. Analytical-grade phenol and sulfuric acid (98% w/w) were used as the liquefaction reagent and catalyst, respectively.

Wood Liquefaction and Liquefied Wood Residues Preparation

Wood powder, phenol, and sulfuric acid were added into a 500-mL three-neck flask reactor attached with a condenser and a stirring setup. The liquefaction procedure was conducted in an oil bath with various phenol-to-wood ratios, catalyst contents, and temperatures. These experimental variables and their levels are listed in Table 1.

The liquefied mixture was collected at six liquefaction time levels (30, 60, 90, 120, 150, and

Level	Phenol-to-wood ratio	Catalyst content* (%)	Liquefaction temperature (°C)	
1	3:1	4	130	
2	4:1	6	150	
3	5.1	8	170	

Table 1. Liquefaction variables and treatment levels.

* Based on the amount of phenol.

180 min), diluted with acetone, and vacuumfiltered. The insoluble moiety was oven-dried at $103 \pm 2^{\circ}$ C to constant weight, and residue content was calculated by Eq 1:

$$\mathrm{RC} = \frac{\mathrm{W_r}}{\mathrm{W_0}} \times 100\% \tag{1}$$

where RC is residue content, W_r is oven-dried weight of residue, and W_0 is weight of the original wood powder.

Scanning Electron Microscopy Characterization

An S-3400 scanning electron microscopy (SEM) was used to observe the surface morphology of liquefied wood residues. The samples were first oven-dried at $103 \pm 2^{\circ}$ C for 4 h and then sputter-coated with gold prior to the SEM observations.

Surface Fractal Dimension Determination

CCM was applied to calculate surface fractal dimension of the liquefied wood residues. The method was first proposed by Zhou and Xie (2003), using 3D cubes to cover an irregular surface. As shown in Fig 1, a regular square grid is placed on plane XOY. In each grid cell with scale δ , four intersection points correspond to four heights of the irregular surface area within the scale



Figure 1. Cubic covering method.

 δ : h (i, j), h (i, j+1), h (i+1, j), and h (i+1, j+1), where $1 \leq i, j \leq n-1$, and n is the total number of sampling points on each individual profile on the surface. If a cube with scale δ is used to cover the surface, the maximum difference among h(i, j), h(i, j+1), h(i+1, j), and h(i+1, j+1) will determine the number of cubes needed. The number N_{i,j} of cubes needed to cover the irregular surface in the field of the (i, j)th grid unit on the reference plane XOY is given by Eq 2: following steps: 1) two-dimensional SEM images of liquefied wood residues were analyzed by the software, pure fiber area in the SEM images was selected to avoid calculating errors caused by the condensation products formed during latter liquefaction stage, and gray matrixes of the selecting area were identified and transferred into the corresponding height matrixes; and 2) surface fractal dimension was then estimated using Eqs 2-4.

$$N_{i,j} = INT \begin{cases} \frac{1}{\delta} [max(h(i,j), h(i,j+1), h(i+1,j), h(i+1,j+1)) \\ -min(h(i,j), h(i,j+1), h(i+1,j), h(i+1,j+1))] + 1 \end{cases}$$
(2)

where INT is the integration function. The total number $N(\delta)$ of cubes needed to cover the entire irregular surface is determined by Eq 3:

$$N(\delta) = \sum_{i,j=1}^{n-1} N_{i,j}$$
 (3)

Apparently, $N(\delta)$ depends on the sampling interval δ . For a fractal surface, the relation between $N(\delta)$ and δ is given by Eq 4:

$$N(\delta) \sim \delta^{-D} \tag{4}$$

where D is the surface fractal dimension, which can be estimated by taking the logarithm of Eq 4. Therefore, by changing the scale δ ($\delta = 2^k$, k = 1, 2, 3, 4, 5), different values of N(δ) can be obtained, and D is the slope (absolute value) on the plot of logN(δ) against log δ from linear regression.

Based on this idea, Wang et al (2006) developed fractal analysis software that has been widely applied to determine the fractal dimension of rough surface in many fields of studies: rocks (Zhou and Xie 2003), sediment particles (Wang et al 2006), granular activated charcoal (Du et al 2006), and flocs (Yu 2011). In this study, the software was used to calculate the surface fractal dimension of liquefied wood residues by the

RESULTS AND DISCUSSION

Scanning Electron Microscopy Characterization

SEM images ($3000 \times$ magnification) of liquefied wood residues at six time levels (with 4:1 phenol-to-wood ratio and 6% catalyst content at 150°C) are shown in Fig 2. The proportional relationship between particle dimension and liquefaction time is apparent. The fact that the residue geometry approached the plane structure as treating time increased justifies the use of the fractal geometry method to characterize liquefied wood residues.

Surface Fractal Dimension

Figures 3, 4, and 5 demonstrate relationships among fractal dimensions and liquefaction times under different scenarios of phenol-to-wood ratios, catalyst contents, and liquefaction temperatures. The surface fractal dimensions were between 2.27 and 2.30 under all liquefaction conditions, suggesting the liquefied wood residues had fractal characteristic. As liquefaction time increased, surface fractal dimension gradually decreased toward 2.0, indicating the elevation of the liquefaction degree. This suggests



Figure 2. Scanning electron microscopy images of liquefied wood residues at different liquefaction time levels with 4:1 phenol-to-wood ratio and 6% catalyst content at 150° C.

that the surface fractal dimension was sensitive to the liquefaction treatment and hence was a viable index to represent degree of wood liquefaction. In addition, the rates of surface fractal dimension decreasing were generally faster at shorter liquefaction time levels, which corresponded to the more intense reactions at early liquefaction stages. With respect to the effects of liquefaction conditions according to Figs 3, 4, and 5, it appears that at a given liquefaction time, surface fractal dimensions decreased with the increase of phenol-towood ratio, catalyst content, and liquefaction temperature. However, this trend reversed for 150 and 170°C when liquefaction time goes beyond 120 min (Fig 5). This may be related to the fact





Figure 3. Effects of phenol-to-wood ratio on surface fractal dimension of liquefied wood residues at different liquefaction time levels (6% catalyst content, liquefaction temperature 150°C).

Figure 4. Effects of catalyst content on surface fractal dimension of liquefied wood residues at different liquefaction time levels (4:1 phenol-to-wood ratio, liquefaction temperature 150° C).



Figure 5. Effects of liquefaction temperature on surface fractal dimension of liquefied wood residues at different liquefaction time levels (4:1 phenol-to-wood ratio, 6% catalyst content).

that condensation reactions occurred at higher temperatures during the latter stage of wood liquefaction (Niu 2011) and the products formed on the residue surfaces caused a rise in the roughness and accordingly the surface fractal dimension. Also, it may have had to do with lignin's glass transition temperature (Hillis and Rozsa 1978; Kelley et al 1987) beyond which the decrease of surface fractal dimension begins to slow down for this specific system.

Correlations between Surface Fractal Dimension and Residue Content

Figure 6 presents the relationship between surface fractal dimension and liquefied wood residue contents (with 4:1 phenol-to-wood ratio and 6% catalyst content at 150°C). It is clear that the surface fractal dimension and residue content follow a linear relationship with a high R^2 value. The same relationship between the two is observed for other conditions as well and can be expressed as Eq 5:

$$RC = aD - b \tag{5}$$

where RC is residue content, D is fractal dimension, a and b are constants, and their values under different liquefaction conditions are listed in Table 2. The regressions have high R^2 values under all conditions (with minimum of 0.940), indicating a strong proportional linear relationship between residue content and fractal dimen-



Figure 6. Relationship between surface fractal dimension and liquefied wood residue content (4:1 phenol-to-wood ratio, 6% catalyst content at 150°C).

sion, suggesting that surface fractal dimension is a reliable alternative to represent wood liquefaction degree.

CONCLUSIONS

Wood liquefaction of Chinese fir was conducted under various conditions, the surface fractal dimensions of the liquefied wood residues were determined at different liquefaction time levels using the cubic covering method, and the relationship between residue contents and fractal dimensions was quantitatively examined. The primary conclusions are

1. Liquefied wood residues had fractal characteristics; their surface fractal dimensions

Table 2. Constant a and b in Eq 5 and the corresponding R^2 values under different liquefaction conditions.

Phenol-to- wood ratio	Catalyst content (%)	Liquefaction temperature (°C)	а	b	R^2
3:1	6	150	837	1094.3	0.940
4:1	6	150	574.58	1304.4	0.987
5:1	6	150	764.17	1736.1	0.990
4:1	4	150	682.49	1550.7	0.991
4:1	8	150	534.2	1212.5	0.995
4:1	6	130	855.78	1946.4	0.945
4:1	6	170	721.46	1640.4	0.955

were between 2.27 and 2.30 under different liquefaction conditions.

- 2. Surface fractal dimension was inversely related to liquefaction time, and the fractal dimension drops were generally faster at early liquefaction stages.
- 3. Surface fractal dimension was inversely related to phenol-to-wood ratio, catalyst content, and liquefaction temperature.
- 4. Surface fractal dimension and liquefied wood residue content followed a linear relationship that can be described by RC = aD b with high R^2 values. This suggests that surface fractal dimension could serve as a reliable alternative to represent the wood liquefaction degree.

ACKNOWLEDGMENTS

We thank the National Special Fund for Forestry Scientific Research in the Public Interest (Grant No. 201004057) for financial support.

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