

Kinetic Modeling of Formic Acid Pulping of Bagasse

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Organic solvent or organosolv pulping processes are alternatives to soda or kraft pulping to delignify lignocellulosic materials for the production of paper pulp. Formic acid, a typical organosolv system, has been presently examined under atmospheric pressure to pulp bagasse fibers. It was shown that efficient bagasse pulping was achieved when the formic acid concentration was limited to 90% (v/v). A statistical kinetic model based on the experimental results for the delignification of bagasse during formic acid pulping was developed that can be described as follows: D (delignification) = $0.747 \times C_{\text{formic acid}}^{1.688} \times (1 - e^{-0.05171t})$, an equation that can be used to predict the lignin content in formic acid during the pulping process. The delignification of bagasse by 90% formic acid was almost completed after approximately 80 min, while extended pulping did not improve the delignification but tended to degrade the carbohydrates in bagasse, especially the hemicelluloses, which were rapidly hydrolyzed at the onset of pulping.

KEYWORDS: Bagasse; formic acid; kinetic pulping model

INTRODUCTION

Forest resources are diminishing globally, while world paper and allied materials consumption is continuously increasing. It has therefore become incumbent to seek strategies that not only compensate for the diminution of dwindling forest resources but also provide local economic value. It is imperative, therefore, given the scarcity of accessible wood reserves around the globe, to explore nonwoods as potential raw materials for paper production (1).

Bagasse is among the candidates to provide nonwoody value for papermaking; it is an agricultural residue that is the byproduct of refining in the sugar industry, best described as a lignocellulosic biomaterial composed of approximately (m/m) 30–40% cellulose, 20–25% hemicellulose, and 15–25% lignin, while the remainder is a number of other components (2, 3). Given the similar composition to hardwood species, bagasse can serve as a raw material for the pulp and paper industry, which is particularly important in developing countries that fall far short of adequate forest resources (4).

Traditionally, nonwoody materials are pulped according to variations of the soda process, that is, with alkali metal-based chemicals. However, the process of delignification releases nonprocess elements (chemicals) such as silicon (Si) that are naturally found in nonwoody agricultural materials

in relatively high amounts. Si, therefore, is codissolved with lignin into the alkali pulping medium, impeding the efficiency of the chemical recovery process, because Si tends to aggregate over the course of industrial processing streams, often leaving behind intractable scale and large deposits (klinkers). It is often the case that many agricultural-based pulping operations do not attempt to recover the residual process stream (composed of lignin and nonprocess elements), instead discarding it into local receiving waterways, causing severe pollution issues and ecological hazards.

Thus, conventional alkali-based pulping methodologies are not attractive options for many nonwoody species. These technological, economic, and environmental difficulties have in general adversely affected the prospects of employing nonwoody materials for pulp production.

Recently, the concept of a forest-based biorefinery has become popular among traditional pulping operations; it is an industrial facility that is able to convert biomass, including lignocellulosic materials, into a broad range of material, chemical, and energy products, not unlike traditional petroleum-based refineries (5). Therefore, critical to the success of the biorefinery is addressing “biomass fractionation,” ways to efficiently process the biomass to its useful components, which may find its realization in organosolv (organic solvent) pulping strategies (6).

Among the possible organic solvents, formic acid displays interesting features as a potential agent to successfully address fractionation, including its ability to achieve extensive delignification with simultaneous hemicellulose degradation and good pulp yield (7).

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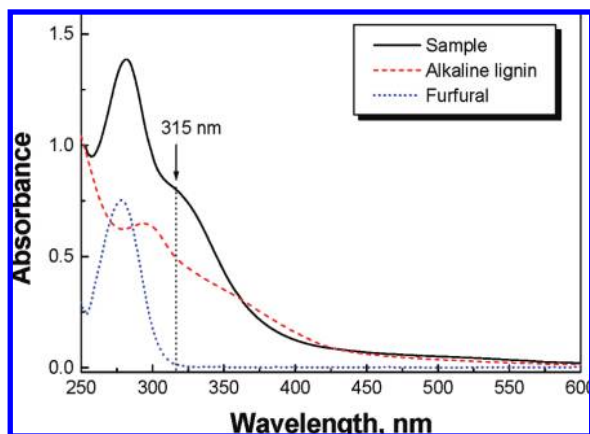


Figure 1. Spectra of lignin and furfural in the spent formic acid liquor.

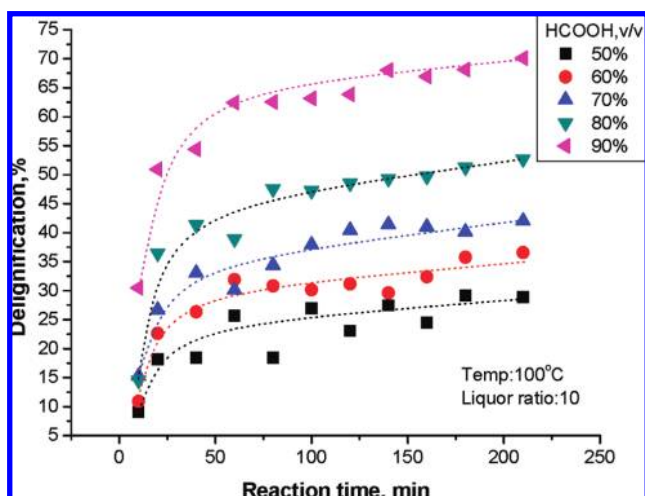


Figure 2. Effect of reaction time and formic acid charge on the pulping of bagasse.

Several approaches have reported fractionation with formic acid media, including acid-catalyzed aqueous formic acid and formic acid–peroxyformic acid mixtures in aqueous media (8–12). However, there are few reports on the utilization of formic acid–water media for suitable lignocellulosic materials.

Thus, the kinetics of delignification of bagasse and the degradation mechanism of carbohydrates were studied in the current report through a series of laboratory experiments using a formic acid–water media model. Finally, a kinetic model for the ensuing delignification was also developed to predict the extent of delignification.

EXPERIMENTAL PROCEDURES

Pulping of Bagasse with Formic Acid. Bagasse from GuangXi Province was air-dried and cut into 2 cm strips for formic acid pulping. The composition of the bagasse was determined using the standard literature method (w/w, oven dry): hollocellulose, 73.9%; lignin, 21.4%; pentosanes, 18.8%; hot water extractives, 17.5%; ethanol–benzene extractives, 1.9%; and ash, 0.7% (20).

Bagasse was cooked in a flask with an aqueous solution of formic acid by refluxing under atmospheric pressure. The cooking was carried out in batches of 50 g dry bagasse samples in a 1 L, flat-bottom, and wide-mouth boiling flask equipped with a condenser. After cooking, the spent cooking liquor was separated and collected by filtration.

Analytical Methods: Delignification Method. The method used was described by Dence (13). The lignin content in cooking liquor was determined by UV spectroscopy at 315 nm. K , the coefficient of absorbance as shown in eq 1, was obtained by measuring the absorbance

of purified formic acid lignin using UV spectra described previously (13). The extent of delignification (D) was determined according to eq 2:

$$B = \frac{A}{K} \times M \quad (1)$$

$$D(\%) = \frac{B}{\text{the total lignin}} \times 100 \quad (2)$$

where B is the lignin content, A is the absorbance, K is the coefficient of absorbance, D is the extent of delignification, and M is a multiple factor of dilution.

Determination of Carbohydrates in Cooking Spent. The spent cooking liquor was sufficiently diluted with distilled water to precipitate the lignin dissolved during pulping, which can be removed, and then reacted with concentrated sulfuric acid (98%, v/v) for 10 min. The content of carbohydrates in the pulping liquor was measured by a double wavelength method (21).

RESULTS AND DISCUSSION

General Aspects of the Delignification of Bagasse. One of the species generated during bagasse pulping that interferes with the analysis of lignin is furfural. If present in the spent liquor, it has a distinct absorbance range (250–310 nm) that overlaps that of lignin. Thus, an appropriate wavelength must be chosen to measure lignin in the final formic acid liquor to avoid the interfering absorbance of furfural. As shown in Figure 1, the absorbance at 315 nm in the spent liquor is mainly from dissolved lignin and lignin-related substances, such as phenolics, while furfural possesses almost no absorbance in this range. Therefore, the content of lignin can be determined. The rate of delignification from bagasse can therefore be calculated once the dissolved lignin concentration is known (relative to the starting amount of native lignin).

During the pulping experiments, dissolved lignin was collected and measured. It was demonstrated in Figure 2 that most of the lignin removal occurred in the first 80 min of pulping under all pulping conditions. However, variations in the extent of delignification were minimal from 80 to 180 min. During this latter phase, residual lignin removal was very slow for all reaction conditions. Some research (13–16) has reported for similar systems that lignin polymer recondensation reactions occur during extensive pulping time (greater than 80 min); these results are in agreement with our experimental data.

In general, a good delignification medium must have nucleophilic species to promote the cleavage of lignin and to dissolve the lignin fragments. The addition of water is able to promote the delignification reaction but reduces the ability of the solvent to dissolve the lignin generated in the process because lignin is a hydrophobic biopolymer and thus induces adsorption of lignin fragments onto the surface of a pulp fiber. To prevent lignin reprecipitation in formic acid liquor, a suitable concentration of formic acid is critically important. As Figure 2 illustrates, a formic acid liquor having a 90% (v/v) concentration had a positive effect on the delignification. If the formic acid charge was less than this in the reaction mixture, the extent of delignification decreased significantly.

Kinetic Model Development. The atmospheric formic acid pulping process involves mass transfer of cooking chemicals into the bagasse structure and complex heterogeneous chemical reactions between various bagasse components and the pulping chemicals. A proper generic chemical reaction equation for delignification may be considered as follows:

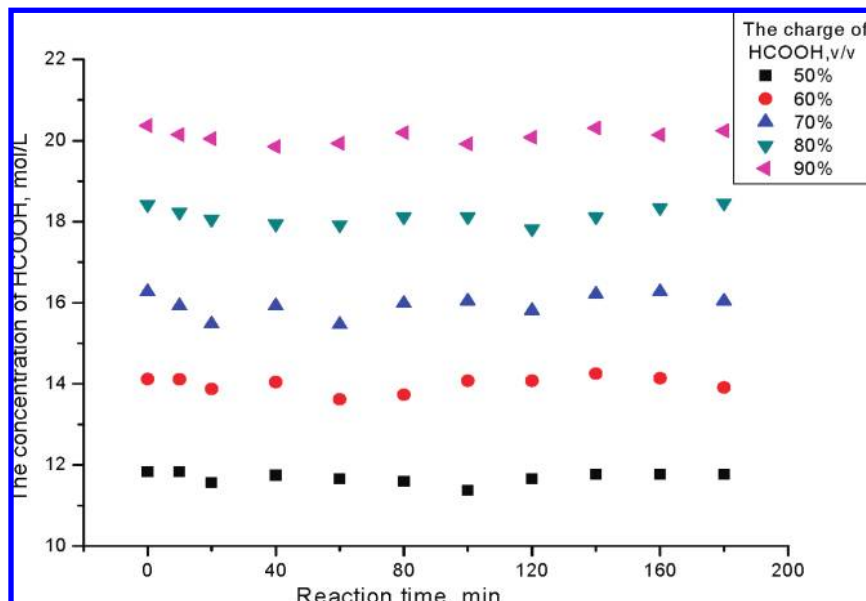


Figure 3. Concentration of formic acid at different reaction times.

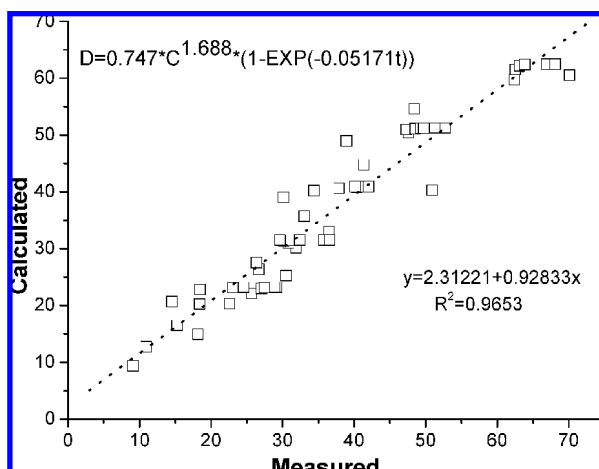
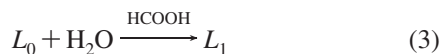


Figure 4. Linear relationship between the calculated and the measured delignification for the formic acid pulping of bagasse under atmospheric conditions.



where L_0 is the starting lignin concentration, HCOOH is formic acid, and L_1 is the final lignin concentration; the kinetic equation for the above chemical reaction is as follows:

$$v = \frac{dc_Y}{dt} = k' c_A^\alpha c_B^\beta \quad (4)$$

In which c_Y is the concentration of L_1 , c_A represents the concentration of protolignin, c_B represents the concentration of formic acid, k' is the constant of chemical reaction, and α, β are the orders of reaction.

During the cooking of bagasse with formic acid, the concentration of formic acid in the cooking liquor always kept the same level from 10 to 180 min at each situation with a different initial concentration as shown in Figure 3, which indicates that the concentration of formic acid is not diminished by the available, reactive lignin.

If $c_B \gg c_A$, then c_B^β can be considered a constant in the reaction process. Thus, when the concentration of formic acid is almost invariable as shown in Figure 3, eq 5 holds

$$k' c_B^\beta = k \quad (5)$$

Thus, from eqs 4 and 5, a kinetic equation describing the delignification of bagasse by formic acid can be derived as follows:

$$\frac{dc_Y}{dt} = k c_A^\alpha = k(c_0 - c_Y)^\alpha \quad (6)$$

where c_0 is the total content of lignin.

Integrating eq 6 yields

$$\int_0^{c_Y} \frac{dc_Y}{(c_0 - c_Y)^\alpha} = \int_0^t k dt \quad (7)$$

Delignification by formic acid has been adequately interpreted as a first-order reaction by Dapia (15). Thus, eq 8 can be derived from eq 7:

$$c_Y = c_0(1 - e^{-kt}) \quad (8)$$

However, a good delignification medium must also have the ability to dissolve lignin fragments. From Figure 2, we know that the ability of 90% (v/v) formic acid is obviously the most superior.

Therefore, eq 8 should add an additional concentration term, and thus, the rate of delignification can be described by eq 9:

$$D = K \times C^a \times \frac{c_Y}{c_0} \times 100\% \quad (9)$$

where, C is the concentration of formic acid and "a" represents the exponent of C . Substituting eq 8 and eq 5 into eq 9, the following expression is obtained

$$D = K \times C^a \times (1 - e^{-kt}) \times 100\% \quad (10)$$

To use this expression for the prediction of spent formic acid lignin concentration, the parameters in eq 10 need to be estimated. By virtue of the experimental data for the formic acid concentrations and the reaction time, the parameters of k , a , and b were deduced and are 0.747, 1.688, and 0.5171, respectively, for eq 5.

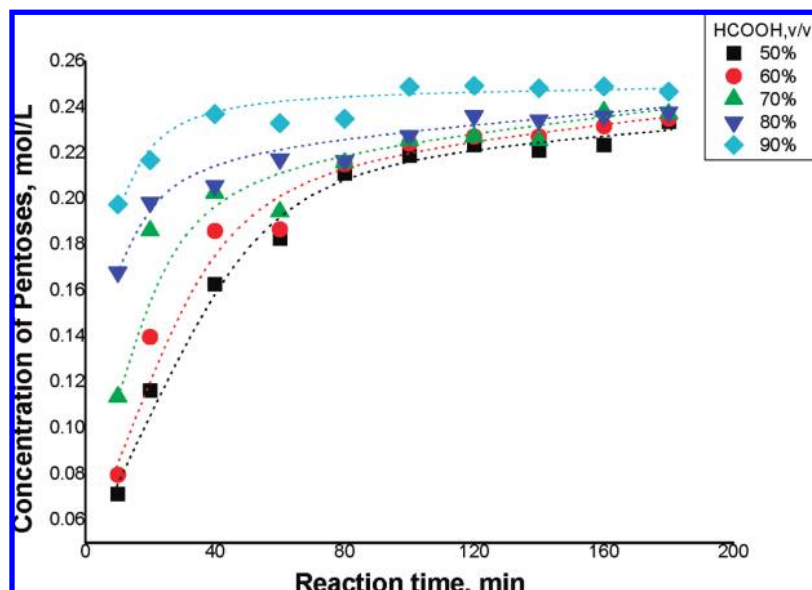


Figure 5. Content of pentoses in formic acid spent liquor at different reaction times.

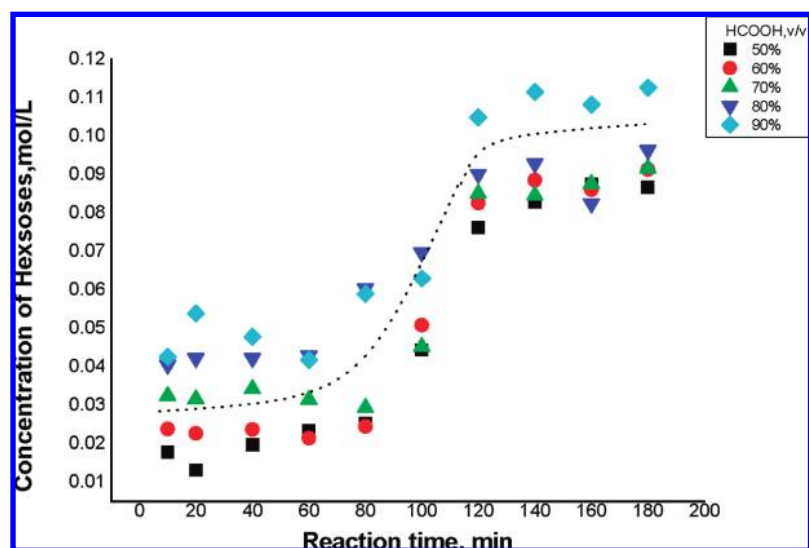


Figure 6. Content of hexoses in formic acid spent liquor at different reaction times.

Prediction of Lignin Content in Formic Acid Liquor.

During the delignification, exposure of bagasse to formic acid for prolonged reaction times obviously results in the degradation of lignin and the solubilization of lignin fragments. Clearly, the extent of lignin removal varies according to the process conditions, including formic acid concentration and reaction time. A calculated delignification has been graphically presented in Figure 4.

A linear regression was applied to estimate the parameters (k , a , and b) of the mathematic model based on eq 10. This plot shows a regression coefficient of 96.53% to confirm that eq 10 can indeed characterize the nature of the delignification with acceptable accuracy.

The experimentally derived equation can be used to develop a kinetic model for control of the delignification. In general, for such applications, model parameters have to be determined experimentally to accommodate for materials in the pulping process.

Hydrolysis of Carbohydrates: Hemicellulose. By contrast to cellulose, which is a very crystalline polymer composed of glucose, hemicelluloses are polydisperse polymers of five different sugars. During chemical treatment, hemicelluloses are

easily degraded and dissolved by virtue of their noncrystalline nature. The effects of variables such as cooking time and formic acid concentration on the hydrolysis of carbohydrates during atmospheric pressure formic acid pulping were studied.

The results in Figure 5 showed that the rate of hydrolysis gradually increased as the formic acid concentration increased. The bulk of removal of pentoses in spent liquor was achieved during the first 30–40 min of the pulping reaction, when the formic acid concentration was 90% (v/v). A comparison to the literature data showed that a single stage of formic acid pulping of beech wood achieved a higher degree of hemicellulose removal than Acetosolv or Milox treatments of the same raw material (17–19).

Hydrolysis of Carbohydrates: Cellulose Degradation. The bond between C₁ and O in an exposed cellulose chain can easily be attacked by acid to cause a hydrolysis reaction. To explore cellulose degradation, the hexoses content in the pulping liquor was measured. The results are depicted in Figure 6.

Because the hemicelluloses were rapidly hydrolyzed during the initial phase of reaction, they partly contribute to the total hexoses concentration. Besides, it is probable that the initial hexoses from the water extractives were from incomplete

removal of sucrose during sugar extraction. However, as the reaction time increased, the content of hexoses in spent liquor sharply increased between 80 and 120 min, which meant that the cellulose contribution was more significant. Thus, the pulping time should optimally be no longer than 80 min to avoid cellulose degradation and compromised final pulp properties.

CONCLUSIONS

The pulping of bagasse in uncatalyzed formic acid media allowed both extensive delignification and excellent pulp yield under the following conditions: 90% (v/v) aqueous formic acid, at a ratio of liquor to straw (L/S) = 10 (v/w), temperature = 100 °C, and pulping time = 80 min.

The typical delignification process is clearly characterized by an initial fast phase followed by the onset of a slow second phase of delignification. A kinetic model of lignin dissolution by formic acid may be described as follows: $D = 0.747 \times C^{1.688} \times (1 - e^{-0.05171t})$.

Meanwhile, carbohydrates were also degraded, especially hemicellulose, which was quickly hydrolyzed into smaller molecules during 90% (v/v) aqueous formic acid pulping. The degradation of cellulose was not severe before 80 min, but became much more drastic afterward, in accordance with the observed intractability of the delignification presumably arising from lignin condensation reactions.

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