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Tetrahydrofurfuryl Alcohol (THFA) Pulping of Rice Straw

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Abstract: A 80–95% solution of tetrahydrofurfuryl alcohol (THFA) added with 0.15–0.5% catalytic hydrochloric acid (HCl) was used to pulp rice straw. The pulping conditions applied for organosolv digestions of the straw at atmospheric pressure and 120°C cooking for 4 h. The characteristics of the digestion, chemical properties of the resulting pulp, and the handsheet physical properties were evaluated. As for the pulp yields, the method has high delignification specificity, at kappa number 20, the yield was ca. 60%, about 15–20% higher than the traditional alkaline pulping method. Furthermore, with increasing THFA concentrations, efficacies of delignification also increased. Increasing the catalyst dosage also caused an increase in delignification. Delignification rate of 120°C cooking are not so appreciable, but high yield were retained. If cooking temperatures were increased to 130 and 150°C, although even higher delignification rates were achievable, the yield decreased as well. During the cooking the dissolution of carbohydrate was low, at most 23%, consisting of mostly hemicelluloses, which was as high as 78% of the dissolved carbohydrates. The optimal conditions of the THFA/HCl cooking applied 95% THFA, 0.50% HCl, temperature of 120°C, and cooking time of 240 min. Residue lignin in the resulting pulp was low, and can be bleached to high brightness easily with a conventional bleaching sequence. If, however, energy and operation efficiency was a primary consideration, then a procedural heating scheme could be employed. The physical properties of the THFA pulp handsheets were inferior to those of the kraft pulp. The main reason was the damage to cellulose sustained during the acidic cooking condition.

Keywords: Organosolv pulping, pulp properties, rice straw, tetrahydrofurfuryl alcohol pulping

INTRODUCTION

Shortage in supply of wood resources in recent years causes the effective utilization of agroforestry wastes to be reexamined and reconsidered. The use

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of rice (*Oryza sativa*) straw, wheat straw, and corn stovers in the Poaceae family as raw materials for pulping has received increasing attentions. The main impetus is the worldwide shortage of fiber materials and their high costs. Agroforestry wastes have long been used for making pulp, substituting wood with proven potential. Statistics stated that the production of pulp from non-wood sources worldwide makes up 5–7% of pulps.[1] Many countries of the world use rice straw in their pulp production. The major pulping methods are mostly chemical and semi-chemical processes such as kraft,[2] soda,[2,3] or NSSC (neutral sulfite semichemical) pulping.[4] However, these methods generally face difficulties in recovering waste cooking liquors and have low pulp yields.[5] Thus, developing novel and low polluting pulping process in order to realize the complete utilization of non-wood resources possesses significance both in material utilization and environmental protection.

Organosolv pulping processes have been developed with the aim of extracting lignin from the wood and allowing full utilization of various chemical components. In these processes, organic solvents are used for the separation,[6–9] with the modern purposes of producing various biomass materials and bioenergy.[10] The organic solvents used for the purposes include phenols;[11–14] methanol;[15] ethanol;[16–18] butanol;[19] ketones;[20–22] organic acids.[23–26] These methods were applied mainly to the pulping of softwood and hardwood, and were rarely used in agroforestry wastes. There were very few papers using organosolv methods to pulp rice straw; these included Ghose et al.[27] using butanol; Navaee-Ardeh et al. [1,28] using ethanol, soda-ethanol-water, and dimethyl formamide; Pourjoozi et al.[29] using ethanol-water; Mohammadi-Rovsshandeh et al.[30] using dietylene glycol, a mixture of diethylene glycol and ethylene glycol, and a mixture of diethylene glycol, ethylene glycol, and 2% NaOH; Ghozatloo et al.[31] using dimethyl formamide; and Rodriguez et al.[2] using potassium hydroxide for pulping. Among the aforementioned organosolv pulping, although most had low residual lignin content as manifested by their kappa numbers, the yields were on the low side as well.

Among the organosolv processes, the tetrahydrofurfuryl alcohol (THFA) system can be carried out under atmospheric condition, allowing energy saving and low capital cost requirement. THFA boils at 176°C, has low volatility, low toxicity; is biodegradable and water miscible. After pulping, THFA can be recovered from waste liquor extraction. After organic layers were separated, the water layers were treated with acid to separate lignin and carbonhydrate, then pentose and hexose were divided separately, THFA in water layer was then recovered by another solvent; the consumed THFA can be replenished by converting the dissolved pentosan in the liquor to furfural and then hydrogenated to generate THFA.[32,33]

This digestion method will not generate combustible organic solvents like methanol and ethanol, and will not generate malodorous gas or liquids.[34] This technology, however, has not yet seen industrial applications. Bogomolove et al.,[35–37] Johansson et al.,[34] and Aaltonen et al.[38] had reported using

THFA solutions to delignify birch and pine, and to pulp birch, spruce, and eucalyptus. These were pulping of softwoods and hardwoods, whereas there appears to be no report of applying the method to agroforestry waste like rice straw. In this study, we carried out pulping of rice straw using the THFA method and examined its pulping characteristics and the chemical and physical properties of the pulp in order to establish the feasibility of THFA pulping of rice straw. The pulp can be used for making base paper for corrugating medium, liner board, and pulp substitutes. Upon verification of the pulp's bleachability, using this pulp for paper and board of bleached grades are feasible. The lignin and hexosans isolated from the waste liquor can be transformed into biofuels, and materials for lactic acid and polylactide (PLA). Biomaterial productions are also potential considerations. Thus the multipurpose utilization of a largely wasted raw material such as rice straw, wheat straw, corn stalk, sugar corn stalks, and so on appears to be highly feasible.

EXPERIMENTAL

Materials

Rice (*Oryza sativa*) straw, obtained from commercial rice straw ropes of Taiwan, were dissected into segments of ca. 3 cm. The material was air dried before use. The chemical compositions of the rice straw are shown in Table 1.

Atmospheric Pressure THFA Pulping of Rice Straw

One hundred g (oven-dry mass) of the 3 cm rice straw segments were place in a round-bottom flask and added with 80–95% THFA in water solution having differing amounts of catalyst (HCl, 0.1–0.5%). Adjusting the liquor to material ratio to 10 and 12 (kg L^{-1}), and carrying out digestion at 120°C for 4 h, respectively. After cooking, the pulp was washed thoroughly with water and a

Table 1. Chemical composition of rice straw for experiment

	Composition (%)
Holocellulose	68.2
α-cellulose	50.2
$\beta + \gamma$-cellulose	18.0
Lignin	20.1
Ash	12.6
Extractive	2.6

2% solution of NaOH at 70°C to obtain the pulp. Yields were then determined. In order to compare the delignification rates and yields, digestions at 130 and 150°C were also carried out. All test data shown are the average of triplicate analyses.

Evaluation of Pulp Properties

After pulping, the washed pulp were subjected to chemical analyses, including the kappa number (TAPPI T236 om-85), ash (TAPPI T211 om-93), alcohol-benzene extractives (TAPPI T204 os-76), holocellulose (the Wise method, as stipulated by the Japan Wood Association, 1985), cellulose and hemicellulose content (JIS P9001), and lignin (TAPPI T222 om-88). All test data shown are the average of triplicate analyses.

Carbohydrate Analysis of the Pulps

Based on the method of Borchardt and Piper[39] and using inositol as an internal standard and prepared acetyl derivatives of the sugars in order to carry out gas chromatographic analysis. A HP 6890N GC and 5973N MSD mass spectroscopy were used for the analysis. The separation column used was a DB-5 capillary column (30 m $\times$ 0.25 mm $\times$ 0.25 μm), the carrier gas was helium, flow rate 1.0 mL min^{-1}, split ratio 1:10, temperature of the injection port 270°C, ionizing pressure 70 eV, mass range m/z was 41–400 a.m.u. The starting temperature of the analysis was 50°C, temperature rise at 5°C min^{-1} to 230°C. Compounds were identified by comparing the mass spectra with those of National Institute of Standard and Technology (NIST) and Wiley libraries and by comparing to the known standards. All test data shown are the average of triplicate analyses.

Evaluation of the Physical Properties of the Pulps

The air-dried handsheets made from the pulps were conditioned in a constant temperature and humidity room kept at 50% relative humidity and 23°C for more than 24 h before conducting the physical tests. The properties tested included tensile strength (TAPPI T404 om-92), bursting strength (TAPPI T403 om-97), tearing strength (TAPPI T414 om-98), folding endurance (TAPPI T511 om-96), zero-span tensile strength (TAPPI T231 cm-96), light-scattering coefficient (TAPPI T220 sp-06), and a composite strength index was calculated according to the method stipulated by Sekine[40] which was: Strength index = breaking length + burst factor $\times$ 10.2^{-1}+ tear factor $\times$ 17.9^{-1}+ folding endurance $\times$ 665^{-1}. All test data shown are the average of triplicate analyses.

RESULTS AND DISCUSSION

The THFA Pulping Characteristics of Rice Straw

The relationship between the pulp kappa number and yield are shown in Figure 1 for the atmospheric pressure THFA cooking of rice straw. The graph indicates that a liquor to material ratio of 10 gave higher delignification efficiency with lower pulp kappa number as low as 17.3 and yield of 59.2%. Along with increased THFA concentrations, the kappa number and pulp yield tended to decrease. Furthermore, increase in the HCl catalyst dosage led to increase in delignification efficiency. This result was in agreement to those of Johansson et al.[34] who used the same method to pulp birch, spruce, and eucalyptus wood chips, that is, along with increasing HCl dosage, a higher delignification and lower yield of the pulp will be produced.

Figure 2 shows the pulp yields and kappa numbers of 95% THFA cooking of rice straw with varying amounts of catalyst dosages. The specific yield versus kappa number regression equations of various catalyst dosages indicated that the higher the catalyst dosage, the greater the slope of the regression equation, which means higher delignification efficiency and relatively lower yield loss. As a consequence, at the highest catalyst dosage of 0.5%, digestion of rice straw proceeded very well, and could be considered to be a high delignification efficiency and high yield pulping condition. Rodriguez et al.[2] conducted rice straw pulping using kraft, soda, soda-anthroquinone (soda-AQ), soda-parabenzoquinone, and potassium hydroxide. At pulp kappa numbers 21–34, they got yields between 33 and 43%. Bhardwaj et al.[3] conducted rice straw

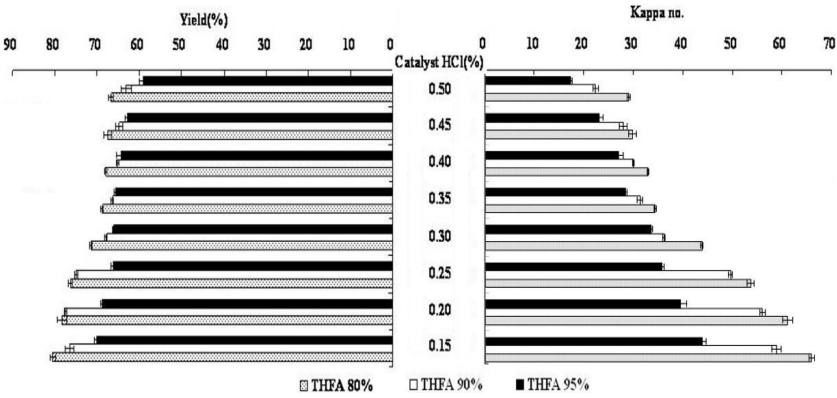

Figure 1. Effects of different concentrations of THFA and the addition of catalyst (HCl) on the rice straw pulp yields and Kappa no. The pulping conditions applied a THFA concentration of 80, 90, and 95%; HCl dosages 0.1–0.5%; liquor to solids ratios 10 (kg L^{-1}); cooking temperature of 120°C; cooking time of 4 h.

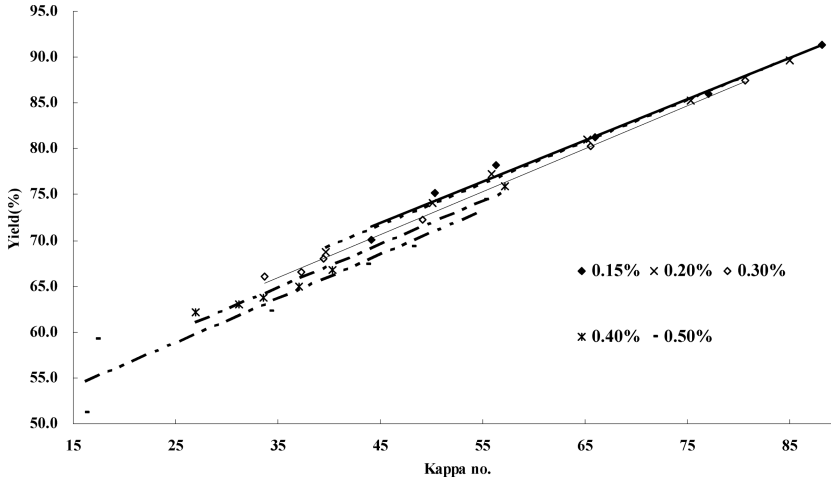

Figure 2. Graphs of yield versus kappa number regression equations for rice straw pulped with THFA/HCl methods. Note: 1. The pulping conditions applied a THFA concentration of 95%; HCl dosages of 0.1–0.5% (w/v); liquor to solids ratios of 10 (kg L^{-1}); cooking temperature of 120°C.
2. The regression equations of yield versus kappa number

Mark	HCl (%)	Equation	R^2
♦	0.15	$y = 0.4503x + 51.683$	0.9849
×	0.20	$y = 0.4544x + 51.219$	0.9969
◇	0.30	$y = 0.4676x + 49.573$	0.9979
∗	0.40	$y = 0.4725x + 48.298$	0.9788
–	0.50	$y = 0.4809x + 46.774$	0.9063

pulping using soda and soda-AQ processes. They obtained 42.9 to 51.6% pulp yields with kappa numbers of 18.3 and 26.6. Deniz et al.[41] did kraft pulping of wheat straw; the pulp yields were 42.6% when the kappa numbers were 31 to 32. These reports show that the other chemical pulping processes produced pulp yields at similar kappa numbers much lower than the THFA method, as we obtained yields around 60% at kappa number of 20, this was 15–20% higher than the traditional alkaline pulping processes. Furthermore, by comparing the results to other organosolv pulping of rice straw for the yields and kappa numbers, such as Ghose et al.[27] who used butanol to pulp rice straw and obtained yields of 60–72% but with kappa number as high as 51.3–58.7; Navaee-Ardeh et al.[28] who pulped rice straw with ethanol and obtained yields of 50–61% at kappa numbers of 51.6–104; and Kham et al.[42] who used peroxoacids to pulp wheat straw and obtained pulp yield of 43.0% at kappa number of 50.4, our results were also superior with regard to both kappa number and yields. Aaltonen

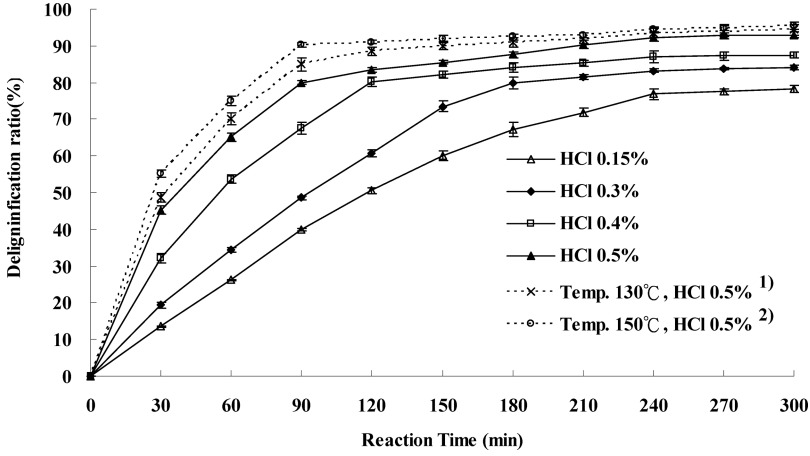

Figure 3. Rice straw delignification in THFA/HCl pulping. The pulping conditions applied a THFA concentration of 95%; HCl dosages 0.15∼0.5% (w/v); liquor to solids ratio 10 (kg L^{-1}); cooking temperature of 120°C; cooking time of 0∼300 min. [1)]Pulping conditions: THFA concentration of 95%; HCl dosages 0.5% (w/v); liquor to solids ratios 10 (kg L^{-1}); cooking temperature of 130°C; cooking time of 0∼300 min. [2)]Pulping conditions: THFA concentration of 95%; HCl dosages 0.5% (w/v); liquor to solids ratios 10 (kg L^{-1}); cooking temperature of 150°C; cooking time of 0∼300 min.

et al.[38] conducted THFA/HCl pulping of Japanese cedar and observed that the chemicals attack mainly the lignin in middle lamella. These characteristics can be assumed to occur at the THFA/HCL delignification of rice straw as well, and the preferential removal of lignin at middle lamella resulted in a high yield and low residue lignin.

The residual lignin content in pulp was measured every 30 min for a cooking time of 300 min using 95% THFA and various catalyst dosages; the results are shown in Figure 3. The graph indicates that the digestion had high initial delignification rates, but for the lowest catalyst dosage (0.15%), a cooking time of 240 min was required to reach the plateau stage. The delignification rate increased with the HCl concentration, with the highest rate resulting in the highest delignification efficiency. For instance, at HCl concentration of 0.15%, after 240 min of cooking, 76% of the lignin was removed; whereas at increased HCl concentration of 0.50%, cooking for 90 min removed 80% of lignin already. Among the 4 catalyst dosages, the 0.50% HCl cooked for 90 min produced the highest delignification efficiency. Thus, the cooking reaction stage differed from typical kraft pulping of wood chips. Zhai and Lee[43] noted that lignin of grasses is mainly distributed at middle lamella and cell corner of the fiber, which have lignin content higher than that in woody plants. The portion of lignin tended to dissolve quickly at the initial cooking stage. Aaltonen et al.[38] pulped Japanese cedar using THFA/HCl and observed that

the chemicals attack mainly the lignin in middle lamella. Also, Huang et al.[44] using NH_4OH-KOH to pulp rice straw, noted a high initial delignification rate and thought that rice straw was a more porous structure than wood. We deduced that in THFA/HCl pulping, the liquor easily penetrated the porous straw substrate and attacked the lignin in middle lamella. The large-scale delignification of middle lamella lignin during the start to 90 min of cooking at HCl dosage of 0.50% thus caused a high delignification efficiency. Regardless of the cooking temperature of 120, 130, or 150°C, the subsequent cooking stage (90∼300 min) rendered little additional delignification. The probable cause for the lack of further delignification was the recondensation of dissolved lignin under the acidic condition. And the condensation reaction usually occurred after 80 min of digestion. These results are similar to those of Tu et al.[45] Additionally, if enhanced delignification is desired to make purer cellulose, a condition using 95% THFA, 0.50% HCl, and digestion at 150°C for 90 and 150 min could be used, which allows a delignification efficiency of 90%, but also causes drastic reduction of pulp yields to 43.2% and 32.1%; the dissolution rate of holocellulose also reaches 45.7 and 57.3%, respectively. The reduction probably reflected acid hydrolysis of cellulose. These results were similar to those of Huang et al.[44] From the above, we have established that the optimal pulping conditions for rice straw were using 95% THFA, HCl dosage of 0.50%, temperature of 120°C, and cooking time of 240 min, as they produced high yield, good delignification, and relatively mild carbohydrate dissolution. If energy conservation is a consideration, a programmed temperature profile could be employed to increase the initial cooking temperature, then reducing the temperature at the later stage and by shortening the digestion period. As shown in Figure 4, the scenario of 95% THFA, temperature of 130°C, and HCl dosage of 0.3% resulted in poorer delignification than the optimal conditions noted earlier; whereas, the scenario of using 95% THFA, temperature of 130°C, and HCl dosage of 0.40% produced similar delignification efficiency as the optimal conditions. However, its carbohydrate dissolution rate was higher after 210 min of digestion. In a scenario using 95% THFA, temperature of 130°C, and HCl dosage of 0.50% after 90 min of cooking, the delignification rate was 86%, yield was 58%, and carbohydrate dissolution rate was 27%, which was acceptable. Thus, this set of conditions could be substituted for the aforementioned optimal conditions to conserve cooking time and obtain excellent delignification efficiency.

From the aforementioned, it is notable that using THFA cooking to rice straw not only produced yields higher than the traditional chemical and some organosolv pulping methods; the kappa number of the pulp was also lower than those methods. The results are in agreement with Herbert,[46] who noted that THFA pulping provided higher yields. Thus we deemed the THFA process a high yield and low kappa number process, with excellent applicability to pulp rice straw.

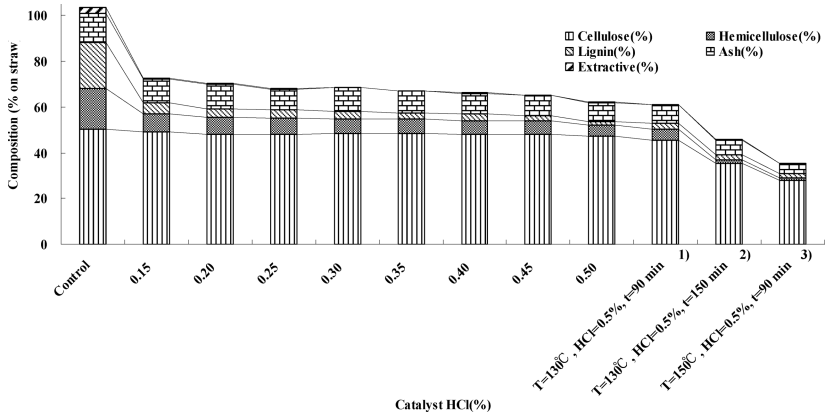

Figure 4. Residual lignin and carbohydrate dissolved during THFA/HCl pulping of rice straw. The pulping conditions applied a THFA concentration of 95%; HCl dosages 0.3–0.5% (w/v); liquor to solids ratios 10 (kg L^{-1}); cooking temperature of 120–130°C; cooking time of 0–300 min.

Comparisons of the Chemical Composition of the Pulps

The rice straw pulp obtained by THFA organosolv pulping has chemical compositions as shown in Figure 5. The pulps cooked at 120°C for 240 min showed that along with increasing THFA concentrations (80–95%), and catalyst HCl dosages (0.15–0.5%), delignification efficiency increased notably as well. The delignification was accompanied by dissolution of hemicelluloses, with lower amount of cellulose dissolution. Revealing all the experimental concentrations of the THFA and the acidic catalyst dosages used for cooking showed the solvent attacked mainly lignin and hemicelluloses. These observations were similar to the results of spruce THFA pulping by Aaltonen et al.[38] Furthermore, a 130°C cooking for 90 and 130 min caused holocellulose dissolution reached 26.5% and 45.8%, respectively; whereas cooking at 150°C for 90 min resulted in more degradation of the holocellulose to the extents of 57.4%. These values are higher than that of 120°C cooking for 240 min. In other words, the cellulose and hemicelluloses of the pulp showed drastic reductions under those conditions (Figure 4). As for the delignification efficiency, the higher the catalyst dosages, the greater the delignification ratio (Figure 6). At THFA concentration of 95%, and catalyst dosage of 0.50%, the delignification ratio peaked at a maximum of 92%; dissolution of carbohydrates, however, also increased with increasing THFA concentration and catalyst dosage, with a maximum ratio of 23% (Figure 6). In addition, by comparing the ratio of delignification to carbohydrate dissolution, the higher the THFA concentration, the less the ratio became. The same was true for the catalyst dosages. Thus, from the aforementioned results, the THFA pulping chemicals attacked mainly lignin in the substrate and dissolved

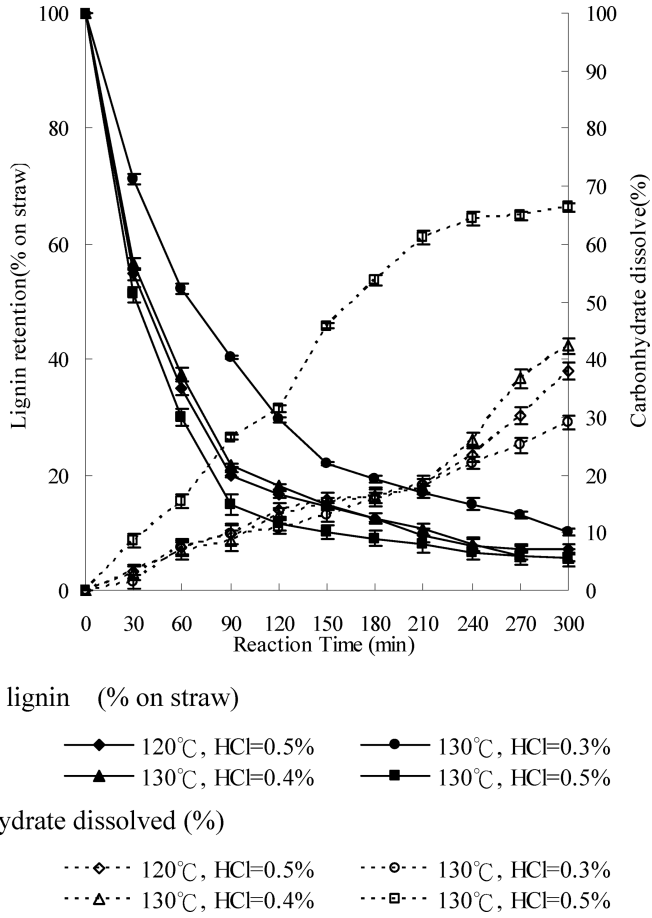

Figure 5. Residual lignin and carbohydrate dissolved during THFA/HCl pulping of rice straw. The pulping conditions applied a THFA concentration of 95%; HCl dosages of 0.3∼0.5% (w/v); liquor to solids ratios of 10 (kg L^{-1}); cooking temperature of 120°C∼130°C; and cooking time of 0∼300 min. [1)] Pulping conditions: THFA concentration of 95%; HCl dosages 0.5%(w/v); liquor to solids ratios 10 (kg L^{-1}); cooking temperature of 130°C; cooking time of 90 min. [2)] Pulping conditions: THFA concentration of 95%; HCl dosages 0.5%(w/v); liquor to solids ratios 10 (kg L^{-1}); cooking temperature of 130°; cooking time of 150 min. [3)] Pulping conditions: THFA concentration of 95%; HCl dosages 0.5%(w/v); liquor to solids ratios 10 (kg L^{-1}); cooking temperature of 150°C; cooking time of 90 min. Control: Composition of rice straw.

carbohydrate only moderately. However, at higher temperatures and prolonged cooking time, the carbohydrate dissolution increased drastically, resulting in lower pulp yields. This phenomenon is observed for THFA/HCl pulping of rice straw for the first time.

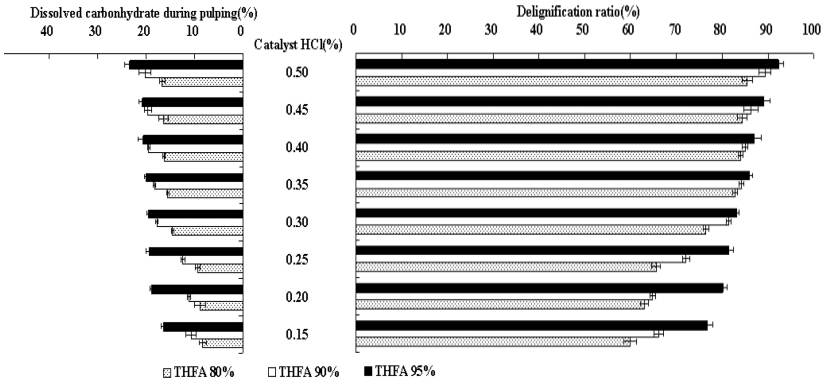

Figure 6. Comparisons of delignification efficiencies and dissolved carbohydrate when different catalyst dosages (0.15–0.50% HCl) were added. Note: The pulping conditions are the same as in Figure 1.

Figure 7 shows the compositional analysis of hydrolyzed carbohydrates produced by different conditions of the THFA cooking of rice straw. Among the hydrolyzates, glucose made up the bulk, followed by xylose, then galactose, arabinose, and mannose in decreasing amounts. In Figure 8, we grouped the sugars as hexosan and pentosan for comparison. Cooking at different liquor to material ratios, either at 10 KgL^{-1} or at 12 KgL^{-1}, all showed the dissolution rates of pentosan higher than those of the hexosan. Although increases in both THFA concentrations and catalyst dosages led to increases in hexosan and

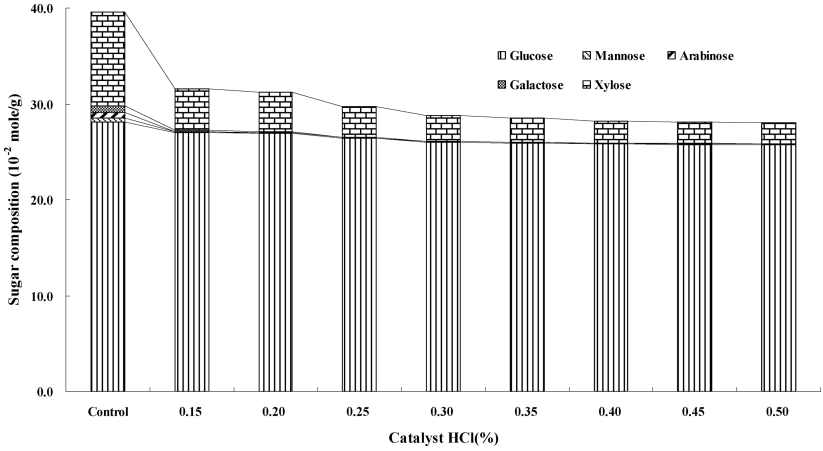

Figure 7. Sugar composition for resulting rice straw pulp when pulped with THFA/HCl methods. Note: The pulping conditions are the same as in Figure 4.

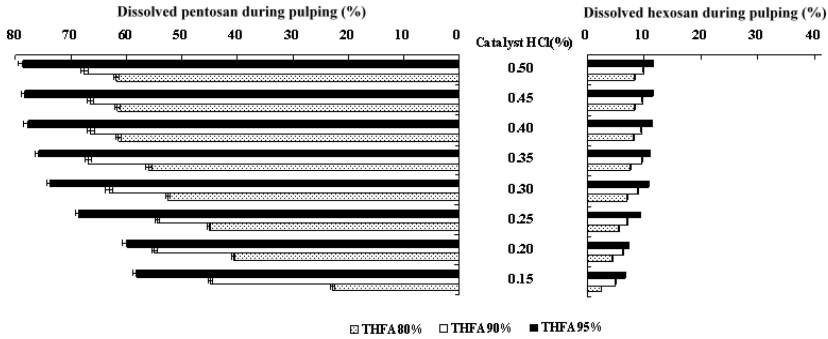

Figure 8. Dissolution ratios of pentosan and hexosan under different THFA concentration and catalyst dosages. Note: The pulping conditions are the same as in Figure 1.

pentosan dissolution, pentosan always outstripped hexosan in rates. At catalyst dosages between 0.15 and 0.25%, the pentosan to hexosan dissolution ratio was about 8–10, when pentosan was dissolved more proportionally; at catalyst dosages of 0.30% or more, however, the pentosan to hexosan ratio became constant at about 6–7. Thus, the increases in catalyst dosages produced the similar trend. From the aforementioned results, we deemed that hemicelluloses were easier to dissolve in the liquor, and the main constituent of hemicelluloses, xylose, accounted for a maximum of 78% of the dissolved sugars. The dissolution of cellulose was much lower; for instance, the maximum glucose dissolution ratio was only 11.8%. The results indicated that THFA organosolv pulping of rice straw had very high selectivity and the catalyst dosage could be selected depending on the use, and the best condition generally resulted from the condition using HCl at 0.50%.

Fiber Morphology and Physical Properties of the Pulp Handsheets

THFA and kraft pulps were beaten with a PFI mill; the results are shown in Figure 9. The beating characteristic of the THFA pulp was excellent, requiring only ca. 400 revolutions to achieve a 400 mL CSF. Conversely, the KP needed ca. 2500 revolutions to obtain the same degree of freeness. Based on these results, we surmised that in the initial stage of THFA cooking, substantial amounts of lignin were removed from middle lamellae, allowing the cooking liquor to penetrate into the interior of fibers, resulting in a pulp with relative low freeness (ca. 490 mL CSF), which was substantially lower than the 580 mL CSF of the equivalent KP. The results were similar to those obtained by Johansson et al.,[34] who cooked Japanese cedar and birch wood chips using the THFA method. In addition, the THFA pulp beaten to 400 mL CSF showed

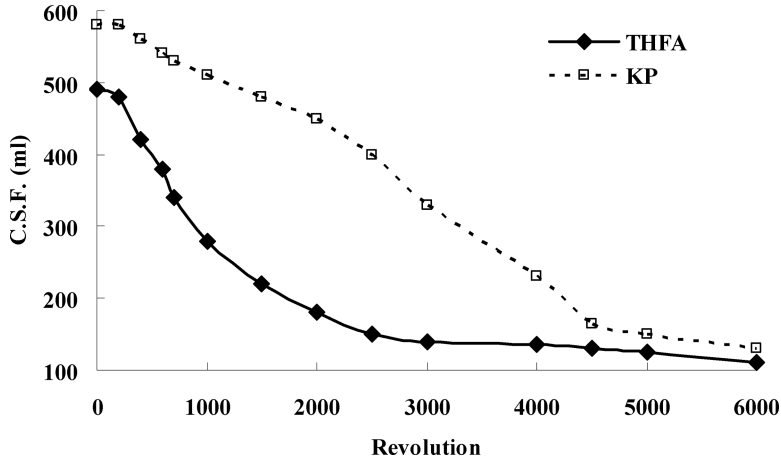

Figure 9. Beating characteristics of THFA and Kraft pulps. The pulping conditions: THFA pulping: Liquor/dry straw = 10, THFA 95%, HCl 0.5%, pulping time 240 min. Kraft pulping: Liquor/dry straw = 4, sulphidity 25%, active alkali 16%, pulping temperature 160°C, pulping time 3 h (to temp. 160°C, 90 min, at temp. 160°C, 90 min).

only marginally improved paper strengths compared to the unbeaten pulp. This observation was again similar to that of Johansson et al.[34] These results suggest that under the acidic THFA cooking conditions, fiber properties were degraded by the acid and became weaker. Thus, despite beating to improve fiber bonding, the effect was obscure. Table 2 shows the fiber morphological characterizations

Table 2. Comparison of fiber morphology of THFA and Kraft pulps

	Before beating			After beating		
Property	Max.	Min.	Ave.	Max.	Min.	Ave.
THFA[1)]						
Fiber length (mm)	1.9	0.6	0.94 ± 0.28	1.7	0.5	0.88 ± 0.27
Fiber width (μm)	15.2	2.6	6.01 ± 0.54	14.0	2.4	5.96 ± 0.55
KP[2)]						
Fiber length (mm)	2.1	0.9	1.18 ± 0.36	1.8	0.8	1.12 ± 0.31
Fiber width (μm)	16.2	3.0	6.33 ± 0.62	14.8	2.6	6.28 ± 0.58

[1)]Liquor/dry straw = 10, THFA 95%, HCl 0.5%, pulping time 240 min, Kappa no. 17.3.

[2)]Liquor/dry straw = 4, sulphidity 25%, active alkali 16%, pulping temperature 160°C, pulping time 3 h (to temp. 160°C, 90 min, at temp. 160°C, 90 min), Kappa no. 19.2.

Table 3. The physical properties of handsheets from various pulps

Treatment	Freeness (mL CSF)	Kappa no.	Tensile index ($Nm \cdot g^{-1}$)	Tear index ($mN \cdot m^2 g^{-1}$)	Burst index ($kpa \cdot m^2\ g^{-1}$)	Folding endurance (d. folds)	Zero-span tensile strength ($N\ m \cdot g^{-1}$)	Light scattering coefficient ($m^2 kg^{-1}$)	Strength index[1)]
THFA	490	17.3[2)]	33.5	7.40	2.1	16	73.6	17.2	9.15
	400	17.3[3)]	35.5	7.45	2.3	19	82.6	18.6	10.19
	400	36.3[4)]	31.6	7.86	2.65	26	76.5	19.5	10.38
	400	49.8[5)]	28.5	7.62	2.5	24	72.8	20.6	10.06
KP	580	19.2[6)]	52.1	7.36	3.62	40	98.2	18.3	12.97
	400	19.2[7)]	55.4	7.25	3.51	46	110	19.9	13.36
	400	30.6[8)]	51.2	7.57	2.47	199	100	20.9	12.3
	400	45.6[9)]	52.6	7.68	2.53	182	95	21.3	12.4

[1)]Strength index = breaking length + burst factor $\times\ 10.2^{-1}$ + tear factor $\times\ 17.9^{-1}$ + folding endurance $\times\ 665^{-1}$.[40].

[2)]Liquor/dry straw = 10, THFA 95%, HCl 0.5%, pulping time 240 min.

[3)]Liquor/dry straw = 10, THFA 95%, HCl 0.5%, pulping time 240 min, beating.

[4)]Liquor/dry straw = 10, THFA 90%, HCl 0.30%, pulping time 240 min, beating.

[5)]Liquor/dry straw = 10, THFA 90%, HCl 0.25%, pulping time 240 min, beating.

[6)]Liquor/dry straw = 4, sulphidity 25%, active alkali 16%, pulping temperature 160°C, pulping time 3 h (to temp. 160°C, 90 min, at temp. 160°C, 90 min).

[7)]Liquor/dry straw = 4, sulphidity 25%, active alkali 16%, pulping temperature 160°C, pulping time 3 h (to temp. 160°C, 90 min, at temp. 160°C, 90 min), beating.

[8)]Liquor/dry straw = 4, sulphidity 25%, active alkali 14%, pulping temperature 160°C, pulping time 3 h (to temp. 160°C, 90 min, at temp. 160°C, 90 min), beating.

[9)]Liquor/dry straw = 4, sulphidity 25%, active alkali 12%, pulping temperature 160°C, pulping time 3 h (to temp. 160°C, 90 min, at temp. 160°C, 90 min), beating.

of the THFA and kraft pulps. The kraft fibers generally had greater lengths and widths than those of the THFA fibers. The shorter and more slender THFA fibers showed more drastic changes after beating than the kraft fibers did. Care must be taken to prevent THFA pulp from excessive shortening or breakage.

Table 3 shows the comparison of the mechanical strengths of the THFA and kraft pulps; the tensile strength of the pulp was inferior to that of kraft pulp. The tensile strength of paper correlates with that of the intrinsic strength of fiber and the interfiber bond number and strength. Page[47] noted that tensile strength, single fiber strength (manifested by zero-span tensile strength), and the strength of interfiber bonding has a relationship of $1/T = 1/F + 1/B$. In the equation, T is the tensile strength; F is the fiber strength; and B is the interfiber bonding strength. The interfiber bonding strength is often proportional to the bonded area. The bonded area in turn is negatively correlated with the light scattering coefficient of the paper. Hence, Table 2 shows that the THFA rice straw pulp handsheets had poorer zero-span tensile strength, indicating a weaker fiber strength. The possible reason was the addition of acidic catalyst, which might damage fiber more than did the kraft process. As for the light-scattering coefficient, the THFA pulp was similar to that of the kraft pulp, indicating both had similar bonded area, and potentially comparable bonding strengths. The weaker tensile strength of the THFA pulp was thus a manifestation of the weaker fiber strength. The THFA pulp had similar tear strength to that of the kraft pulp. As for the bursting strength, the determinants were similar to the tensile strength, hence the THFA pulp was weaker than the kraft pulp. In addition, the THFA pulp had inferior performance than that of the kraft pulp, indicating a less tough fiber. Finally, the strength index comparison between the handsheets of the THFA and kraft pulps suggested that the former is about 20–30% weaker than the latter. The relative weakness of the THFA/HCl pulp had been noted by Johansson et al.[34] and Aaltonen et al.[38] before, and the rice straw results were no exception. Despite this, the pulp should perform satisfactorily in practical applications.

CONCLUSIONS

In this study, we conducted THFA organosolv pulping of rice straw at THFA concentrations of 80–95%, and catalyst (HCl) dosages of 0.15–0.5%; digestions were carried out at 120°C for 4 h. At pulp kappa number around 20, pulp-calculated yields of 60% or more were obtained, more than 20% higher than those provided by kraft pulping; and the process had excellent pulp ability. In the chemical compositions of the resulting pulps, the higher the THFA concentration, the lower the lignin content tended to become. The higher the catalyst dosage, the greater the degree of delignification was as well. Optimally, 95% THFA with 0.5% HCl at 120°C 4 h cooking of rice straw produced a maximum delignification rate of 92% (kappa number 17.3). When digestion

was extended to 300 min, the lignin content change indicated that at the initial stage of the pulping, rapid delignification occurred, which differed from typical kraft pulping of wood chips. If 95% THFA and catalyst dosage of 0.5% were employed at 130 or 150°C cooking, the delignification rate was even faster; however, the pulp yield loss and holocellulose dissolution rate were drastically increased as well. At the conditions with 95% THFA, HCl of 0.5%, temperature of 120°C, and cooking time of 240 min easily bleachable pulp with kappa number of 17.3 and 59.2% yield of pulp can be obtained. However, if energy and operational efficiency is a factor, then a programmed heating scheme such as using 95% THFA, HCl of 0.5%, temperature of 130°C, and cooking time of 90 min can produce very good results as well. Additionally, the analysis of sugars in the pulps indicated that in THFA pulping, hemicelluloses were more liable to dissolve than cellulose, and xylose constituted the main sugar in the dissolved hemicelluloses, which along with increases in the THFA concentration and catalyst dosage, reached as high as 78%. The main constituent of cellulose, glucose, on the other hand, had a dissolution rate of only 11.8% maximum. Finally, on the physical properties of handsheets, the THFA pulp was about 20–30% poorer in strength than the corresponding kraft pulp. This was caused by weaker single fiber strength, but shall not pose any problem in practical application of the pulp.

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