

Pulping of Rice Straw by High Boiling Solvents in Atmospheric Pressure

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ABSTRACT

The pulping of rice straw with diethylene glycol, diethylene glycol+ethylene glycol and diethylene glycol + ethylene glycol + 2% NaOH was studied in order to investigate the effects of the cooking variables (temperature and different organic solvent mixtures) on the properties of obtained pulp (cooking yield, Kappa number, freeness (CSF)) and paper (breaking length, burst index, folding endurance, tear index). Delignification was increased by increasing of the temperature and hand sheet papers with better bondability of fibres were obtained but the strength or length of the fibres with increasing temperature were decreased. With the use of 2% sodium hydroxide in cooking solvent, papers with superior mechanical properties were obtained. Properties that are sensitive to bondability of fibres, such as, breaking length, burst index, folding endurance, were increased with increasing of temperature, but another property sensitive to the length or strength of fibres, that is, tear index, was decreased with increasing of temperature.

Key Words:

organosolv pulping;
rice straw;
diethylene glycol;
ethylene glycol;
pulp and paper properties.

INTRODUCTION

Many cereal straws, particularly rice straw, have been used as raw materials for paper production. Non-wood raw materials account for 5-7% of the total pulp and paper production worldwide [1]. These raw materials were gradually replaced with wood

products after World War II.

However, straw is still a good source of raw material in areas where wood supplies are scarce. The main reasons for the decreased use of straw in the paper industry are: difficulties in using straw pulp in

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paper machines as compared to wood pulp and the specific properties of the black liquors resulting from straw cooking in basic environments, makes them hard to use in recovery systems [2]. These deficiencies are primarily due to the presence of large amounts of pentosanes in the pulp and black liquors, which also contain silica [3]. The development of new technologies for cereal straw pulping is the only solution to avoid the current industrial problems and to put to better use these generally under-valued agricultural resources.

A wide variety of organic solvents including alcohols, ketones, glycols, esters and organic acids have been proposed for the delignification of lignocellulosic materials in organosolv pulping processes [4]. The most used solvents are low molecular weight aliphatic alcohols, given the industrial interest on ethanol and methanol due to their relatively low cost. In fact, three of the four processes that have been operated at pilot plant or commercial scale use either ethanol or methanol as the delignifying agent. In the ALCELL process, where the pulping medium is a mixture of ethanol and water, pulps with Kraft equivalent quality are obtained [5]. In the Organocell and ASAM processes, the most relevant industrial applications of methanol pulping, the alcohol is used in an alkaline medium [6,7]. One of the main drawbacks of low molecular weight organic solvent is the high pressure generated during the pulping stage. Besides, they are highly volatile and flammable. The investments required to reduce the risk associated with the use of alcohol would increase the production cost [8-12].

In this study for the reduction of cooking pressure to atmospheric pressure, solvents with high boiling points (ethylene glycol, diethylene glycol and their mixtures) were used to pulping of rice straw and the properties of pulp and hand-made paper sheets were characterized.

EXPERIMENTAL

Analysis of Raw Materials, Pulps and Handsheets

Sun-dried stem rice (*Oryza sativa*) straw, the composition of which was determined to be 58.65% holocellulose, 13% lignin, 18.35% ash, was used as raw material.

The starting materials and the products obtained from them were characterized according to the following standard methods: Holocellulose [13], lignin Tappi

T 222 om-88), Kappa number (Tappi T 236 om-99), handsheet forming (Tappi T 205 sp-95), freeness (CSF) (Tappi T 227 om-99), breaking length (Tappi T 494 om-96), burst index (Tappi T 403 om-97), folding endurance (Tappi T 511om-96), tear index (Tappi T 414 om-98), pulp yield (Scan-C 3:78).

Methods of Pulping and Handsheet Making

Raw material, the rice straw, was initially cut to equal sizes of about 1.5 cm. This straw was dried at 105°C for 24 h. Three combinations of organic solvents were used: 1- Diethylene glycol (DEG) 2- diethylene glycol (50%) + ethylene glycol (50%), (DEG+EG) and, 3- diethylene glycol + ethylene glycol + 2% NaOH (DEG+EG+SH). In a typical experiment, the oven-dried straw was weighed and charged into a 1000 mL flask at atmospheric pressure. The liquor/dry straw ratio (L/S) in cooking was fixed (10/1). A 50 g of straw was used in each assay. After the vessel loaded with straw and the cooking liquor, it was heated directly to the operating temperature, which was then maintained throughout the experiment. A laboratory hot plate was used for cooking of straw at atmospheric pressure. At the end of the cooking time, the vessel was cooled to room temperature, then, the cooked pulp was washed with warm water and, finally again carefully in cold water (on a 230 mesh sieve), afterwards the dried and pulp yield was calculated gravimetrically following drying at 105°C ± 2 for 24 h.

The pulps were first disintegrated (with 3000 rpm and 2.5 min) in a standard disintegrator (Tappi T 205 sp-95). The number of revolutions was 75000. Afterward, the pulps were beaten in a stainless-steel PFI mill under standard conditions (Tappi T 248 sp-00). Paper sheets were prepared with a British pulp handsheet making machine according to Tappi standard (Tappi T 205 sp-95) [14].

Measurements of physical and mechanical properties of sheets were performed using standard procedures.

The cooking time used in all the experiments was 150 min. The temperatures and cooking solvents used in the different experiments are given in Table 1.

RESULTS AND DISCUSSION

The pulping of lignocellulosic resources with and with-

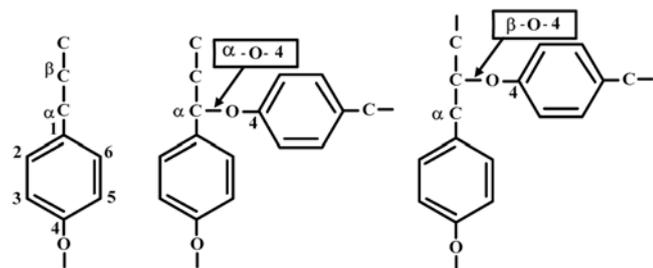
Table 1. Conditions used in the organosolv pulping of rice straw and experimental results for the properties determined in the pulps and hand-sheets.

CS (mL)	T (°C)	YI (%)	KN	F (mL)	TR (s)	BL (m)	BF	FE	TF
DEG	180	70.56	45	285	90	5550	28.5	43	77
	190	65.80	37	235	15	6860	33.5	45	73
	200	60.56	35	250	15	7220	42.5	70	68
DEG+EG	180	65.80	39	225	90	5670	28	25	67
	190	64.00	37	250	30	7340	37.5	70	65
	200	62.50	34	240	15	7800	42	46	62
DEG+EG+SH	180	70.50	32	285	60	4330	26	30	75
	190	66.43	28	270	60	7860	46	110	70
	200	64.57	21	210	15	8140	47	130	63

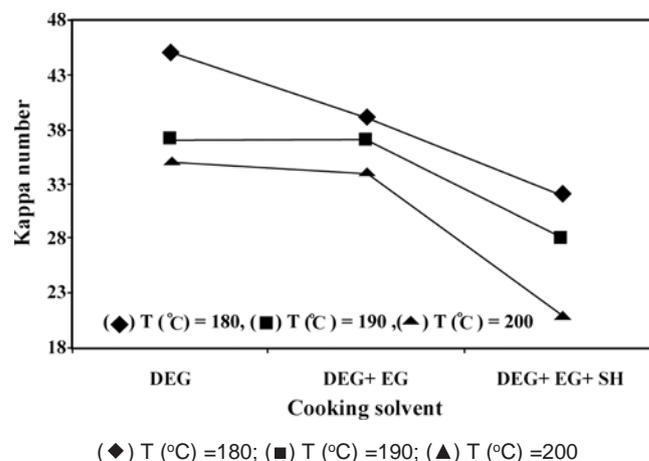
CS: Cooking solvent, T: Temperature, YI: Yield, KN: Kappa number, TR: Time of refining, BL: Breaking length, F: Freeness (C.S.F), BI: Burst index, FE: Folding endurance, TI: Tear index, DEG: Diethylene glycol, DEG + EG: Diethylene glycol + Ethylene glycol, DEG+EG+SH: Diethylene glycol + Ethylene glycol + 2%NaOH.

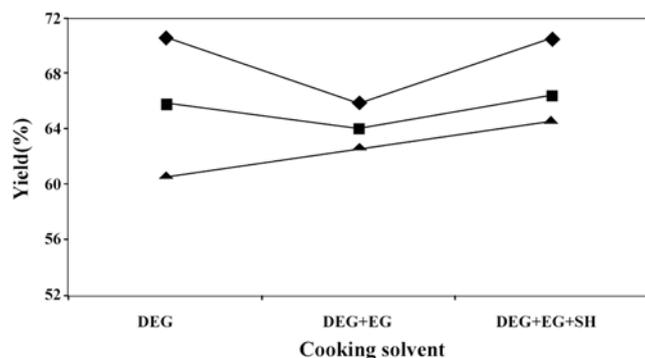
out catalyst can be done by organic solvents. At high temperatures in the presence of water, many of ether bonds in lignin and bonds between lignin and carbohydrates (cellulose and hemicelluloses) are broken and the fragments of lignin with low molecular weight are dissolved in organic solvent. Apparently the alpha aryl ether bonds (α -O-4) are broken faster than the beta-aryl ether bonds (β -O-4) [15]. Also these bonds can be broken by protic solvents with solvolysis. It is expected that because of the protic nature of our solvents (ethylene glycol and diethylene glycol) mechanism of solvolysis is significant in delignification process (Figure 1).

The characteristics of pulp and handsheet papers in the cooking of rice straw with three solvent mixtures in different temperatures at atmospheric pressure are shown in Table 1. Figures 2 and 3 show the relationships between the extent of delignification (*Kappa number*: The Kappa number is the volume (in milliliters) of 0.1N potassium permanganate solution con-


Figure 1. Phenyl propane unit bonds in lignin structure.

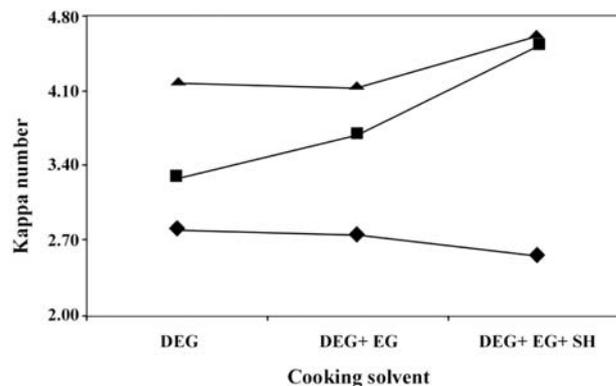
sumed by one gram of moisture-free pulp under the conditions specified in this method so that the results are corrected to 50% consumption of the amount of permanganate added.) and yield with cooking solvent, respectively. It is found that delignification of rice straw can be done successfully in all cases of cooking solvents. Increasing temperature to 200°C lowers the Kappa number and the yield indicates that at high temperature more delignification reactions such as hydrolysis and solvolysis of ether bonds of lignin or lignin-carbohydrate linkages are performed. The similarity of Figures 2 and 3 indicates that the cooking chemicals selectively remove the lignin and carbohydrates (cellu-


Figure 2. Effects of cooking solvents and variation of cooking temperature on Kappa number of pulp.



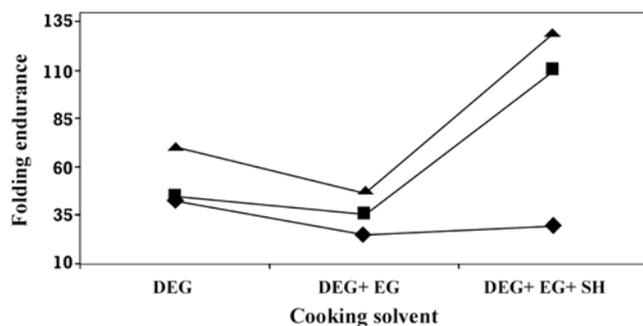
(◆) T (°C) = 180; (■) T (°C) = 190; (▲) T (°C) = 200

Figure 3. Effects of cooking solvents and variation of cooking temperature on pulp yield.



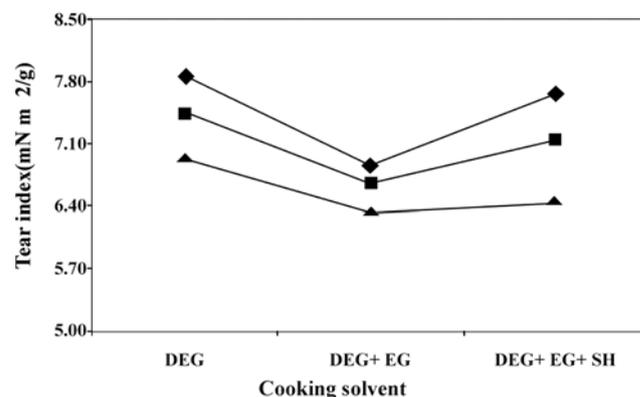
(◆) T (°C) = 180; (■) T (°C) = 190; (▲) T (°C) = 200.

Figure 6. Effects of cooking solvents and variation of cooking temperature on burst index of hand-sheet.



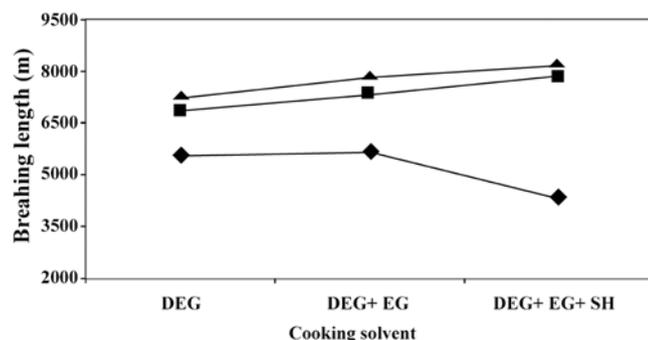
(◆) T (°C) = 180; (■) T (°C) = 190; (▲) T (°C) = 200

Figure 4. Effects of cooking solvents and variation of cooking temperature on folding endurance of hand-sheet.



(◆) T (°C) = 180; (■) T (°C) = 190; (▲) T (°C) = 200.

Figure 7. Effects of cooking solvents and variation of cooking temperature on tear index of hand-sheet.



(◆) T (°C) = 180; (■) T (°C) = 190; (▲) T (°C) = 200

Figure 5. Effects of cooking solvents and variation of cooking temperature on breaching length of hand-sheet.

lose and hemicelluloses) are not attacked significantly by the chemicals. Figures 4-7 show the relationships between mechanical properties of hand-sheet paper (folding endurance, breaking length, burst index and tear index) with cooking solvent. The first three

mechanical properties especially burst index are sensitive to the degree of hydrogen bonding between the fibres but the last property, that is, tear index, is more sensitive to fibre length and fibre strength. Increasing temperature with removal of lignin, better hydrogen bonding is formed between fibres and the first three properties are increased as there are no significant differences between 190°C and 200°C. Apparently, with increasing temperature some of the fibres are damaged and their strength and length decrease. This phenomenon causes the last mechanical property, that is, tear index to decrease with increasing of the temperature. The other aspect of the Figures 4-7 is the effect of the presence of 2% sodium hydroxide in cooking solvent. Hand-sheet papers obtained with this cooking solvent have superior mechanical properties especially in higher temperatures. This is because of the better delignify-

ing character of this reagent and subsequently superior hydrogen bonding of fibres in the absence of lignin.

CONCLUSION

Rice straw pulping can be successfully performed in diethylene glycol, diethylene glycol + ethylene glycol and diethylene glycol + ethylene glycol + 2% NaOH at atmospheric pressure. Hand-sheet papers with superior mechanical properties were obtained at 190°C with a mixture of two solvents together and 2% NaOH. The fibres are damaged at high temperature and at low temperature delignification is incomplete.

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