

ORGANOSOLV PULPING OF WHEAT STRAW BY GLYCEROL

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Pulping of wheat straw was studied with an organic solvent (glycerol) and 2% NaOH as a catalyst, and without catalyst, at various cooking times (180, 90, 45 and 30 min), and at reflux temperature (195-205 °C) as cooking temperature, to investigate the properties of the obtained pulp (cooking yield, kappa number, freeness (CSF), fiber length, α -cellulose, γ -cellulose, ash) and paper (breaking length, burst index, fold endurance, tear index). The best properties of the handsheets were obtained with 2% sodium hydroxide in the cooking solvent, at 30 min as cooking time. As a result of using the processing variables over the variation ranges considered, the following optimum values of the dependent variables were obtained: 64.1% (yield), 64 (kappa number), 300 mL CSF (freeness), 11.89 km (breaking length), 60.38 (folding endurance), 9.27 mNm²g⁻¹ (tear index) and 4.60 kNg⁻¹ (burst index) for pulps and handsheets. The results obtained showed that, under the cooking conditions applied, either including the use of a catalyst or not, delignification increased by increasing the cooking time, although the brightness of the handsheets was reduced. These results involved a secondary reaction between the organic solvent glycerol and the micro-fragments of fibers during cooking.

Keywords: organosolv pulping, wheat straw, non-wood fiber, glycerol, kappa number, papermaking

INTRODUCTION

Non-wood plants represent an important alternative fiber source for the pulp and paper industry. The role of agro-fiber biomass is particularly prominent in countries with limited wood resources. In some regions of Asia, Africa and Latin America, this is the only source of industrial papermaking fibers.¹ Recently, there has been a growing interest in using non-wood fibers for the production of cellulose for paper and other industrial applications.² In the last decade, special attention of the world agricultural research has been given to non-wood materials with a focus on possible environmentally-friendly industrial utilization. In this way, wheat straw, bagasse, reed, rice straw and kenaf have been studied as important non-wood fiber sources for pulping and papermaking.³⁻⁷ Meanwhile, the paper industry is constantly facing mounting resis-

tance from conservationists and environmental groups. To maintain the paper industry growth, governments, as well as industry executives, have to establish and implement policies and plans to ensure a sustainable fiber supply, including reforestation programs, plantation management, recycling, and development of non-wood fibers.⁸

The pulping process of raw materials produces large amounts of highly polluting waste water, especially the sulfite- and sulfate-based processes. For environmental considerations, new methods, such as organosolv pulping, with a potential of reducing the unpleasant effects would be desirable. Organosolv (solvent-based or solvolysis) pulping is a chemical pulping method involving the delignification of the biomass (usually wood) in an organic solvent

or in a solvent plus water system. Organosolv processes have been applied with varying success to hardwoods and softwoods and also, to a lesser extent, to non-wood materials.⁸ The main advantages of the organosolv processes over the conventional ones are the following: low environmental impact, higher pulp yield, ease of bleaching, easy solvent recovery, low capital for a new plant, and recovery of lignin and sugars for profitable utilization.^{3,7,9,10}

A wide variety of organic solvents, including alcohols, ketones, aldehydes, glycols, esters, ketones, dioxane, phenols, thiocompounds, organic acids and bases, dimethyl sulfoxide and organic peroxides, has been proposed for the delignification of lignocellulosic materials in organosolv pulping processes.¹⁰⁻¹² The earliest scientific references to delignification with organic solvents date from 1893, when Kason used ethanol and hydrochloric acid. Subsequently, in the 1930s, Aronovsky and Grotner carried out interesting experiments on this topic, followed by those of Brounstein in the 1950s and those of Kleinert in the 1970s. Since then, a number of authors have investigated the potential of various organic solvents.⁹ The most prominent among the processes that use alcohols for pulping are those carried out by Kleinert (with ethanol or methanol, in the absence of a catalyst) – Alcell (ethanol-water), MD Organocell (ethanol-soda), Organocell (methanol-soda-antraquinone), ASAM (alkali-sulphite-antraquinone-ethanol), the one using sodium bicarbonate-ethanol-water and that using oxygen-alcohol. Other processes based on different alcohols, also worthy of note, are those of ester and phenol pulping – Acetocell (acetic acid-water), Milox (formic acid-hydrogen peroxide), Formacell (acetic acid-water-formic acid), and those using formic acid, glycerol, oxygen-acetone-water, water, glycerol-acetic acid, and ammonia and amine bases.¹³ Therefore, a new pulping process would be more attractive, if suitable for a variety of different types of fiber raw materials, such as softwoods, hardwoods and non-wood materials. Also, the recovery and regeneration of the cooking solvent and of other chemicals should be simpler compared to those of the presently used chemical process.¹⁴ However, one of the main drawbacks of low-molecular weight, low-boiling-point organic

solvents, such as methanol, ethanol and acetone, is that they are restricted to laboratory- or pilot-scale operation for several reasons, including the risk of 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.^{8,10,15,16}

Wheat straw is one of the main cereal raw materials produced in large quantities worldwide every year.¹⁷

Glycerol was selected as an organic solvent, with a high boiling point, for wheat straw pulping, considering the results obtained in preliminary experiments and due to its physico-chemical properties. In the present study, an 85% aqueous solution of glycerol was selected for wheat straw delignification. The solvent was applied under reflux conditions, at atmospheric pressure and a reflux cooking temperature of 195-205 °C. The effects of cooking time and catalyst concentration on pulp properties (cooking yield, kappa number, freeness (CSF), fiber length, α -cellulose, γ -cellulose) and handsheet paper properties (breaking length, burst index, folding endurance, and tear index) were investigated.

EXPERIMENTAL

Raw material

The wheat straw was obtained from the local wheat field in Ardebil, Iran. Before pulping, the raw material was cleaned, cut and sample pieces of approximately 3 cm in length were selected. The chemical composition of wheat straw was determined as follows: 43.1% cellulose, 19.31% lignin, 72.12% holocellulose, 6.8% ash and 1.64% ethanol/dichloromethane extract, on an oven-dry weight basis (moisture content 7.8%).

Analysis of raw materials and pulps

The starting materials and the products obtained from them were characterized according to the following standard methods: cellulose – by the Kirschner-Hoffer method,¹⁸ Klason lignin – by TAPPI T222 om-02, holocellulose¹⁹ and ash content – by TAPPI T 211 om-02. Pulp yield was determined²⁰ gravimetrically, after drying at 105±2 °C for 24 h. Also, the obtained pulps were characterized according to the following standard methods: kappa number – by TAPPI T 236 om-99, α -cellulose – by TAPPI T 203 cm-99, γ -cellulose – by TAPPI T 203 cm-99 and fiber classification was

carried out according to TAPPI 233 cm-06. Handsheets of 60 g/m² were formed and their properties were evaluated in accordance with TAPPI standard methods [TAPPI Committee (2006-2007)]: base weight – by TAPPI T 410 om-02; brightness – by TAPPI T 525 om-06; breaking length – by TAPPI T 404 cm-92; burst index – by TAPPI T 403 om-02; tear index – by TAPPI T 414 om-04; folding endurance – by TAPPI T 511 om-02. The handsheets were conditioned at 23 °C and 50% RH for at least 24 h before testing.

Pulping and papermaking

The pulp was obtained in a 2000 mL balloon placed under reflux conditions. In each experiment, 70 g of oven-dried wheat straw (moisture content 7.8%) was weighed, charged into the balloon and refluxed. The solid/liquor ratio was fixed to 1/10. Glycerol (85% aqueous solution) as a cooking liquor was set by weight. Then, the balloon was loaded with wheat straw and the cooking liquor and the mixture were mantle-heated to the reflux temperature, maintained (controlled) throughout the whole experiment. Wheat straw was cooked in the balloon. Next, the cooked pulps were washed with warm water and disintegrated (at 3000 rpm and 2.5 min) in a standard disintegrator model LTD (TAPPI T 205 sp-02). Further on, the pulps were refined in a laboratory stainless steel PFI mill, model 277, under standard conditions (T 248 sp-00), directly to the specified level of CSF (Canadian Standard Freeness) in agreement with standards T 227 and T 248. After pulp refining, the average fiber length was measured by classification of the BAUER BROS Company. Then, handsheets were prepared with a Semi-Automatic Sheet Machine Series 300, LABTEC Company.

To obtain more precise and acceptable experimental data, the cooking of wheat straw was reproduced in three and two replications, with and without catalyst, respectively, and their properties were measured carefully.

RESULTS AND DISCUSSION

The characteristics of the pulps obtained in the 18 pulping runs are summarized in Table 1. Two sets of experiments – with catalyst (2% NaOH): cooking times 180, 90, 45 and 30 min, and without it: cooking times 90, 45 and 30 min – were done with a glycerol solvent (85% aqueous solution) and, respectively, at a reflux cooking temperature of 195-205 °C. Based on the primary trials performed, the cooking was not accomplished properly at cooking temperatures lower than 195-205 °C. The main effects of cooking time and catalyst on kappa number and yield are shown in Table 1.

As expected, the results obtained reveal that, by using organic solvent glycerol (85% aqueous solution), both with and without catalyst, kappa number and yield decreased along with increasing cooking time. It should be noted that the variation of cooking time was the most influential in relation to yield and lignin reduction of pulps, followed, in the order of importance, by the catalyst. Indeed, the effect of using a catalyst was comparatively low. The present study showed that, by increasing the cooking time up to 6 times (with a catalyst), from 30 min to 180 min, the yield and kappa numbers decreased with 10 and 15 units, respectively. Moreover, on cooking without catalyst, the yield and kappa number decreased with 7 and 15 units, respectively, when increasing cooking time from 30 to 90 min, *versus* 180 min as discussed above. Actually, when using the catalyst, the yield reduction was around half of the yield reduction without catalyst, for the same cooking time (from 30 to 90 min). The effects of the cooking time on the kappa number and yield, both with or without catalyst, are shown in Figures 1 and 2.

Processing under higher reaction conditions increased the delignification ability of the pulping systems. It is well known that a certain ratio of α -O-4 and β -O-4 linkages within the lignin macromolecule should be cleaved to dissolve lignin during pulping, thus permitting its further degradation to lower molecular weight fragments soluble in solvents.¹⁴ A notable observation in this investigation is that, in both cases (with and without catalyst), an increase in the brightness of the handsheets is expected with decreasing the kappa number in pulps, even if it increased with decreasing cooking time and kappa number. The observed increase in brightness is attributed to the glycerol reactions with degraded lignin during cooking. Indeed, the secondary (condensation) reactions between lignin- and sugar-derived degradation products are very intensive under these extremely drastic (for wheat straw) conditions, which explains the dark color and poor delignification. The effect of cooking time on brightness at reflux temperature for both cases of wheat straw pulping is shown in Figure 3. The relation between brightness and kappa number with cooking time is illustrated in Figure 4. However, at a cooking time of 90

min, this is an unusual relationship. Apparently, this behavior could be explained by an uncontrolled influence determined by the same results obtained both with and without catalyst.

Generally, paper strength properties increase with fiber length, L . For wood fibers, it is generally believed that this effect is more pronounced in the case of tear strength *versus* tensile and burst strength values:²¹ for wood fibers, tensile strength was found²² to be proportional to the square root of fiber length, $L^{0.5}$, burst strength to L and tear strength to $L^{1.5}$. Generally, shorter fibers result in decreased paper mechanical properties, as a result of the lower strength of the individual fibers, and *vice versa*. The results of fiber length classification are shown in Table 1. In this study, fiber length increases with decreasing cooking time. Also, the results were more favorable when no catalyst was employed. However, it was expected that the treatment by NaOH might induce damage to fibers. Figure 5 shows the effect of the catalyst on fiber length during cooking.

The freeness of pulps before handsheet making was adjusted by refining in a PFI mill around 300 CSF (Table 1). Refining tends to increase interfiber bonding by fibrillation (increasing the surface area) and hydration of fibers (making them more flexible for better molding around each other), even if the strength of the individual fibers decreases.²³ Then, pulp suspensions were used to make handsheets. The study on the physical properties of the produced handsheets indicates that both breaking length and burst index decrease with increasing cooking time – both with and without catalyst. The percents of decreasing, with and without catalyst, were of 6.9 and 9.7%, respectively. The dependence of breaking length and burst index on cooking time – two important parameters in industrial papermaking – is presented in Figures 6 and 7. As shown in Figure 7, the variation of the burst index during cooking was not remarkable in the absence of the catalyst.

Tearing strength, however, requires a certain minimum fiber bonding, increased fiber bonding causing reduction in tearing strength,¹⁴ which means that the difference in tearing index is more closely related to fiber length. Consequently, as shown in Figure 8,

the catalyst has a marked influence on the tear index at long cooking times, in comparison with short cooking times. On the other hand, compared to Figure 5, it may be noted that fiber length decreases, not only with increasing cooking time, but also with the use of NaOH. Accordingly, the negative effect of the catalyst is slowed down with increasing cooking time. It is understood that the increase in cooking time causes a reduction in kappa number and, consequently, an increase in fiber flexibility. Therefore, the tear index improves when using longer cooking times.

The results of ash also showed that approximately all silica ash present in wheat straw was kept in the glycerol pulp (Fig. 10). Besides, the constant difference in the ash content of the pulps when using a catalyst, in comparison with the absence of the catalyst, is related to reducing the other chemicals of the obtained pulp, *e.g.* the lignin content. However, ash might function as a filler, being thus beneficial to paper printability.²⁴ Additionally, high silica levels create problems in the chemical recovery systems and paper quality. If silica ends up in the paper, it makes the sheet more abrasive, which creates problems in the converting equipment. If silica is removed from the wheat straw fibers during alkaline (soda and Kraft) pulping processes, it appears in the black liquor as sodium silicate and/or other complex siliceous compounds. A high silica content may lead to scaling in the evaporator and recovery boiler tubes, thus interfering with the chemical recovery process. Moreover, the amount of α -cellulose is higher at longer cooking times (Fig. 11). Conversely, compared to α -cellulose, γ -cellulose shows a quite expected reverse behavior (Fig. 12).

In spite of the fact that the strength properties of organosolv pulps are usually lower than those of the corresponding Kraft pulps, their properties may be improved by treatment with various chemicals.¹⁶ A comparison of the results of wheat straw cooking with organosolv glycerol with those of Kraft pulping of wheat straw with 20% active alkali charge and 14% sulphidity,¹¹ and those of soda-AQ pulping of wheat straw with 15% NaOH, 0.05% AQ²⁴ shows that the main properties of wheat straw are improved, particularly % yield, breaking length and tear index (Table 2).

Table 1
Values of independent variables and mechanical chemical properties of the pulp and paper obtained by using the proposed experimental design and papermaking with a catalyst (2% NaOH) and without it

Run	Time (min)	Rep	YI (%)	PFI	KN	FL (mm)	CSF (ml)	BW (g)	Br (%ISO)	BL (km)	BI (kN/g)	TI (mNm ² /g)	FE	Ash (%)	α -C (%)	γ -C (%)
1	180	1	58	114	52	0.285	300	60	8.5	11.5	4.29	10.83	45.94	4.2	71.52	2.35
2		2	57	114	52	0.281	300	60	8.4	11.1	4.20	10.95	46.35	4.2	71.55	2.15
3		3	55	114	49	0.279	300	60	8.5	10.9	4.28	10.88	46.11	4.2	71.46	2.24
4	90	1	61	144	55	0.29	300	60	8.6	11.5	4.48	10.51	51.81	4.2	70.77	2.81
5		2	61	144	54	0.289	300	60	8.6	12.2	4.40	10.42	50.98	4.2	70.73	2.85
6		3	62	144	55	0.301	300	60	8.6	11.3	4.34	10.47	51.21	4.2	70.81	2.74
7	45	1	62	178	62	0.306	300	60	8.8	12.28	4.53	9.94	58.51	4.2	69.86	3.98
8		2	63	178	63	0.321	300	60	8.7	13.19	4.66	10.00	58.32	4.2	69.83	4.02
9		3	62	178	62	0.31	300	60	8.7	11.92	4.51	9.80	57.98	4.2	69.83	4.05
10	30	1	64	266	64	0.321	300	60	9.3	11.89	4.60	9.27	60.38	4.2	69.51	4.54
11		2	64	266	64	0.337	300	60	9.3	12.78	4.72	9.38	60.11	4.2	69.46	4.61
12		3	65	266	64	0.343	300	60	9.4	13.61	4.56	9.32	59.82	4.2	69.57	4.51
13	90	1	63	176	71	0.321	300	60	8.5	11.18	3.46	9.58	29.95	6.8	70.12	2.51
14		2	63	176	71	0.313	300	60	8.5	10.38	3.42	9.65	30.57	6.8	70.02	2.62
15	45	1	66	176	84	0.372	300	60	9.2	11.3	3.49	9.24	32.69	6.8	69.27	3.32
16		2	67	249	84	0.382	300	60	9.2	10.89	3.45	9.29	32.31	6.8	69.31	3.27
17	30	1	71	249	86	0.388	300	60	9.7	11.35	3.52	9.16	35.89	6.8	68.63	4.05
18		2	70	249	85	0.391	300	60	9.6	11.11	3.50	9.10	35.52	6.8	68.57	4.09

Rep: repeat; YI: yield (values referred to pulping process); PFI: refined time; KN: kappa number; FL: fiber length; CSF: Canadian freeness of pulp (after refining); BW: base weight handsheets; Br: brightness of unbleached pulp; BL: breaking length; FE: fold endurance; TI: tear index; BI: burst index; Ash: ash in pulp; α -C: α -cellulose; γ -C: γ -cellulose; runs 1 to 12 – with a catalyst, runs 13 to 18 – without catalyst

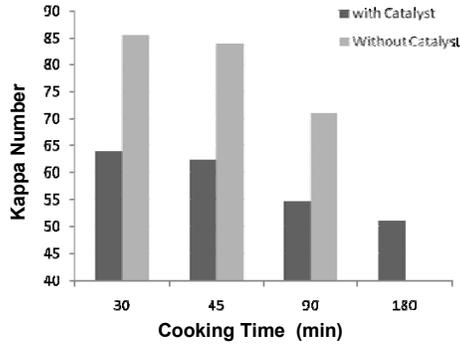


Figure 1: Effect of cooking time on kappa number at 200 °C (pulping of wheat straw with and without catalyst)

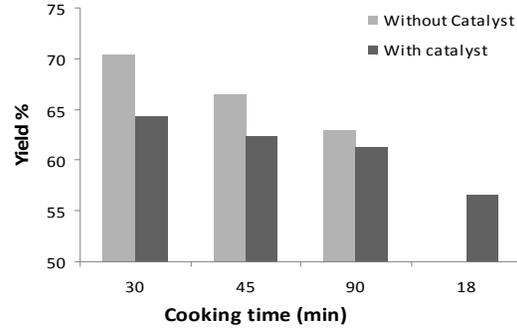


Figure 2: Effect of cooking time on % yield at 200 °C (pulping of wheat straw with and without catalyst)

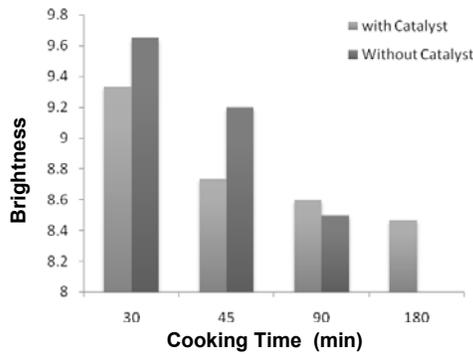


Figure 3: Effect of cooking time on brightness (%ISO) at 200 °C (pulping of wheat straw with and without catalyst)

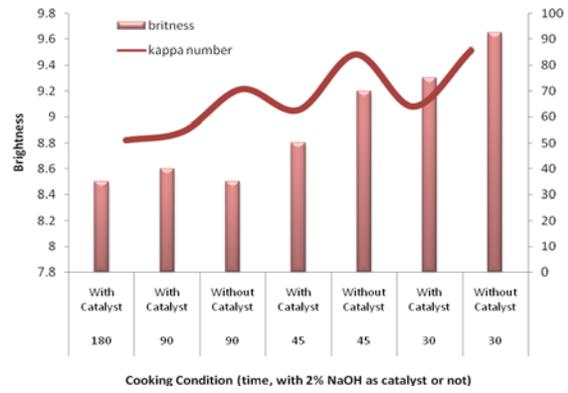


Figure 4: Relation between brightness and kappa number of pulps at 200 °C (pulping of wheat straw with and without catalyst) and handsheets

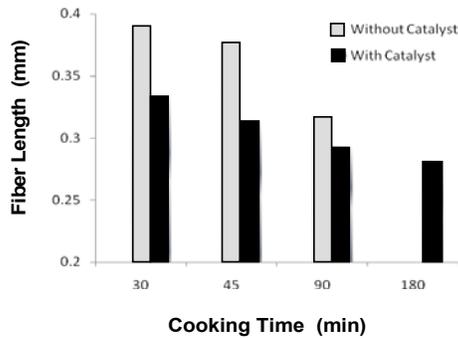


Figure 5: Effect of cooking time on fiber length at 200 °C (pulping of wheat straw with and without catalyst)

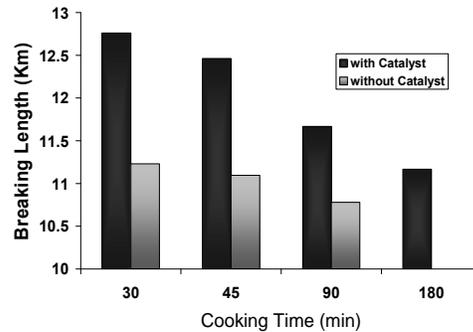


Figure 6: Effect of cooking time on breaking length (km) at 200 °C (pulping of wheat straw with and without catalyst)

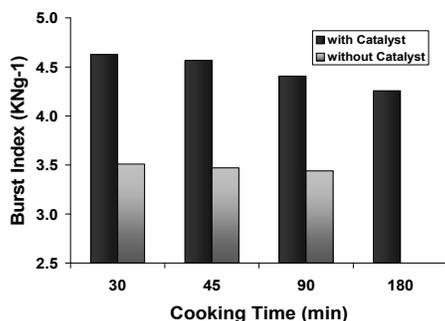


Figure 7: Effect of cooking time on burst index (kNg⁻¹) at 200 °C (pulping of wheat straw with and without catalyst)

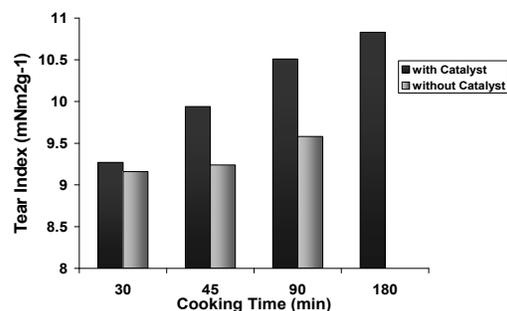


Figure 8: Effect of cooking time on tear index (mNm²g⁻¹) at 200 °C (pulping of wheat straw with and without catalyst)

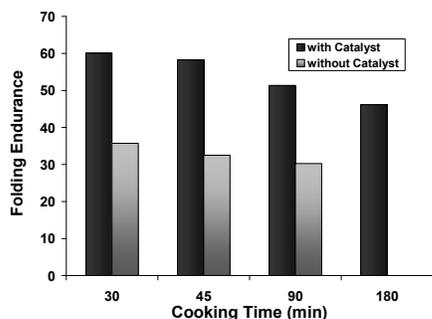


Figure 9: Effect of cooking time on fold endurance value at 200 °C (pulping of wheat straw with and without catalyst)

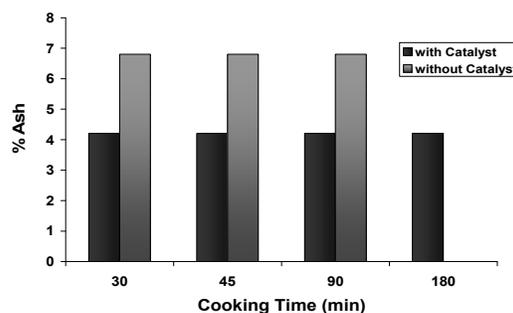


Figure 10: Effect of cooking time on ash content at 200 °C (pulping of wheat straw with and without catalyst)

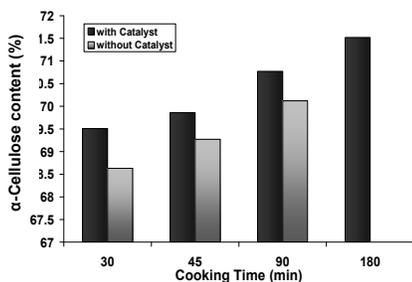


Figure 11: Effect of cooking time on α-cellulose content at 200 °C (pulping of wheat straw with and without catalyst)

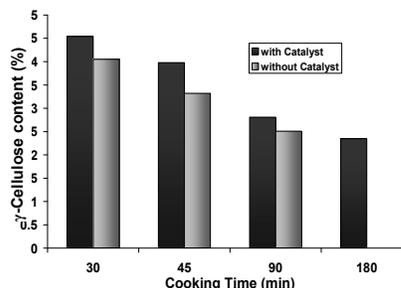


Figure 12: Effect of cooking time on γ-cellulose content at 200 °C (pulping of wheat straw with and without catalyst)

Table 2
Comparison between organosolv glycerol, Kraft and soda-AQ pulps from wheat straw

Parameters	Glycerol pulp + cat.	Glycerol pulp	Kraft pulp	Soda-AQ pulp
Pulping temperature (°C)	200	200	160	160
Pulping time (min)	30	30	40	120
Time to maximum	60	60	55	60
Pulping temperature (min)				
Liquor/straw	10/1	10/1	4/1	6/1
Kappa number	64	85.75	31	15.4
% Yield	64.13	70.48	42	42.3

Breaking length (km)	12.76	11.23	9.8	9.2
Burst index (kNg ⁻¹)	4.62	3.51	4.09 (kpam ² /g)	7.4
Tear index (mNm ² g ⁻¹)	9.32	9.13	4.57	7.5
Brightness (%)	9.33	9.7	29	22.6

In spite of the fact that the strength properties of organosolv pulps are usually lower than those of the corresponding Kraft pulps, their properties may be improved by treatment with various chemicals.¹⁶ A comparison of the results of wheat straw cooking with organosolv glycerol with those of Kraft pulping of wheat straw with 20% active alkali charge and 14% sulphidity,¹¹ and those of soda-AQ pulping of wheat straw with 15% NaOH, 0.05% AQ²⁴ shows that the main properties of wheat straw are improved, particularly % yield, breaking length and tear index (Table 2).

Moreover, the results obtained show that the yields of organosolv pulping are higher than those of Kraft and soda-AQ pulping. The protective action of organosolv on noncellulose polysaccharides wheat straw against degradation under Kraft pulping conditions has been considered the main reason of the fairly high yield of organosolv pulps.¹⁶ Moreover, the results obtained show that the yields of organosolv pulping are higher than those of Kraft and soda-AQ pulping. The protective action of organosolv on noncellulose polysaccharides wheat straw against degradation under Kraft pulping conditions has been considered the main reason of the fairly high yield of organosolv pulps.¹⁶

CONCLUSIONS

The behavior of glycerol as a delignifying agent has been investigated with 2% sodium hydroxide as a catalyst during organosolv pulping of wheat straw, the subsequent effects of the cooking time being evaluated. Generally, glycerol led to good results, both with or without catalyst, used at a short cooking time. In fact, due to its highly polar polyalcohol structure, it can easily penetrate the wheat straw tissue. Glycerol provided an effective reaction medium for wheat straw delignification. The study of glycerol recommends it as an excellent solvent,

particularly when NaOH was used as a catalyst. The study of the physical specifications of the handsheets produced by using a catalyst showed that their physical properties are not considerably improved with increasing the cooking time. Consequently, for pulping wheat straw with 2% sodium hydroxide in glycerol as a cooking solvent, a relatively short cooking time (around 30 min) is recommended, as well as a reflux cooking temperature around 195-205 °C.

Additionally, the dependence of kappa number on cooking time in the presence of 2% NaOH as a catalyst showed that, even if delignification increased with increasing cooking time, the brightness of the handsheets was reduced. Apparently, this is caused by the secondary reaction between lignin- and sugar-derived degradation products during cooking. According to the experimental results, one can obtain optimal conditions of temperature (200 °C) and cooking time (30 min) for producing a light weight board used as a liner, or corrugated box with acceptable properties: 64.1% (yield), 64 (kappa number), 300 mL (freeness), 11.89 km (breaking length), 60.38 (folding endurance), 9.27 mNm²g⁻¹ (tear index) and 4.6 kNg⁻¹ (burst index).

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