EFFECT OF ALKALINE PRE-HYDROLYSIS ON SODA PULPING OF WHEAT STRAW

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The influence of alkaline pre-hydrolysis on hemicelluloses removal and the impact of the treatment on soda pulp quality were investigated. The pre-hydrolysis conditions were selected as NaOH – 5 and 7.5% based on the oven dry weight of the sample, time – 30, 60 and 90 minutes, and temperature – 60 and 90 °C. Each treated sample was divided into two portions: one-third was used for chemical analysis and the other two-thirds for soda pulping. The influence of the pre-hydrolysis conditions was determined by measuring the cellulose and lignin content and the removal of hemicelluloses. The lignin and cellulose content increased under the intense treatment conditions and the hemicellulose removal was higher at higher dosages of NaOH, temperatures and times, varying between 4.55% and 8.31%. The treated sample was subjected to soda pulping during 20 minutes pulping time, at 175 °C temperature and 16% sodium hydroxide (based on dry weight). Then, the pulping yield, kappa number and strength properties of the unbleached pulp were determined by corresponding Tappi standard test methods. The pulping yield and kappa number ranged from 41 to 46.6% and from 41.6 to 61.85, respectively. The highest values of tensile strength, tear strength and burst strength indices were determined as 75.35 Nm/g, 17.9 mN.m^2/g and 3.31 kPa.m^2/g, respectively.

Keywords: hemicelluloses, pre-hydrolysis, cellulose, lignin, yield, strength

INTRODUCTION

The worldwide demand for paper and paper products has significantly increased during the last decades.[1] Even though the per capita consumption of paper and paper products in developed countries is fairly stabilized, due to social, cultural and economic criteria, in many countries, especially those with potential as regards raw material availability, the consumption has increased and the consumption rate has reached far higher than expected. Therefore, the demand for the raw material required for paper production has imposed increasing pressure on forests, which, along with land conversion, has resulted in extensive deforestation, especially in underdeveloped regions. This situation has led to shortage of wood, which is the most suitable raw material for paper and paper products production. Therefore, the tendency towards the utilization of different lignocellulosic biomass, such as agricultural residues, in the pulp and paper industry has been intensified. Indeed, non-woods were primarily used in paper production since the start of paper making attempts and the early papers were produced from non-woods even in North America.[2] However, this trend did not last and within a short period, wood fibers started to dominate paper production.

Since 1970, non-wood pulping capacities have picked up the momentum and increased 2-3 times faster than the wood pulping capacity on global basis.[3] At the same time, research on non-wood pulping has expanded worldwide. Such research activities cover a wide range of pulping processes and raw materials, such as conventional soda and kraft pulping of bagasse and cereal straw, giant reed, high yield pulping of cotton stalks, flax and chemi-mechanical pulping of canola straw.[4-8]

Among agricultural crop residues, wheat straw has gained a higher position among cultivated crops throughout the world. Although the prime intention of wheat cultivation is the seed, the activity also produces lignified straw, which is not usually suitable for cattle feed. Therefore, different pulping processes have been applied to wheat straw at a laboratory scale to investigate its potential for pulp and paper production.

Paper industry is not the only one facing shortage of raw materials, other industries especially the energy and chemical sectors are facing limitations of resources as well. Until the 19th century, renewable resources were the main source of energy, then coal and later petroleum gained prominence. With industrial revolution, the predominant feedstock for the energy and chemical industries consisted in non-renewable oil and natural gas resources, and therefore both of them are now facing increasing consumption and limitations of supply. Hence, there is a continuous search for alternative sources of feedstock, with a focus on renewable resources and on the biorefinery concept.

The biorefinery concept is considered as a path to sustainability for partial fulfillment of the future demand for chemical feedstock and energy.[9] A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuel, power and value-added chemicals from biomass. The biorefinery concept is analogous to today's petroleum refinery, which produces multiple fuels and products from petroleum. Thus, nowadays, new bioproducts are continuously emerging on the chemical material and pharmaceutical markets. The use of biomass in biorefinery facilities is showing a promising perspective, although further technological development for achieving more efficient processes, which can reduce the high cost of production, is still necessary.[10]

The paper industry has also been concerned about the multiple utilization of raw material to reach efficient production practices. Since its beginnings, the paper industry has been continuously developing new procedures and technologies towards the complete utilization of the raw material. Pulping processes, especially chemical pulping, are not only energy self-sufficient, but also some surplus energy is provided to the communities, thanks to modern chemical and energy recovery systems. Moreover, this industry aims at an even more efficient utilization of the lignocellulosic raw material, based on the consideration that both wood lignin and carbohydrates are valuable feedstock for value-added chemicals. Even though the residues from pulping are usually burned to generate energy, the heat value of dissolved carbohydrates, especially hydrolyzed hemicelluloses, is low, which requires an alternative utilization of these compounds.

The utilization of pulping residues as feedstock for the production of chemicals has been conducted following two possible paths: 1) by conversion of residual lignin and hydrolyzed carbohydrates from spent liquor (black liquor) prior to burning it, and 2) by pre-hydrolysis of the raw material and the extraction of the hydrolysate before pulping. The first path has been used for a long period in the production of sugars intended for human consumption from soft wood pulping and other derivatives. The second path is new and has been pursued extensively in the last two decades following the biorefinery concept.

The available literature presents a wealth of research on acid and alkaline pre-hydrolysis of different lignocellulosic raw materials to extract the carbohydrate hydrolysate to be used in bioethanol production. Cheng *et al.*[11] investigated the effect of alkaline pre-hydrolysis of depithed corn stover on the hemicellulose extraction and the performance of pre-hydrolyzed corn stover in soda/AQ pulping. Kurian *et al.*[12] enzymatically fermented the xylose and other hemicellulose products from sweet corn stalks in the production of bioethanol. Teherzadeh and Karimi[13] reviewed the acid pre-hydrolysis of various lignocellulosic materials and Yan *et al.*[14] used acidic hot water treatment to improve extraction and characterized the value-added non-carbohydrate compounds from poplar wood. Mirahmadi *et al.*[15] applied mild alkaline pre-hydrolysis on spruce and birch wood to extract sugar compounds for the production of both bioethanol and biogas, while Jian *et al.*[16] applied acid and alkali pretreatment on pine wood to enhance the bio-oil yield. Sugarcane bagasse[17-18] and softwood[18] have been studied for ethanol production.

The importance of chemical feedstock production from lignocellulosic raw materials, in conjunction with pulping, directed this research to investigate the alkaline pre-hydrolysis of wheat straw to extract the carbohydrate hydrolysate and to determine its effect on soda pulping of pre-hydrolyzed wheat straw.

EXPERIMENTAL

Raw materials

Wheat straw was collected from Jehad-d-Agriculture experimental wheat fields in Ahvaz, Khuzestan, and was transferred to the Pulp and Paper Research Laboratory, Islamic Azad University, Karaj Branch. The leaves and debris were removed, and then the straw was chopped into 3 to 4 cm long pieces. The clean chopped straw was dried at ambient temperature until it reached equilibrium moisture content and was stored in plastic bags until use.

Chemical analysis

The chemical components of the wheat straw, including cellulose, lignin and extractives, were determined using the following Tappi test procedures: Powder preparation; T257 cm-20, extractive free powder; T264 cm-07, Cellulose; Kurschner-Hoffer, Lignin; T222 om-06.[19]

Alkaline pre-hydrolysis

First, the preliminary alkaline pre-hydrolysis of wheat straw was performed applying different dosages of sodium hydroxide, temperatures and times. Then, the weight loss of the wheat straw was determined and it was found that the effect of low and high dosages of NaOH is not detrimental.

Based on the preliminary experiment, each wheat straw sample weighing 150 grams (bone dry) was mixed with 1500 mL distilled water, containing the required NaOH, in a plastic bag and was heat sealed. Then, the sample was treated at pre-determined temperature and time in a hot water bath at constant temperature and under occasional shaking to ensure uniformity. At the end of the treatment time, the content of the plastic bag was discharged on a screen (200 mesh) and the hydrolysate (filtrate) was collected for determining the residual sodium hydroxide and dissolved hemicelluloses. The pre-hydrolyzed wheat straw was divided into two portions: one-third for determining the chemical composition and the other two-thirds for soda pulping experiments.

Alkaline pre-hydrolysis conditions were selected as follows: wheat straw to liquor ratio: 1:10, sodium hydroxide charge: 5 and 7.5% (based on oven dry weight of straw), time: 30, 60 and 90 minutes and temperature: 60 and 90 ºC.

The chemical components of pre-hydrolyzed wheat straw were determined based on Tappi standard test methods, as mentioned above.

Hemicelluloses precipitation

The dissolved hemicelluloses were determined as described below. First, the pH of the filtrate was adjusted to 5 using 4N H_2So_4 and the solution was kept refrigerated for 24 hours to precipitate the dissolved lignin. Then, 100 mL of the liquor above the precipitated lignin was transferred to a 1000 mL beaker and 400 mL of 96% ethanol was added. The solution was refrigerated for 24 hours. At the end of this period, the solution was centrifuged for 5 minutes at 7500 rpm. The hemicelluloses were separated and dried in an oven set at 40 ºC for 24 hours. Then, the weight of the hemicelluloses was determined and the percentage based on original straw was calculated.

Pulping

Soda pulping was used on pre-hydrolyzed wheat straw. Pulping conditions were kept constant: sodium hydroxide: 16% based on the oven dry weight of straw, cooking temperature: 175 ºC, cooking time after reaching the cooking temperature: 20 minutes, and straw to liquor ratio: 1:5. Untreated wheat straw was pulped as a control sample. In each cooking, two-thirds of the pre-hydrolyzed wheat straw sample were used (oven dry), in a 4-liter rotating digester (Ghomes Wood and Paper Equipment Manufacturing Co.). At the end of each pulping trial, the content of the cylinder was discharged on a 200 mesh screen, and the spent liquor was collected for consumed alkali determination. Then, the cooked straw was defibrated using a 25 cm laboratory single disc refiner (Ghomes Wood and Paper Equipment Manufacturing Co) in three passes. The defibrated cooked straw was screened using a set of two screens, a 14-mesh screen on top of 200 mesh screens. The material retained on the 14-mesh screen (R14) was considered as "reject" (shives), and the fibers that passed through the 14-mesh screen and remained on the 200-mesh screen (P14-R200) were considered as "accept" (screened yield).

The following TAPPI standard test methods were used for pulp and handsheet evaluation: Kappa number, T236 om-06; PFI; Drainage, T227 om-04; Handsheet preparation, T205 om-06; Tear strength, T414 om-04; Tensile strength, T494 om-06, and Burst strength, T403 om-02, Brightness, T452 om-08, Opacity, T425 om-06.[19]

Statistical analysis

The analysis of variance (ANOVA) was used for statistical analysis of the data and, in case a significant difference between the averages was observed, the Duncan multiple range test was used for grouping the averages.

RESULTS AND DISCUSSION

Alkaline pre-hydrolysis

Wheat straw was pre-hydrolyzed to demonstrate the impact of sodium hydroxide concentration at different treatment times and temperatures on the dissolution of hemicelluloses and lignin. Preliminary experiments with various dosages of sodium hydroxide revealed that the dosages of sodium hydroxide do not have a detrimental effect on the weight loss of the treated wheat straw. Therefore, two dosages of sodium hydroxide were used and the cellulose and lignin content of the treated wheat straw and the dissolved hemicelluloses were measured. The residual sodium hydroxide after the treatment was also determined. The results of the statistical analysis of the effect of pre-hydrolysis variables on the measured properties are shown in Table 1. The influence of sodium hydroxide dosage and treatment temperature on residual sodium hydroxide and hemicelluloses removal has shown to be statistically significant at a 99% level and the data indicate that about two percent sodium hydroxide is needed for the dissolution of hemicelluloses and part of lignin. Thus, higher dosages of this compound are not required.

The independent and interactive effects of the variables (except time and temperature) on hemicelluloses removal was statistically significant at a 99% level, indicating the effectiveness of alkaline hydrolysis treatment in this case (Fig. 1). The hemicelluloses removal varied between the lowest value of 4.55%, corresponding to the mildest treatment (5% NaOH, 30 minutes and 60 ºC), and the highest removal efficiency (8.31% removal), related to the severe treatment conditions (7.5% NaOH, 90 minutes and 90 ºC). The results of wheat straw alkaline hydrolysis revealed the potential of this treatment to dissolve and remove the hemicelluloses from wheat straw. These hemicelluloses can be used as a source of carbohydrate for bio-ethanol production.

The influence sodium hydroxide, treatment time and temperature on the cellulose content of pre-hydrolyzed wheat straw and the interactive effect of time and temperature and time and sodium hydroxide on the cellulose content of pre-hydrolyzed wheat straw were statistically significant at a 99% confidence level (Table 1). The cellulose content of the treated wheat straw is higher, because of the hemicelluloses removal, otherwise the charged sodium hydroxide is not strong enough to degrade and dissolve the cellulose.[20] Figure 2 illustrates the influence of wheat straw pre-hydrolysis variables on the cellulose content of treated wheat straw.

The impact of variables on the lignin content of pre-hydrolyzed wheat straw was not statistically significant, except in the case of the combined effect of time and temperature (Table 1). The lignin content of the treated wheat straw is higher than in the untreated wheat straw, which is attributed to the removal of the hemicelluloses.

Pulping

For annual plant fibers, mostly soda pulping has been applied. Soda pulping is a well-established process with the potential to process a vast variety of annual plant raw materials, but this process has the particular disadvantage of deteriorating the low molecular weight carbohydrates, which are dissolved in the spent liquor and then burned with lignin.[21] Therefore, the pre-hydrolysis of wheat straw, followed by soda pulping, was performed to discover the impact of pre-hydrolysis and removal of hemicelluloses on the pulp chemistry, yield and strength properties. Identical soda pulping conditions were used and only the wheat straw treatment was varied. Soda pulp from untreated wheat straw was also prepared for comparison. The results of statistical analysis (ANOVA) are presented in Tables 2 and 3.

The results of the chemical analysis showed that between 12.82 and 14.49% sodium hydroxide was consumed during pulping (16% was charged) and the residual alkali after pulping was low. Even though the charge of alkali seems sufficient, for future work, a higher charge of chemicals would be required to ensure efficient dissolution of lignin. The interactive effect of wheat straw pre-hydrolysis conditions on sodium hydroxide consumption was not statistically significant, which indicates the sufficiency of the alkali charge.

Table 1
Analysis of variance of the effect of pre-hydrolysis variables on chemical components of pre-hydrolyzed wheat straw and hemicelluloses removal (F value and significance level)

Properties / Variables	Cellulose	Lignin	Residual NaOH	Hemicellulose removal
Temperature	139.39**	0.51^{ns}	16.44**	37.2**
Time	29.22**	11.62**	0.3^{ns}	0.3^{ns}
NaOH	52.66**	0.13^{ns}	224.73**	224.73**
Temp*time	12.77**	4.86**	2.43^{ns}	1.21^{ns}
Temp*NaOH	5.09^{ns}	0^{ns}	2.50^{ns}	32.21**
Time*NaOH	13.64**	0.8^{ns}	2.16^{ns}	5.09**
Temp*time*NaOH	21.96^{ns}	2.41^{ns}	2.34^{ns}	10.89**

Significance level: **99%; *95%; ns – not significant

Table 2
Analysis of variance of the effect of pre-hydrolysis variables on wheat straw soda pulp properties
(F-value and significance level)

Variables \ Properties	Cellulose	Drainage	Kappa No.	NaOH consumed	Yield
Temp	0.52^{ns}	9.45**	38.84**	15.22**	16.87**
Time	1.55^{ns}	4.13*	19.58**	42.19**	8.37**
NaOH	1.89^{ns}	0^{ns}	10.86**	384.81**	16.87**
Temp*time	0.34^{ns}	64.28**	2.4^{ns}	5.99**	0.05^{ns}
Temp*NaOH	0.11^{ns}	21.26**	3.67^{ns}	0.09^{ns}	2.14^{ns}
Time*NaOH	10.52**	1.77^{ns}	1.04^{ns}	9.59**	1.04^{ns}
Temp*time*NaOH	0.75^{ns}	5.33**	5.33**	0.73^{ns}	2.14^{ns}

Significance level: **99%; *95%; ns – not significant

Table 3
Analysis of variance of the effect of pre-hydrolysis variables on wheat straw soda pulp strength and optical properties
(F value and significance level)

Variables \ Properties	Tensile strength index	Tear strength index	Burst strength index	Brightness
Temp	59.95**	18.86**	2.18^{ns}	247.79**
Time	20.59**	3.32*	5.41**	191.76**
NaOH	4.31**	1.13^{ns}	0.31^{ns}	176.2**
Temp*time	37.37**	10.33^{ns}	10.87**	30.69**
Temp*NaOH	0.46*	2.09^{ns}	47.04**	4.43*
Time*NaOH	6.58**	5.76**	18.95**	13.02**
Temp*time*NaOH	9.64**	0.05^{ns}	2.22^{ns}	95.17**

Significance level: **99%; *95%; ns – not significant

The total yield of the pulps varied between the lowest value of 41% under severe wheat straw pre-hydrolysis conditions (7.5% NaOH, 90 minutes at 90 ºC) and the highest value of 46.6% under the mildest wheat straw pre-hydrolysis conditions (5% NaOH, 30 minutes at 60 ºC). The total yield of the pulp produced from untreated wheat straw was 45%. The pulping yield measurements showed that wheat straw alkaline pre-hydrolysis opens the structure of the wheat straw and dissolves the hemicelluloses (Fig. 1), which facilitates the penetration of alkali into the wheat straw structure and easy removal of lignin. This phenomenon reduces the pulping yield and increases the cellulose content of the pulp.

The effect of wheat straw pre-hydrolysis conditions on the cellulose content of the pulps was not statistically significant, but the independent effect of the variables on the kappa number of the pulps was statistically significant at a 99% confidence level (Fig. 3). The kappa number of the pulps prepared from treated wheat straw was lower than that of the pulp from untreated straw, which indicates the easy removal of lignin from treated straw. The kappa number of the pulps from the treated straw samples varied from the highest value of 59.81 to the lowest value of 41.66. The kappa number variation shows that, as the straw treatment intensifies at higher NaOH charge, longer time and higher temperature, more lignin is removed and the kappa number is reduced (Fig. 3).

The drainage of the pulps does not vary significantly because of the removal of hemicelluloses, which is the hydrophilic component of the pulp (Fig. 4).

Pulp strength and optical properties

The strength properties and brightness of the soda pulps produced from alkaline pre-hydrolyzed wheat straw were determined and the statistical analysis of the data is provided in Table 3. The pretreatment of the wheat straw deteriorated the strength properties of the soda pulps, while pulp brightness was improved.

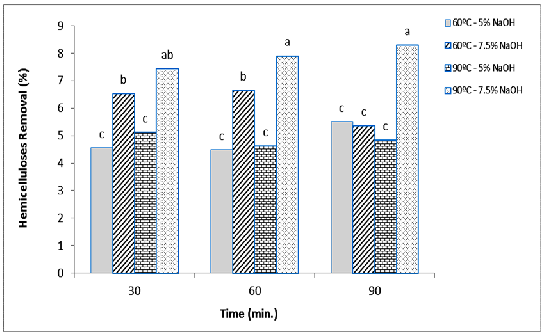

Figure 1: Influence of wheat straw alkaline pre-hydrolysis variables on hemicelluloses removal (lower case letters on the bars – Duncan grouping of the averages)

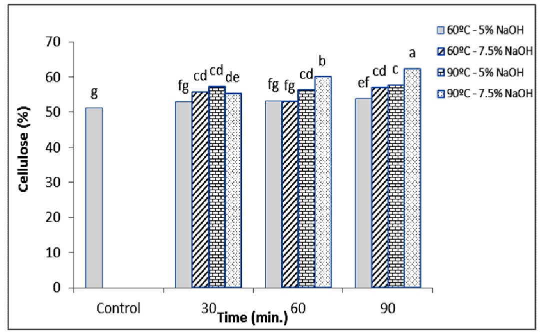

Figure 2: Influence of wheat straw alkaline pre-hydrolysis variables on cellulose content (lower case letters on the bars – Duncan grouping of the averages)

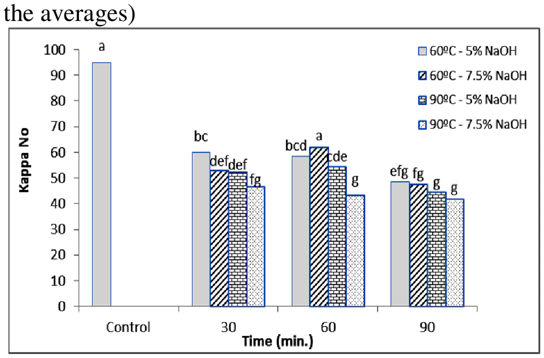

Figure 3: Influence of wheat straw alkaline pre-hydrolysis variables on kappa number of the pulps (constant soda pulping conditions: NaOH: 16% based on bone dry weight of straw, 175 ºC and 20 minutes cooking time after reaching the cooking temperature, straw to liquor ratio: 1:5)

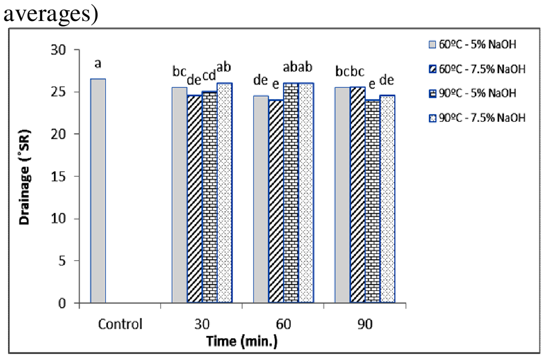

Figure 4: Influence of wheat straw alkaline pre-hydrolysis variables on pulp drainage (constant soda pulping conditions: NaOH: 16% based on bone dry weight of straw, 175 ºC and 20 minutes cooking time after reaching the cooking temperature, straw to liquor ratio: 1:5)

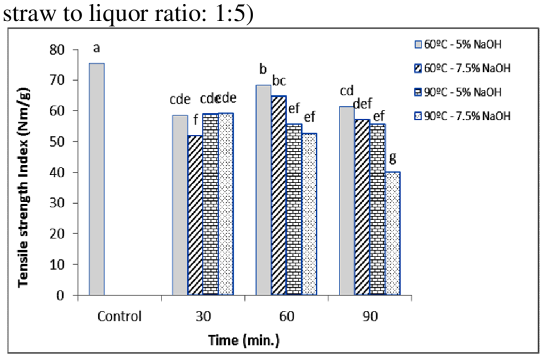

Figure 5: Influence of wheat straw alkaline pre-hydrolysis variables on pulp tensile strength index (constant soda pulping conditions – see Fig. 3)

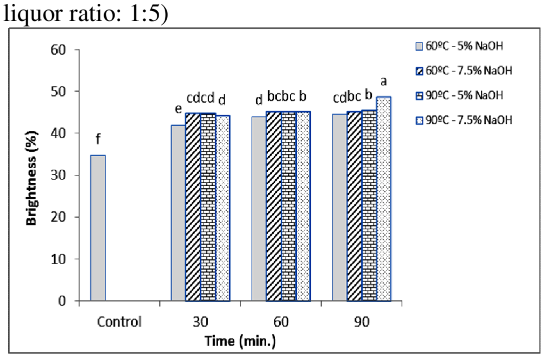

Figure 6: Influence of wheat straw alkaline pre-hydrolysis variables on pulp brightness (constant soda pulping conditions – see Fig. 3)

The effect of pre-hydrolysis variables on the pulp tensile strength index (Fig. 5) is statistically significant at a 99% confidence level. However, only the effect of temperature and the interactive effect of temperature and NaOH on the tear strength index were statistically significant at a 99% confidence level, while the effect of the other variables was not statistically significant (Table 3).

The presence of low molecular weight hemicelluloses in the pulp fibers enhances the bonding potential of the fibers. Hemicelluloses absorb more water, compared to cellulose, and help develop more hydrogen bonds among the cabohydrates. The strength of paper produced from fibers strongly depends on the intensity of the hydrohen bonds and the elimination of hemicelluloses will reduce the number of hydrogen bonds, consequently, will lower the strength of the paper. As observed from this experiment, both the tensile and burst strength indices of the paper produced from the treated pulps were reduced. This happened because the removal of hemicelluloses deteriorated the integrity of the fiber structure and reduced the inherent strength of the fiber. The consequence of this phenomenon is the reduction of paper strength.

In the cell walls of fibers, lignin and cellulose molecules are bound by hemicelluloses, generating the lignin-carbohydrate complex. Any removal of hemicelluloses facilitates the separation and removal of lignin, which improves the brightness of the pulp. The effect of wheat straw pre-hydrolysis variables on the evolution of pulp brightness was statistically significant (Fig. 6).

CONCLUSION

Alkaline pre-hydrolysis of wheat straw effectively removes the hemicelluloses of the straw, which can be used as feedstock for energy generation and chemical production. Alkaline hydrolysis removed 8.31% hemicelluloses, which amounts to 83 kg/ton of wheat straw.

Alkaline pre-hydrolysis and consequently the partial removal of hemicelluloses disrupts the lignin carbohydrate linkages and facilitates the lignin removal. Therefore, the kappa number of the produced pulp is reduced and the brightness of the pulp is increased. The lower kappa number and higher brightness reduce the consumption of bleaching chemicals.

The dissolution of hemicelluloses and their separation from the wheat straw deteriorate the strength of the pulp. However, the strength can be increased by pulp refining.

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