RESOURCE-SAVING WHEAT STRAW PROCESSING TECHNOLOGY

Iryna Trembus[1], Nazarii Mykhailenko[2]

[1]Department of Ecology and Plant Polymer Technologies
National Technical University of Ukraine
[2]"Igor Sikorsky Kyiv Polytechnic Institute"
37 Peremohy Ave., Kyiv, Ukraine, 03056
E-mail: tivkpi@gmail.com

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ABSTRACT

The wheat straw delignification condition influence in the medium "acetic acid-water-hydrogen peroxide-citric acid catalyst" to the yield and cellulose product composition was studied. It was established that the fibrous semi-finished product output and the residual lignin content are decrease with increasing temperature and delignification duration. The oxidative wheat straw delignification process was described by a first-order kinetic equation, and it was characterized by low activation energy values of 16.7 kJ mol^{-1}. The oxidized cellulose sample's structure was studied using IR spectroscopy.

Keywords: wheat straw chaff, oxidative delignification, kinetics, infrared spectroscopy, straw cellulose.

INTRODUCTION

Research in the field of macromolecular materials creates a scientific basis for the rational plant raw materials usage. Considering the long-term global economic growth and the fact that the demand for cardboard and paper products in the world will grow by an average of 1.1 % until 2030 as a result it will requires increasing pulp production [1, 2].

The expanded regenerative biomass strategy usage increases interest in the processes development for obtaining valuable chemical products from various types of lignocellulosic material, primarily wood, agricultural waste, and non-wood plant raw materials. Of the numerous agro-industrial complex wastes the straw of cereal crops like wheat and rye have particular interest. The main advantages of such plant material are its annual reproducibility and the processing possibility by any of the currently known delignification methods [3 - 5].

The main difficulties non-wood plant material cellulose obtaining is the large number of short fibers presence; heterogeneity of the macro- and microstructure; high content of pentosans and in particular ash, silicon compounds; low bulk mass of raw materials. These problems cannot be solved only by improving auxiliary processes and technological equipment (absorption, evaporation, soda regeneration, etc.) as it is happening today [6 - 9].

Existing technologies for obtaining cellulosic material from wood and non-wood plant materials are energy-intensive and environmentally unfriendly due to it requires sulfur and chlorine compounds usage. Industry force requirements for gas emissions and wastewater of industry force to use environmentally friendly plant raw materials delignification methods [10, 11]. Cellulose obtaining with the peroxycarboxylic acids has gained special development. For the lignin oxidation with hydrogen peroxide effective catalysts can be compounds of transition metals as a chromium, molybdenum and tungstate. Peroxycarboxylic acids are chemically unstable mainly due to the influence

of variable valency metals. Increasing the stability of peroxyacids is noticeably more effective with the addition of citric acid [12 - 14].

Developing a resource-saving and economically beneficial catalytic oxidation-organosolvent technology for cellulose obtaining from own raw materials is the main goal of this work.

EXPERIMENTAL

Stems of air-dry wheat straw (*Triticum vulgare*) measuring 15 - 20 mm were used as raw materials. Straw stalks chemical composition by mass absolutely dry raw materials, %: cellulose - 45.6; lignin - 20.8; pentosans - 26.7; resins, fats, waxes (RFW) - 5.2; ash - 6.6. It should be noticed that the investigated plant raw materials contain several times more NaOH soluble components such as starch, pectins, inorganic salts, cyclic alcohols, dyes, tannins, hemicelluloses, and low-molecular cellulose fractions. It can be concluded that such wheat straw stalks chemical composition for oxidative-organosolvent delignification needs lower cooking reagents consumption and shorter temperature treatment duration to compare with traditional another plant raw materials cooking to achieve the same delignification degree.

Delignification was carried out in glass reactors with reflux under constant stirring in the temperature range (T) 80 - 100°C, duration (τ) 60 - 180 min., hydromodule (HM) 10:1. The reaction mixture composition are glacial acetic acid and water in the ratio of CH_3COOH : H_2O - 75 : 25 % by volume with the 50 % H_2O_2 addition by absolutely dry raw materials weight and 0.5 % citric acid as a catalyst [13]. After delignification the cellulosic product was separated from the reaction solution by filtration than washed to a neutral reaction with washing water and dried to an air-dry state.

The residual lignin amount in the cellulose product was determined by the sulfuric acid method in Komarov's modification. The cellulose product yield was determined by the weight method.

The cellulose product IR spectrum was recorded on a spectrophotometer "Specord M80" ("Carl Zeiss", Germany) in the range 300 - 4000 cm^{-1}. For the research the sample was grind with KBr in a ratio of 1 : 9 and pressed into tablets [15].

RESULTS AND DISCUSSION

The research examines the temperature and process duration influence on the quality cellulose product indicators Fig. 1.

It can be seen from data in Fig.1 that at 80°C temperature the wheat straw stalks delignification degree is not high and as a result cellulose contains 4.6 % of residual lignin. A significant delignification process intensification is observed with the temperature rises to 100°C. At this temperature cellulose which contains residual lignin 1.0 % was obtained.

The plant raw materials delignification process in the studied system takes place in mild conditions

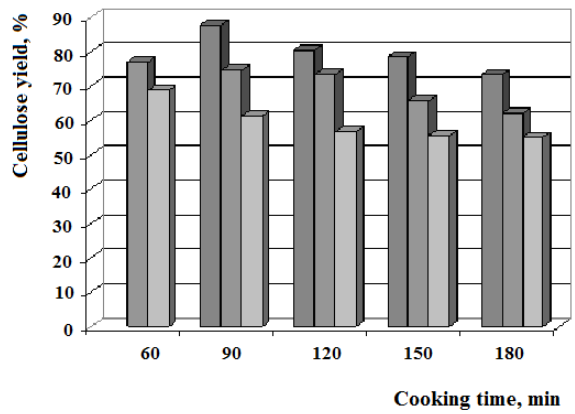

Fig. 1. The impact of technological parameters on the yield of cellulose product: 80°C (■); 90°C (■); 100°C (□).

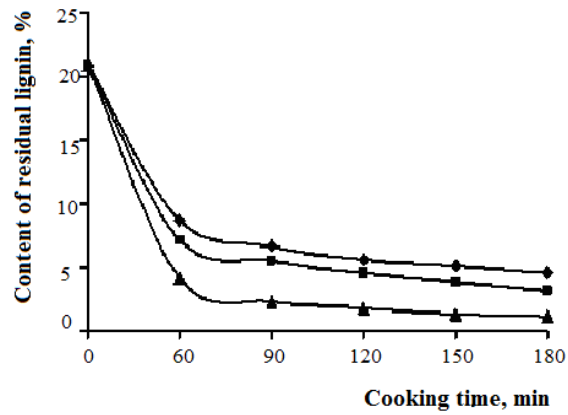

Fig. 2. The lignin content changes dynamics in the cellulose during oxidative wheat straw stalks delignification process: 80°C (♦); 90°C (■); 100°C (▲).

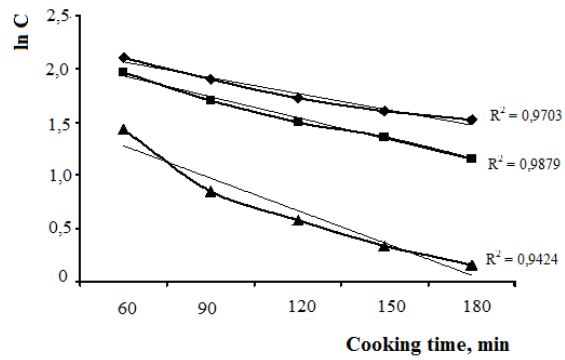

Fig. 3. Logarithm residual lignin content in the cellulose dependence from the wheat straw stalks delignification process duration:80°C (♦); 90°C (■); 100°C (▲).

with significant plant fibers swelling. An increasing temperature accelerates the delignification process which allows to obtain cellulose with a high yield and a low residual lignin content.

To determine rate constants and activation energy of oxidative wheat straw stalks delignification process the dynamics changes in the residual lignin content depending on the duration and processing temperature were studied Fig. 2. The kinetic first order equation was used to calculate the rate constants analytically [3, 16]:

$$\ln\left(1-\frac{[A_o]-[A]}{[A_o]}\right)=k\cdot t, \quad (1)$$

where k - process rate constant; t - the delignification process duration; $[A]$ and $[A_o]$ - initial and current lignin content in plant material and cellulose respectively.

The Arrhenius equation was used to calculate the activation energy [3]:

$$k=k_o\cdot e^{-E/RT} \quad (2)$$

where, k_o - pre-exponential multiplier; E - activation energy; R - universal gas constant; T - temperature in Kelvin degrees.

The order of the wheat straw stalks delignification process was determined graphically by plotting the ln C dependence the delignification process duration where C is the residual lignin content in the cellulose expressed in %. The linear dependence presence of the residual lignin concentration logarithm on the delignification duration indicates the possibility to describe the oxidative wheat straw stalks delignification process by a first-order kinetic equation Fig. 3.

The oxidative wheat straw stalks delignification activation energy was graphically calculated using rate constant which is equal to 16.7 kJ mol^{-1} Fig. 4.

The Table 1 shows the rate constants and

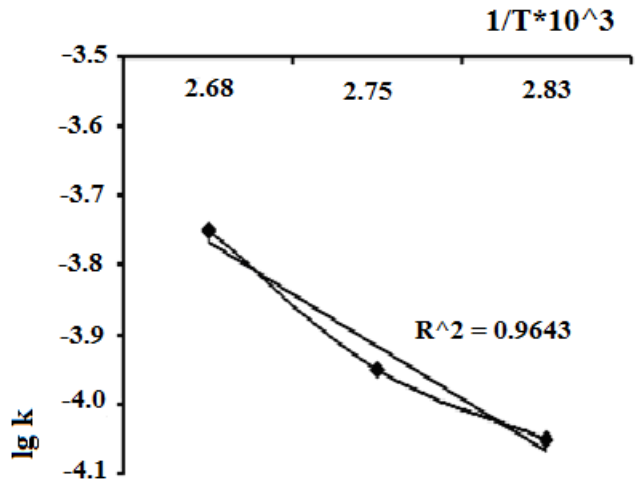

Fig. 4. Logarithm rate constant dependence of the oxidative wheat straw stalks delignification process from the reverse temperature in the temperature range 80 - 100°C.

Table 1. Kinetic oxidative-organosolvent wheat straw stalks delignification characteristics.

Cooking temperature, °C	Graphic method		Analytical method	
	Rate constant k, s^{-1}	Activation energy E, kJ mol^{-1}	Rate constant k, s^{-1}	Activation energy E, kJ mol^{-1}
80	8.88×10^{-5}	16,7	9.01×10^{-5}	19.1
90	1.12×10^{-4}		2.04×10^{-4}	
100	1.76×10^{-4}		2.81×10^{-4}	

activation energy values of the oxidative wheat straw delignification process calculated by graphical and analytical methods.

It can be seen in data from Table 1 that the oxidative-organosolvent wheat straw delignification process rate constants increase with higher temperature which corresponds to the known temperature influence dependence on the delignification reaction rate what is said in Arrhenius law. At the same time the studied delignification process is characterized by lower numerical activation energy values in comparison with the acetic non-wood plant material processing 23 - 48 kJ mol^{-1} [16] and wood - from 82 to 125 kJ mol^{-1} [11]. This is explained by the fact that the annual plants lignin is less polymerized, and it requires less energy to transfer it to the cooking solution.

The cellulose samples' structure obtained by oxidative wheat straw stalks was investigated by IR spectroscopy (Fig. 5). The samples IR spectra were recorded in the range of 400 - 4000 cm^{-1} (Fig. 5). The cellulose sample was characterized by broad absorption band presence in the range of 3000 - 3600 cm^{-1} which corresponds to O-H vibrations and the absorption bands at 2838 and 2914 cm^{-1} correspond to C-H vibrations. Absorption bands presence like these is due to the fact that all three main components of biomass as cellulose, hemicellulose and lignin have hydroxyl groups and C-H bonds in their structure. The plant raw materials treatment with peroxyacid leads to the hemicelluloses and lignin removal and as a result the intensity of the band at 1745 cm^{-1} for the sample is significantly reduced.

Absorption at 1618 cm^{-1} simultaneously corresponds to asymmetric glucuronic acid carboxyl group vibrations in hemicelluloses and C=O vibrations in the lignin structure. As a processing result the intensity of this absorption band is significantly reduced which is confirm the delignification. In addition, the band at 1618 cm^{-1} in the IR spectra of the samples is partially caused by adsorbed H_2O. The bands at 1160 and 896 cm^{-1} arise from C-O-C stretching in β-(1→4)-glycosidic bonds in cellulose and hemicellulose.

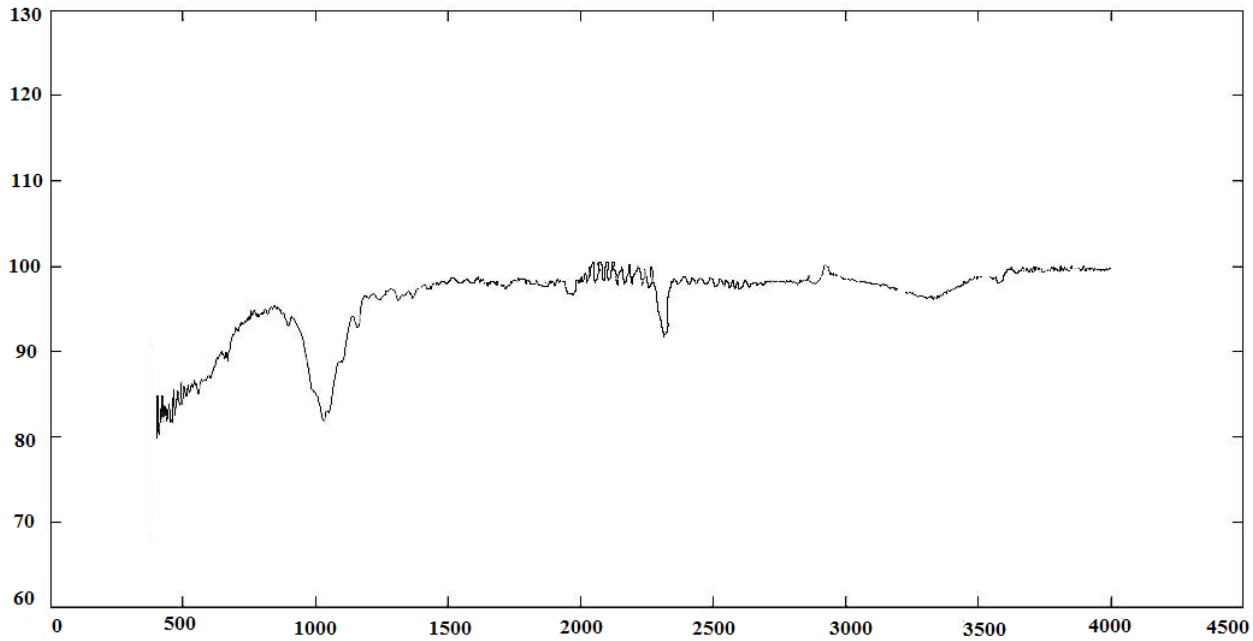

Fig. 5. IR spectrum of a organosolvent cellulose laboratory sample.

CONCLUSIONS

The expediency of using wheat straw as an alternative raw material for the pulp and paper industry and oxidative-organosolvent delignification methods as cooking solutions of non-wood plant raw materials was substantiated. The residual lignin content in the obtained cellulosic product and the cellulose yield decrease with increasing temperature and wheat straw delignification process duration was shown.

The kinetic processing characteristics were calculated and the wheat straw delignification in the acetic acid-hydrogen peroxide-water-citric acid catalyst system is described by a first-order equation was established. According to the graphical and analytical calculation methods the activation energy value is 16.7 and 19.1 kJ mol^{-1}. Low activation energy values indicate the oxidative wheat straw delignification process occurrence in the diffusion region.

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