CELLULOSE CHEMISTRY AND TECHNOLOGY

OPTIMIZATION OF SODA PULPING PROCESS OF CORN STALKS BY RESPONSE SURFACE MODELLING

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Corn (*Zea mays* L.) cultivation generates important quantities of agricultural residues. The chemical composition of corn stalks indicates that these may be used as a raw material for pulping. The goals of the present research include determining the influence of soda process parameters (alkali charge, temperature and pulping time) on corn stalk pulp properties and the optimal conditions for achieving the best results. Therefore, the response surface methodology has been employed for studying the effects of the selected main independent variables (alkali charge, temperature and pulping time) on process yield, pulp Kappa number and intrinsic viscosity, as well as the mechanical strength properties of the corresponding laboratory paper sheets: tensile index, burst index, corrugating medium flat crush resistance and short span compression resistance. The paper strength properties are of much importance in the field of bio-based packaging production. Establishing the proper model equations indicated the influence of each variable on pulp characteristics and paper properties. These equations may provide the basis for selecting the optimal conditions for pulping, depending on the targeted results.

Keywords: corn stalks, fiber sources, packaging, paperboard, paper strength

INTRODUCTION

The pulp and paper industry is facing a continuous need for virgin cellulosic fiber to replace fiber losses during the paper recycling process, to improve the mechanical strength of paper products or to satisfy market demands in terms of health and food safety. Non-wood virgin fiber sources include agricultural lignocellulosic residues, a side-stream of materials resulted from crop cultivation and harvesting.[1,2]

The usage of different agricultural residues as alternative raw materials for pulping and papermaking are an appealing path for the management of this waste category.[3] Corn (*Zea mays*) represents an important crop, with a share of 18.6% of total cultivated cereals in European Union.[4] Romania is an important corn producer, with a production of 14.5 mil. tons in 2017 (second among EU countries). Considering the total cultivated surface of 2.5 mil. ha of corn in Romania (in 2017), important quantities of corn stover are obtained.[5] Corn stover quantities are in the range of 1.7-4.5 t/ha with an average value of 2.49 t/ha.[6] It can be estimated that, in Romania, around 6.25 mil. tons of corn stalks were obtained in 2017. About 30% in mass from this amount is represented by leaves and 70% by stems.[7]

Currently, corn stalks are used as cattle bedding and feedstock, combustion in power plants and chemical processing.[8] Chemical processing methods include the physico-chemical treatment of corn stalks to remove hemicelluloses and lignin, and further use of the cellulosic material in the production of bioethanol.[9,10] The chemical composition of corn stalks includes the known three polymeric constituents: cellulose (30-41.5%), hemicelluloses (18-26%) and lignin (11-20%).[9,11-13] Although the values reported in the literature vary in wide ranges, depending on the variety of corn and the cultivation area, corn stalks are attractive as a raw material for pulping. In this respect, Jahan *et al.*[14] have studied the possibility of alkaline sulfite-anthraquinone-methanol (ASAM) and Kraft pulping of depithed corn stalks, showing the influence of pulping parameters on pulp quality and the characteristics of the obtained sheets before and after bleaching.

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The partial removal of the hemicelluloses from the pith by water pre-extraction shows some minor effects on the strength of the obtained paper sheets.[15]

The main goal of the study has been to determine if corn stalks can be used as a source of fibrous material for bio-based packaging products. In this respect, the effect of soda pulping conditions (active alkali charge, temperature and pulping time) on the corn stalk delignification are studied. The optimal parameters of soda pulping of corn stalks in order to obtain dedicated pulps, in terms of yield and lignin content, are determined.

EXPERIMENTAL

Raw materials

Corn stalks were collected from local farms in the region of Moldova, Romania. The leaves, dirt and biodegraded parts were removed, the stalks were chopped to adequate length (~30 mm) and conditioned to around 10% moisture content. The previously determined chemical composition[14] of corn stalks showed the following values: 64.4% polysaccharides determined as holocellulose by the Wise method;[17] 38.7% cellulose determined by the Kushner–Hoffer method;[19] 19.5% pentosans determined by TAPPI T 223 cm-01; 20.2% acid insoluble lignin (TAPPI T222 om-06); 2.55% extractives (TAPPI T204 cm-07); 5.1% ash at 525 °C (TAPPI T211 om-07); 22.8% hot water soluble components (TAPPI T207 cm-08); 49.3% 1% sodium hydroxide soluble components (TAPPI T212 om-07).

Pulping and experimental design

Pulping experiments were performed in a stainless steel laboratory rotating digester, electrically heated. Each experiment involved an amount of 400 g of raw materials (o.d. mass). The optimization study of corn stalk pulping included the following steps: generation of the experimental design, performing the experiments and analysis of the obtained pulps, generation of the correlation equation, sensitivity analysis and selection of optimal parameter values according to the desired results. Stat-Ease Design Expert® (Software Version 10) was used for generation of the experimental design, data processing and mathematical model evaluation. A three-level factorial, central composite face-centered design and response surface modeling were chosen as methods of optimization.

The considered independent variables were as follows: X_1 – active alkali charge (variation interval: 12-16% NaOH on o.d. raw material); X_2 – pulping temperature (120-160 °C) and X_3 – pulping time (30-90 minutes). The independent variables were normalized according to Equation 1:

$$X_n = 2\frac{(X - X_m)}{(X_{max} - X_{min})} \tag{1}$$

where X is the absolute (natural) experimental value of the variable concerned; X_m is the mean of the extreme values of X, while $X_{\max}$ and $X_{\min}$ are its maximum and minimum value, respectively.

In all the experiments, the solid to liquid ratio of 1:9 and the time of heating to cooking temperature (30 minutes) were kept constant. The obtained pulp was washed and disintegrated and then screened using a vibratory screen with 0.25 mm slots. Pulp yield was determined gravimetrically, while pulp viscosity and Kappa number were determined by standard methods (ISO 5351:2010 and ISO 302:2004, respectively). A Rapid Köthen laboratory sheet former was used for making pulp sheets (ISO 5269-2:2004). The sheets were tested with regard to tensile strength, burst strength, flat crush resistance after laboratory fluting – CMT and short span compression strength – SCT, according to ISO 1924-2:2008, ISO 2758:2014, ISO 7263:2011 and ISO 9895:2008, respectively.

The study concerned the following pulp and paper properties as dependent variables: pulp total yield – Y_{TY} (%); pulp Kappa number – Y_{KN} (cm^3 $KMnO_4$ 0.1N/g of pulp); pulp intrinsic viscosity – Y_{IV} (cm^3/g); obtained paper tensile index – Y_{TI} (Nm/g); burst index – Y_{BI} ($kPa \cdot m^2/g$); corrugated medium test index Y_{ICMT} ($N \cdot m^2/g$); short-span compression index – Y_{SCT} ($N \cdot m/g$).

The data processing software allows testing the adequacy of the model and its adjustment trough the ANOVA tables and Fischer-Snedecor distribution (Prob > F", $p < 0.05$). A second-order quadratic polynomial (Eq. 2) was preferred to express the correlation of responses as a function of the model factors and for multi-criterial optimization:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i<j} \beta_{ij} X_i X_j + \varepsilon \tag{2}$$

RESULTS AND DISCUSSION

Regression analysis

Table 1 lists the obtained experimental values at different levels of independent variables. These data were processed with the mentioned statistical software. In some cases, the insignificant model terms (not counting those required to support hierarchy) were removed. Model reduction improves the obtained models – Equations 3-9 with p-values, R^2 and adjusted R^2 in the parenthesis. By using the generated equations, the contour type plots presented in Figures 1-6 were generated.

$$Y_{TY} = -50.38\ X_1 + 0.69\ X_2 - 0.11\ X_3 + 1.67\ X_1^2 - 3.61 \cdot 10^{-3} X_2^2 - 3.18 \cdot 10^{-4}\ X_3^2 + 5.21 \cdot 10^{-3}\ X_1 X_3 + 387.99 \tag{3}$$

(p = 0.0022; $R^2 = 0.94$; Adjusted $R^2 = 0.88$)

$$Y_{KN} = -0.11X_1 - 0.34X_2 - 0.57X_3 + 0.47X_1^2 + 6.50\cdot10^{-3}X_2^2 + 1.48\cdot10^{-3}X_3^2 - 0.1\,X_1X_2 + 7.07\cdot10^{-3}X_1X_3 + 2.80\cdot\ 10^{-3}X_2X_3 + 60.45 \tag{4}$$

(p = 0.0064; $R^2 = 0.97$; Adjusted $R^2 = 0.92$)

$$Y_{IV} = -765.51X_1 + 15.55X_2 + 52.99X_3 + 34.63X_1^2 + 9.87\cdot10^{-3}X_2^2 - 0.36X_3^2 - 1.38X_1\,X_2 - 0.95X_1X_3 + 4214.05 \tag{5}$$

(p = 0.04; $R^2 = 0.89$; Adjusted $R^2 = 0.73$)

$$Y_{TI} = -89.95X_1 - 5.34X_2 + 0.76X_3 + 2.04X_1^2 + 6.94\cdot10^{-3}X_2^2 - 2.58\cdot10^{-3}X_3^2 + 0.24X_1X_2 - 0.02X_1X_3 + 1.27\cdot10^{-4}X_2X_3 + 1036.90 \tag{6}$$

(p = 0.0012; $R^2 = 0.9$; Adjusted $R^2 = 0.83$)

$$Y_{BI} = -4.11X_1 - 0.23X_2 + 0.05X_3 + 0.09X_1^2 + 2.99\cdot10^{-4}X_2^2 + 0.01X_1X_2 - 2.19\cdot10^{3}X_1X_3 - 7.74\cdot10^{-5}X_2X_3 + 46.18 \tag{7}$$

(p = 0.0075; $R^2 = 0.92$; Adjusted $R^2 = 0.82$)

$$\mathrm{Y_{ICMT}} = 0.17X_1 - 0.05X_2 + 3.35\cdot10^{-3}X_3 - 5.42\cdot10^{-3}X_1^2 + 7.70\cdot10^{-5}X_2^2 - 1.40\cdot10^{-4}X_3^2 + 9.02\cdot10^{-4}\,X_1X_2 - 1.30\cdot10^{-3}X_1X_3 + 2.14\cdot10^{-4}X_2X_3 + 3.72 \tag{8}$$

(p = 0.0253; $R^2 = 0.92$; Adjusted $R^2 = 0.78$)

$$Y_{SCT} = -24.32X_1 - 1.08X_2 - 0.53X_3 + 0.54X_1^2 + 0.07X_1X_2 + 8.67\cdot10^{-3}X_1X_3 + 2.87\cdot10^{-3}\,X_2X_3 + 289.44 \tag{9}$$

(p = 0.0101; $R^2 = 0.87$; Adjusted $R^2 = 0.74$)

Table 1

Experimental design used for the optimization study and experimental values used for modeling

Run number	X_1	X_2	X_3	Y_{PY}	Y_{KN}	Y_{IV}	Y_{TI}	Y_{BI}	Y_{ICMT}	Y_{SCT}
1	12	140	30	37.3	28.8	884	60.3	2.5	1.8	36.5
2	12	160	30	41.1	35.4	1054	53.2	2.4	1.63	30.5
3	14	140	90	34.7	26.8	948	65.0	3	1.94	33.7
4	14	140	60	31.0	25.7	886	62.0	2.6	2.12	34
5	12	140	60	49.2	27.7	1127	66.0	2.9	1.9	32.4
6	14	160	60	27.9	29.3	915	60.0	2.5	2.14	32.5
7	16	120	90	36.1	30.1	578	64.0	2.8	1.81	32.3
8	16	140	60	34.8	21.6	674	70.5	3	2.15	37.2
9	12	160	90	34.0	44.0	1049	68.3	3	1.89	33.3
10	16	160	30	30.1	21.4	747	74.0	3.3	2.1	38.4
11	14	140	30	35.3	21.4	1194	50.4	2.2	1.9	33
12	14	140	60	33.1	25.1	964	63.2	2.6	2.05	33
13	12	120	30	55.1	24.4	997	72.1	3.2	1.98	38.3
14	14	120	60	39.5	21.8	1042	65.1	2.8	2.14	33.8
15	16	140	30	36.3	21.5	1164	60.2	2.8	2.3	36.2

Effect of process variables on model responses

As can be observed from Figure 1, the active alkali charge has an important influence on pulp yield, followed by temperature and time. At constant temperature and pulping time of 140 °C and 60 minutes, respectively, the variation of alkali charge from the lowest to the highest value leads to a decrease in yield of about 13%. The effect of process parameters on Kappa number is displayed in Figure 2. Active alkali charge also influences the final value of Kappa number – by increasing the active alkali charge, at 140 °C and 60 minutes, significant drops in Kappa number occur. In the case of Kappa number, the quadratic term active alkali (Eq. 4) charge shows a significant influence, followed by time, temperature and active alkali charge terms. Interactions, such as that between active alkali charge and temperature, play an almost equal role to that of alkali charge. As seen in both Figure 3 and Equation (5), intrinsic viscosity variation seems to be also influenced by active alkali charge first and second order term. These are followed in the hierarchy of influence by temperature and time.

Observing Figures 1 to 3, we conclude that trying to reduce Kappa number by increasing either active alkali charge or temperature at low pulping time, yield and viscosity losses occur. Furthermore, at lower alkali charges and temperature, extending delignification time has a minor contrary effect on Kappa number – higher pulping time leads to little increases of Kappa number. This phenomenon is a consequence of the lignin condensation reactions, as discussed by different authors.[19,20] Yield and viscosity losses in alkaline pulping are the result of both cellulose and hemicelluloses peeling reactions. Increasing alkali charges or temperature leads to an intensification of these reactions, while prolonging pulping time at constant temperature and alkali charge also leads to yield reduction.[21]

The mechanical properties of the paper sheets obtained from corn stalk pulps are also affected by the variations of the pulping parameters in the studied intervals, but in a different manner. In the case of these properties, Equations 6-9 show that the most important influencing variables are also the alkali charge and temperature, followed by their interactions. Looking at Figures 4 and 5, the tensile index and burst index of the obtained papers seem to decrease for the first interval of alkali charge variation (12-14%) and then to increase in the second part of the interval (14-16%).

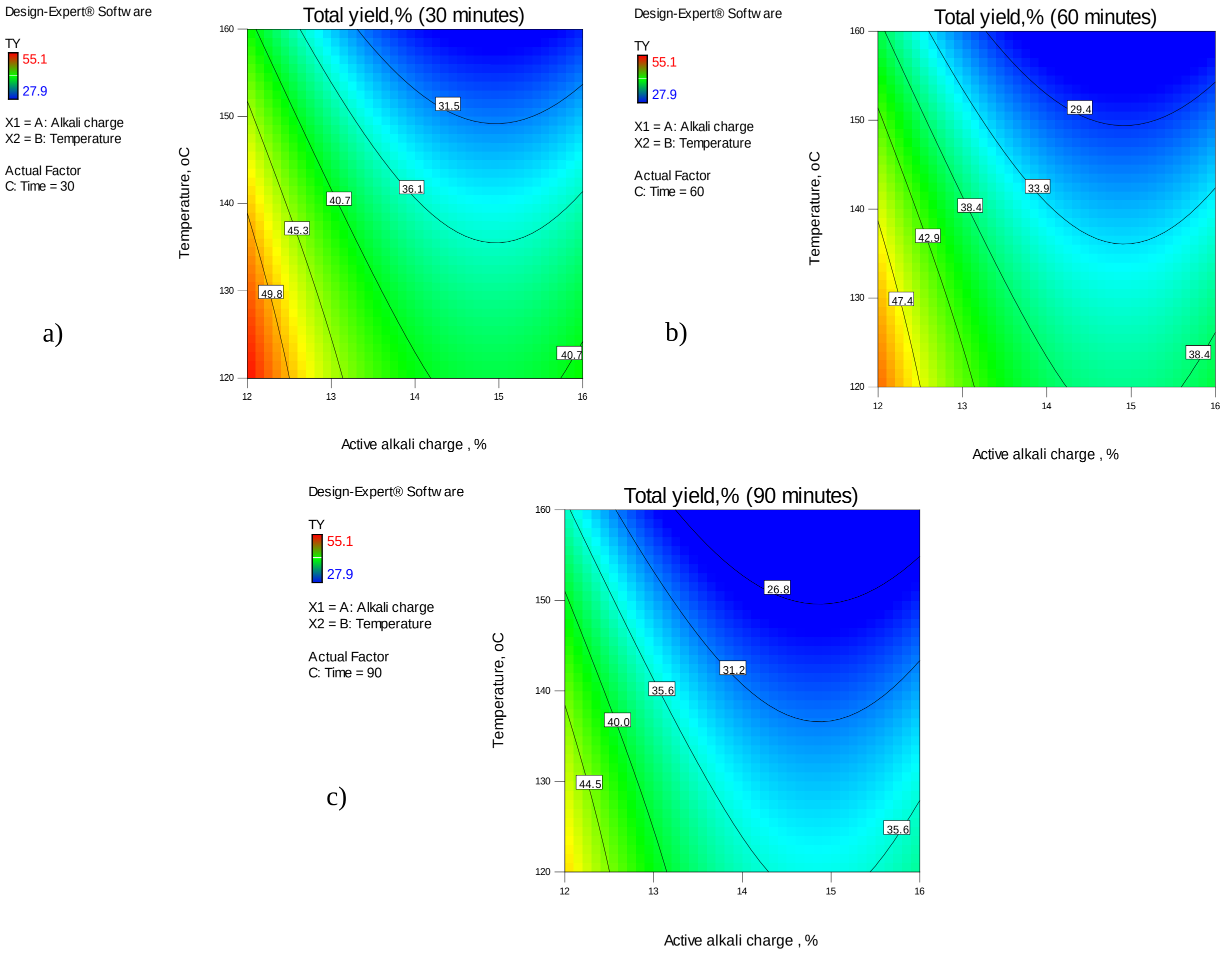

Figure 1: Dependence of total pulp yield on temperature and alkali charge at different constant pulping time values of a) 30 minutes, b) 60 minutes, and c) 90 minutes

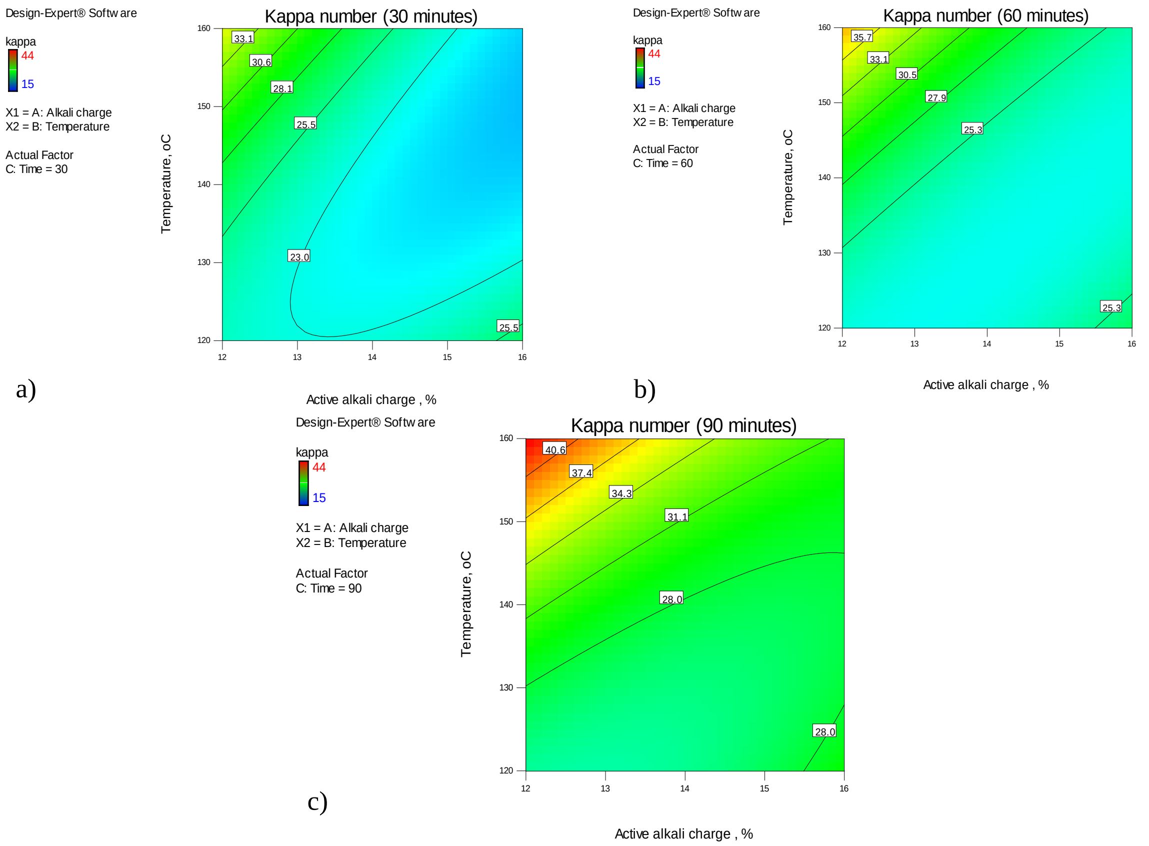

Figure 2: Final Kappa number variation of the pulp as a function of temperature and alkali charge at different constant pulping time values of a) 30 minutes, b) 60 minutes, and c) 90 minutes

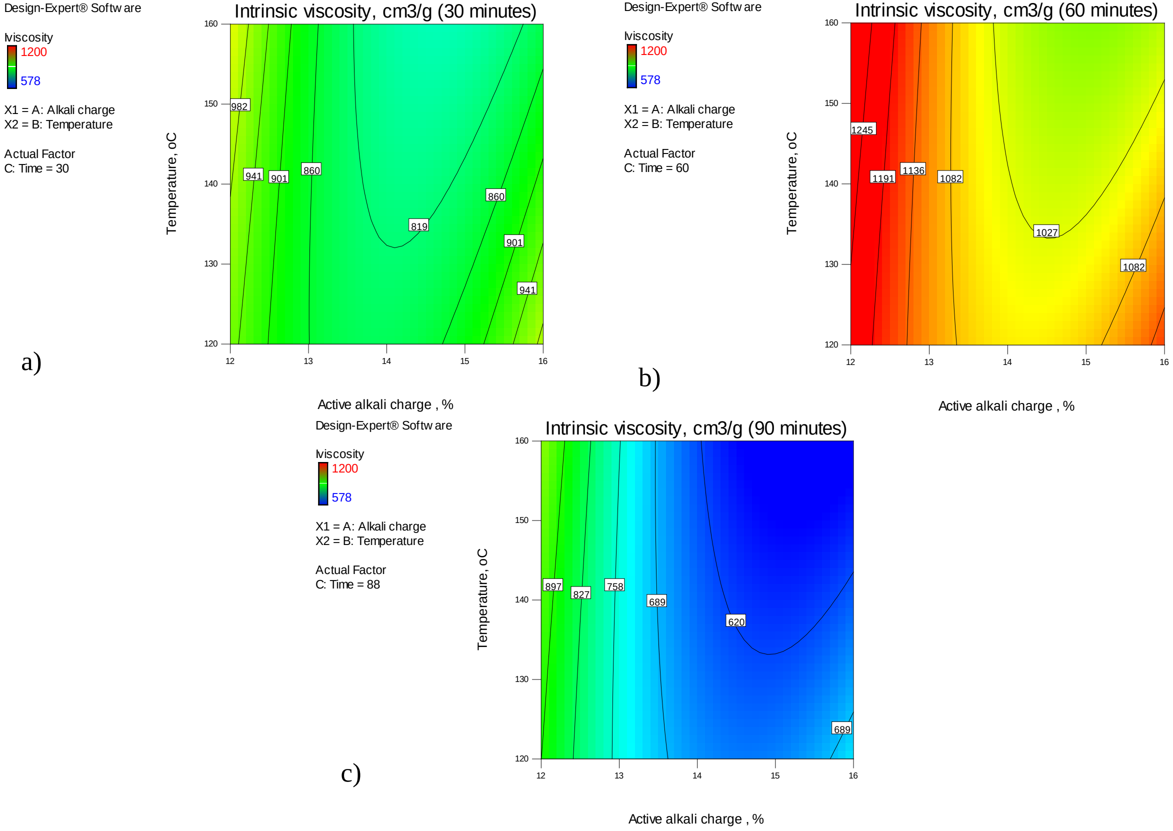

Figure 3: Influence of temperature and alkali charge on pulp intrinsic viscosity at different constant pulping time values of a) 30 minutes, b) 60 minutes, and c) 90 minutes

The CMT and SCT indexes are two important fluting and liner paper characteristics, which have been determined by reporting the absolute values of SCT and CMT to the tested paper basis weight (120 g/m^2). Similar to the case of tensile and burst indexes, CMT and SCT are mainly influenced by alkali charges and temperature. Interaction influences are small. At lower alkali charges and temperature, the increase of pulping time from 30 to 60 minutes seems to induce a positive effect, while at higher alkali charges, this effect is minor. Extending pulping time to 90 minutes leads to decreases of the CMT index (Fig. 6). As it is observable from Figure 7, in the case of SCT, extending delignification time from 30 to 60 minutes leads only to minor increases of the SCT index values at high alkali charge and temperature, while at lower alkali charges and lower temperature, extending pulping time decreases the SCT index values.

The selected statistical software permits multiple criteria optimization by allowing the user to seek for optimal parameters. The optimal parameter values and the intervals of the predicted response values are both presented in Table 2. These values fall within the predicted intervals, showing the adequacy of the model. Thus, in the first scenario, the criteria were optimized in order to obtain a pulp with the maximum yield and the best paper strength, while maintaining low alkali consumption and lower temperature. In terms of costs, this should be the most advantageous situation for producing acceptable quality pulps. In the secondary scenario, no restrictions were imposed on pulping parameters to determine which parameters would lead to maximization of strength properties. In this case, the model showed as optimum the alkali charge of 16% and pulping time of 60 minutes at 160 °C to produce a pulp with low Kappa number, better strength than in the first situation, but with significant losses in yield and viscosity, which would not be economically acceptable.

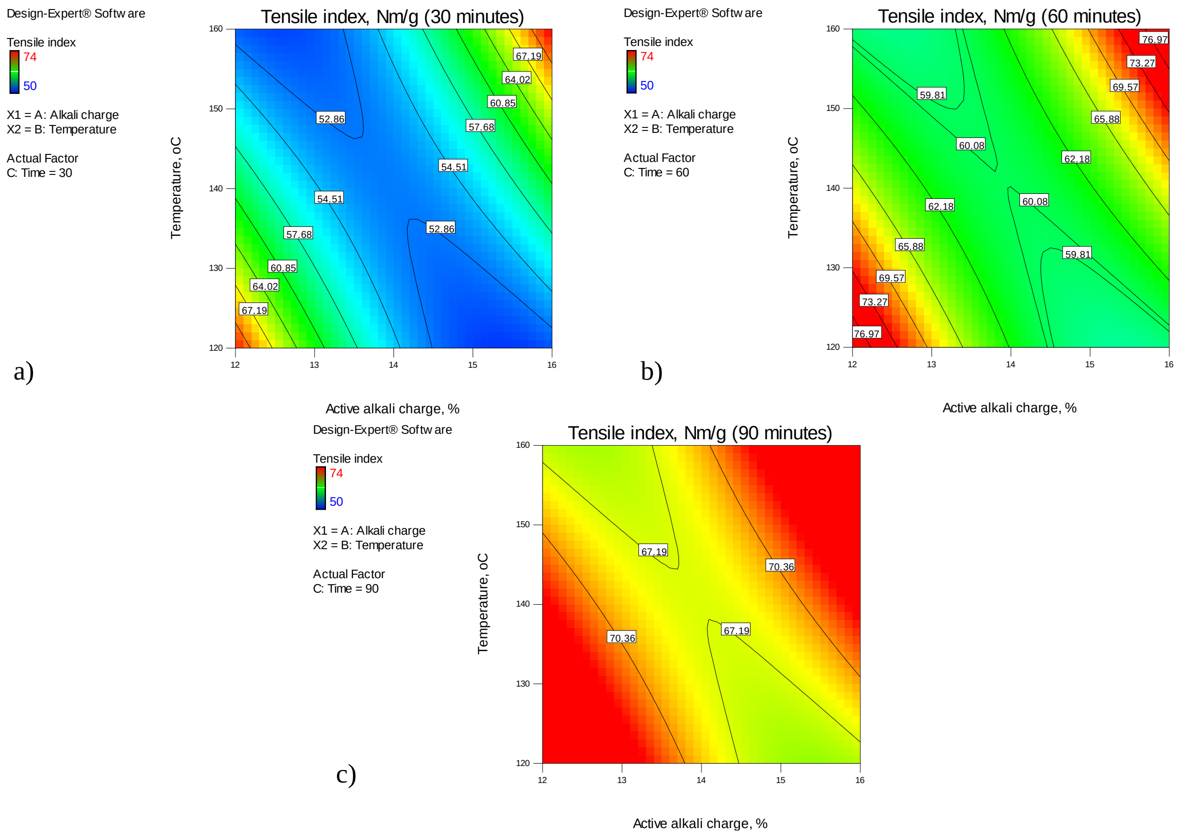

Figure 4: Effect of temperature and alkali charge on tensile strength of the *Zea mays* pulp paper sheets at constant pulping time values a) 30 minutes b) 60 minutes c) 90 minutes

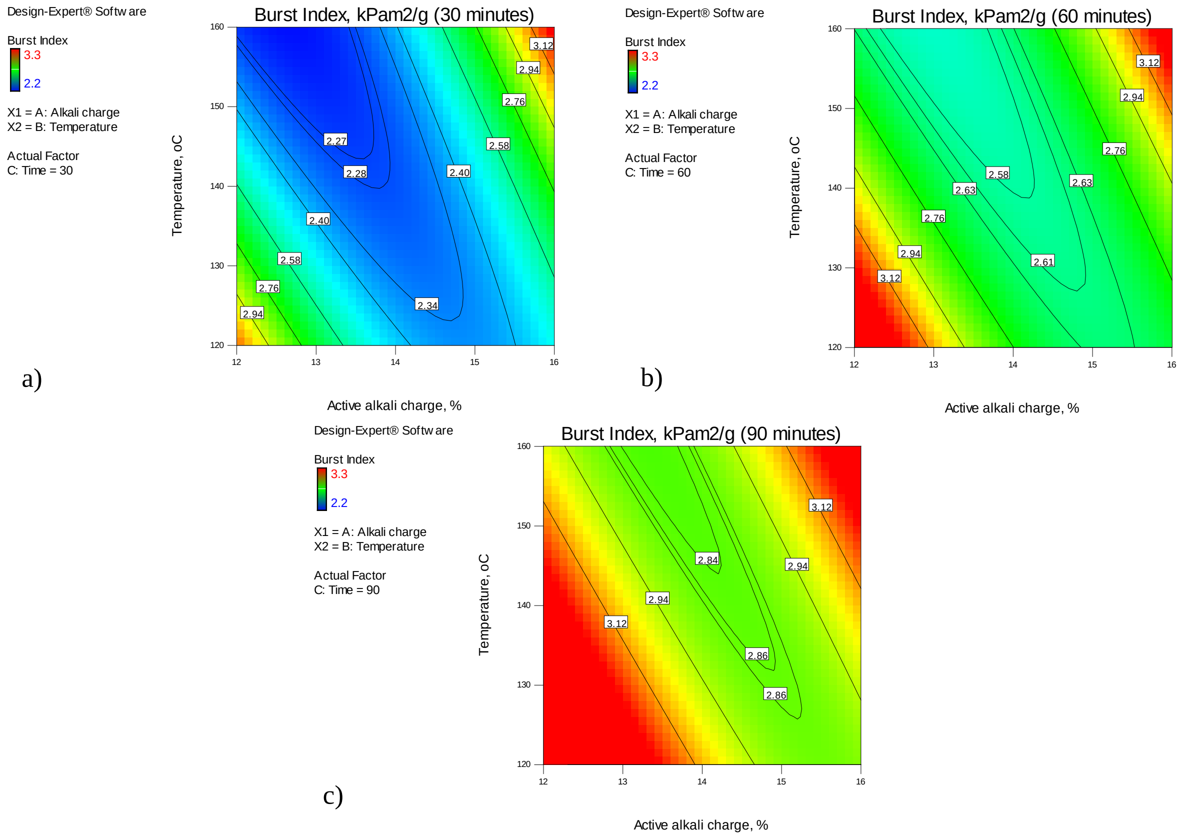

Figure 5: Burst strength variation as a function of temperature and alkali charge at constant pulping time values of a) 30 minutes, b) 60 minutes, and c) 90 minutes

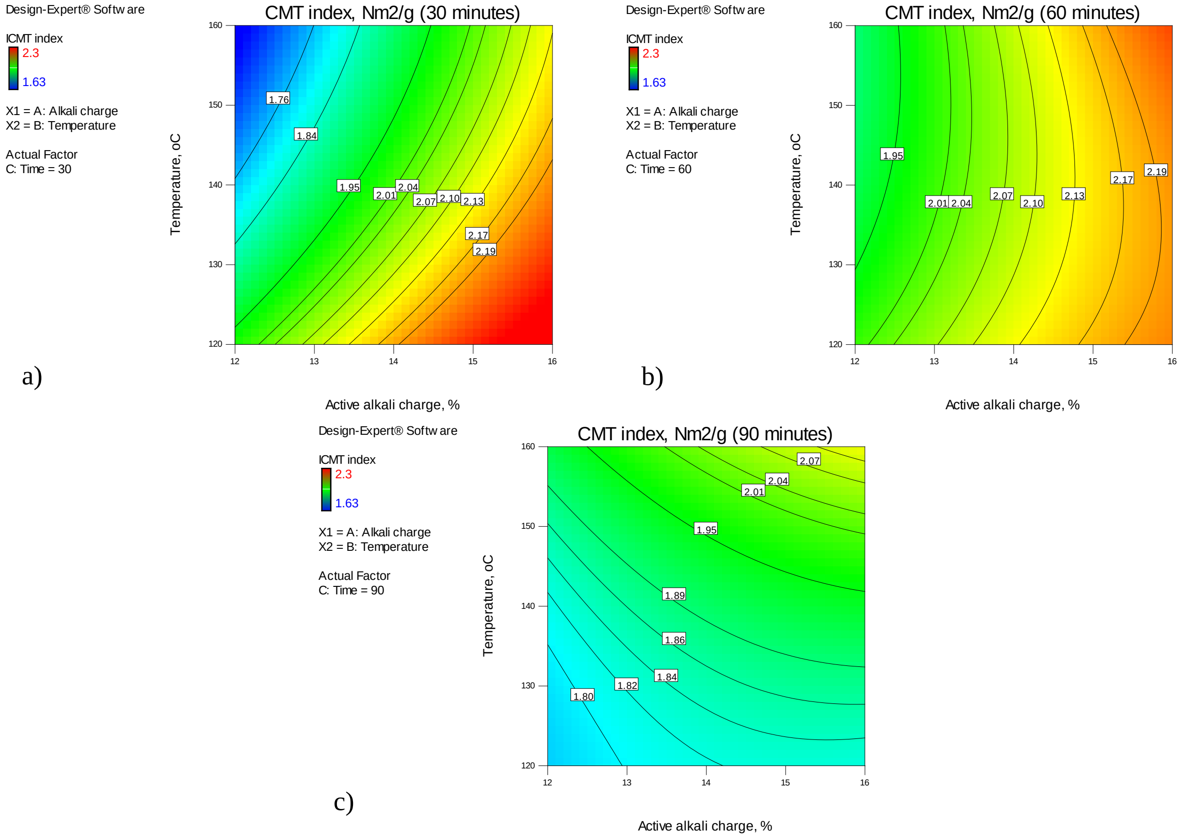

Figure 6: Effect of temperature and alkali charge on corrugated medium resistance of corn stalk paper sheets at constant pulping time values of a) 30 minutes, b) 60 minutes, and c) 90 minutes

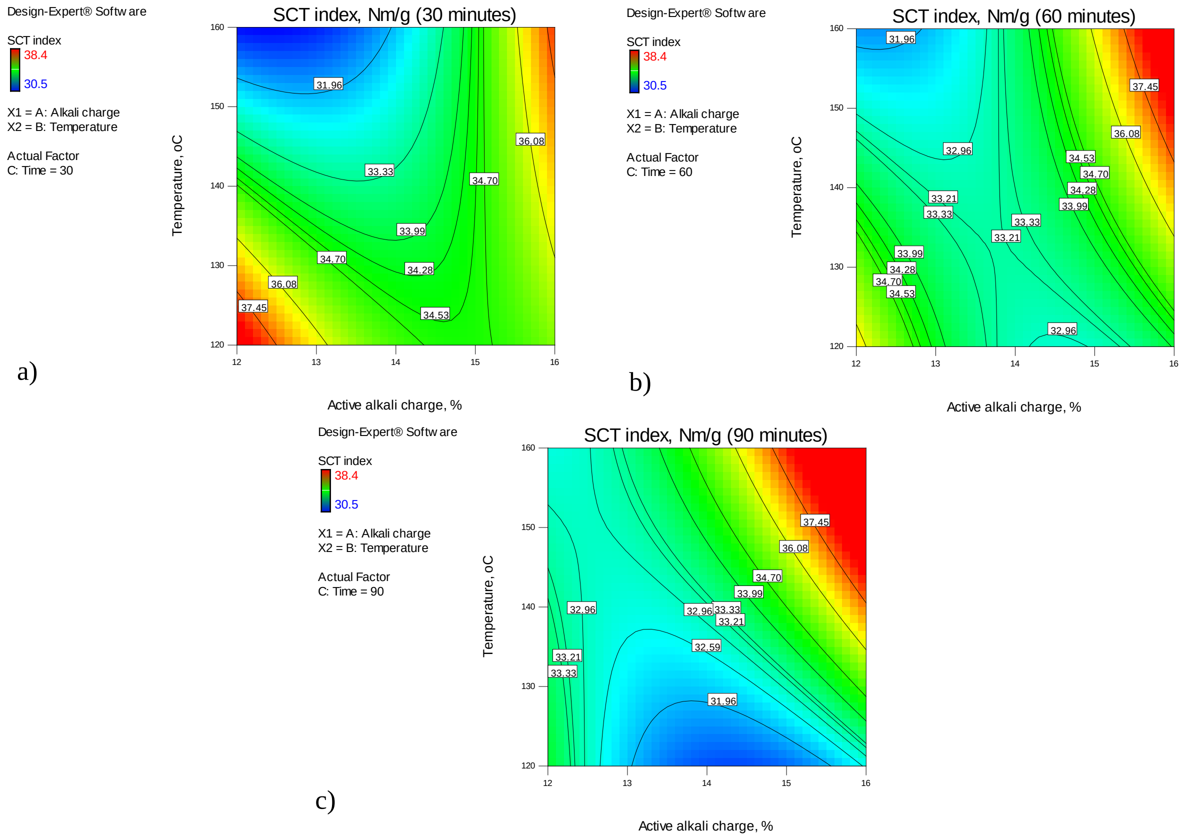

Figure 7: Dependence of short-span compression strength on temperature and alkali charge of corn stalk paper sheets at constant pulping time values of a) 30 minutes, b) 60 minutes, and c) 90 minutes

Table 2
Optimal pulping parameters, interval of predicted results and experimentally determined values

Pulping process parameters	Model response	Predicted value confidence interval (CI)		Determined experimental value
		95% CI low	95% high	
Alkali charge – 12% Temperature – 120 °C Pulping time – 40 minutes	Total yield, %	48.7	58.6	51.2
	Kappa number	23.8	36.5	31.5
	Intrinsic viscosity, cm^3/g	1002	1588	1070
	Tensile index, Nm/g	69.4	82.1	75.2
	Burst index, $kPa\cdot m^2/g$	3.03	3.58	3.1
	CMT_0 index, N·m2/g	1.83	2.20	2.0
	SCT index, N·m/g	35.7	40.4	33.5
Alkali charge – 16% Temperature – 160 °C Pulping time – 59 minutes	Total yield, %	21.30	32.69	32
	Kappa number	18.51	32.62	19.4
	Intrinsic viscosity, cm^3/g	636.36	1500.41	850
	Tensile index, Nm/g	71.05	90.14	74.5
	Burst index, $kPa\cdot m^2/g$	3.01	3.82	3.45
	CMT index, $N\cdot m^2/g$	1.97	2.53	2.5
	SCT index, N·m/g	36.26	43.42	36.2

CONCLUSION

In the present work, corn stalks were successfully used as raw material for soda pulping. By using a central composite face-centered factorial design and response surface methodology, significant statistical models were obtained. The established model equations revealed the dependence between the studied factors (active alkali charge, temperature and pulping time) and the selected responses (pulp total yield, Kappa number, intrinsic viscosity and paper properties, such as tensile strength, burst strength, flat crush resistance after laboratory fluting – CMT, and short span compression strength – SCT).

These models lead to the conclusion that the studied responses are influenced by the process factors in the following order of decreasing importance: alkali charge, temperature and, finally, pulping time. The interactions between the considered parameters were also demonstrated to have different impacts on the responses. Upon the increase of alkali charge, temperature or pulping time in the studied intervals, the yield and viscosity were negatively affected. The variations of pulping parameters also led to modifications in the properties of the obtained paper sheets. Upon delignification, these properties seemed to improve, but the yield and viscosity drops became critical.

Therefore, in order to produce pulps with high yield, moderate to low settings of the studied parameters are recommended. Such conditions (*i.e.* 12% NaOH alkali charge, 30 minutes of pulping at 120 °C) would lead to yields above 50% and sufficient paper strengths. Finally, we analyzed the optimal pulping conditions in two different scenarios and concluded that the scenario with low alkali and low temperature cooking would be more economically acceptable.

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