RESPONSE SURFACE MODELING OF WHEAT STRAW PULPING USING SODIUM CARBONATE AND SODIUM HYDROXIDE MIXTURES

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The paper presents the results of experimental trials regarding pulping of wheat straw by using mixtures of sodium carbonate and sodium hydroxide as pulping reagents. Although sodium carbonate has been proved as potential pulping reagent for obtaining higher yield pulps from wheat straw, the presence of sodium hydroxide improves delignification. Response surface methodology with Central Composite Design has been used as a method for study of process parameters: the temperature, alkali charge and Na_2CO_3/NaOH mass ratio were chosen as independent variables. The studied pulp characteristics were: yield, kappa number, tensile index, burst index, corrugating medium flat crush resistance, short span compression resistance. The influence of each variable on pulp characteristics as well as their interactions has been established. The results of the study and the obtained quadratic equations model equations may provide the basis for selecting the optimal conditions of pulping according to the desired pulp characteristics.

Keywords: straw, pulping, yield, paper strength

INTRODUCTION

The paper-based products account about 34% of the packaging market and represent around 50% of the total European paper production. This share is about to increase in the future due to the change in the consumers preferences towards more environmentally friendly options. The increased demand on paper packaging products at world scale puts up new pressures on pulp and paper industry. According to the Confederation of European Paper Industries – CEPI, about 71.7% of used paper products are recovered in Europe (CEPI, 2016). A major part of paper products cannot be recovered and reused because of severe degradation, destruction during use phase (*i.e.* incineration), or due to their excessive contamination. Other limits of paper recycling include fiber strength loss during paper use and recycling. An important issue regarding paper recycling rate increase is represented by the presence of hazardous contaminants with a wide range of sources including: inks, solvents, additives and their degradation products.[1] These contaminants lead to increased concerns regarding use of recycled paper products in food packaging in the last years.[2,3] A recent study indicates the higher content of substances such as phthalates and phenols of recycled paper products comparative with virgin fiber ones.[4]

Due to these shortcomings, virgin fibers are needed in the paper industry either to replenish the papermaking potential of the recycled fibers but also for the manufacturing of high quality paper products. The virgin fibers share in the fibrous raw materials needed for paper production represent about 44.0%.[5] Most of the virgin fibers are obtained by wood pulping, which implies a series of environmental impacts such as deforestation, resource and energy consumption and pollution.

In theory, many vascular plants may be used as raw material for pulping and papermaking. Attractiveness of non-wood fiber sources as raw materials in pulping resides in their lower lignin content and their availability having in mind their shorter growing cycle.[6-8] Most of these resources are abundantly available as waste from cereals or technical crops harvesting in various regions of the world and either are not reused or are of partially use in other agricultural activities. At present, much of these wastes are returned into soil or incinerated with environmental implications. Among these types of raw materials, wheat straw seems to be the most abundant due to the extended cultivation of wheat. Reports of Romanian Minister of Agriculture and Rural Development show that in the year 2015 wheat was cultivated on 2043 thousands of ha, by thus being the second most cultivated cereal grain after maize.[9] In case of wheat cultures for 1 tonne unit of wheat about 0.6 to 1 tonnes of straws is generated.[10]

There are several factors which prevent the use of straw as raw materials for pulping. These factors include: transportation, storage, processing and chemical recovery. These are caused by the low density of straw, their high content of hemicelluloses and silica minerals.[11,12] Moreover, the selectivity of conventional Kraft pulping is lower than in wood processing, by thus economic efficiency is reduced. Therefore milder reagent pulping processes such as: soda, soda-AQ,[13] organosolv,[14] aqueous ammonia mixed with caustic potash,[15] sodium carbonate[16] are recommended. One literature reported advantage of non-wood pulp fiber, in particular those obtained from wheat straw, is the improvement of paper resistance to strength loss during recycling.[17]

Regarding sodium carbonate usage, in a previous paper[16] we have demonstrated its potential usage as single pulping reagent to produce high yield pulps with strengths suitable for fluting paper. The experimental work presented hereby describes the use of sodium carbonate/sodium hydroxide mixtures as reagents for wheat straw pulping. The aim of the study is to investigate the process factors influence on the pulp characteristics. Temperature, alkali charge and sodium carbonate/sodium hydroxide ratio were chosen as independent variables and their influence on pulp characteristics as well as their interactions has been established.

EXPERIMENTAL

Raw materials

Wheat straws – *Triticum aestivum L.*, were provided by a Romanian farm. The previously determined chemical composition of the straws includes: 43.1% cellulose;[18] 74.4% holocellulose;[19] 27.7% pentosans (TAPPI T 223 cm-10; 17.5% lignin (TAPPI T 222 om-20; 5.5% extractives (TAPPI T 204 om-97 5.3% ash (TAPPI T 211 om-12).[16] These straws were pre-conditioned by drying up to 8-10% moisture, which was determined according to TAPPI T 664 om-07 standard method.

Pulping of straw and pulp characterization

Pulping trials aiming at obtaining papermaking pulps by alkaline pulping using sodium hydroxide and sodium carbonate mixtures as alkali sources were performed. The pulping trials were performed in a 10 L stainless steel laboratory rotating batch digester equipped with electric heating and automatic temperature control. Amounts of 300 g (o.d. mass) of straw and a liquor to solid ratio of 5:1 were used in regular cooking experiment. White liquors were prepared in the laboratory by separately dissolving analytical grade sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3), in tap water. The heating time was 30 minutes, while cooking time was established at 60 minutes.

After cooking, the reactor was degassed and cooled to an appropriate temperature to allow removal of pulp for disintegration, washing and squeezing for water removal up to a consistency of about 30%. Furthermore, yield (gravimetric method) and kappa number (ISO 302:2004) were determined. All specimens were analyzed in triplicates. All chemicals needed for analysis were analytical grade and purchased from Aldrich.

Paper sheets formation and characterization

The obtained pulp samples were used for laboratory sheet forming after 750 rpm beating on Jokro mill according to SR EN 25264-3:1997 procedure. Hand sheets were obtained according to ISO 5269-2:2004 on a Rapid Köthen laboratory sheet former. The following mechanical properties were determined: tensile strength (ISO 1924:2008); burst strength (ISO 2758:2001); corrugating medium flat crush resistance (also called Concora test CMT-ISO 7263:2011) and SCT – short span compression resistance (ISO 9895:2008).

Experimental design and mathematical modeling

Response surface methodology was the empirical statistical technique employed for the study the interactions between factors and possible optimization of operating parameters. A central composite factorial design (CCF) was used. The independent variables were: pulping temperature (X_1 = 150 °C, 160 °C and 170 °C) alkali charge, as NaOH units (X_2 = 16%, 18% and 20%) and the Na_2CO_3/NaOH mass ratio (X_3 = 1, 5 and 9). Each variable was normalized by using equation 2. The independent variables and their normalized values are presented in Table 1. The star point α value was 1.215. We aimed at establishing quadratic models – Equation 1, by using the experimental data; ANOVA was used to test the significance of the obtained models. The experimental design and data processing were performed with the help of the Modde 11 software. The partial least square fitting method was used to validate experimental data and to generate a mathematical equation which could be used for optimization or for forecast of pulping results. The graphical representations of the variations of dependent variables were obtained by Matlab processing of model equations:

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

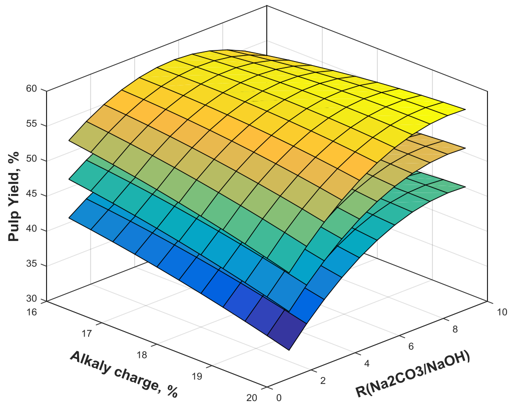
$$X_n = 2 \frac{(X - X_m)}{(X_{max} - X_{min})} \quad (2)$$

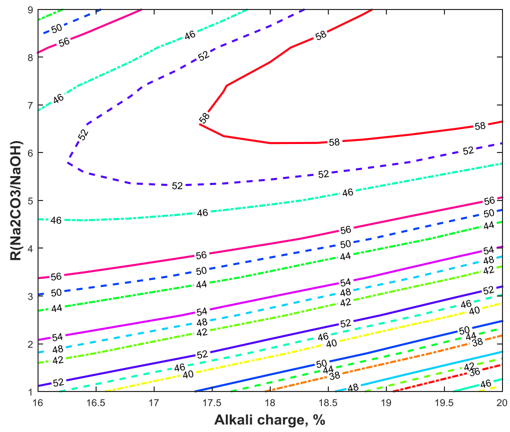
where X is the absolute (natural) experimental value of the variable concerned; X_m is the mean of the extreme values of X while X_{max} and X_{min} are its maximum and minimum value, respectively.

RESULTS AND DISCUSSION

Experimental results obtained for the pulping trials of wheat straw with mixtures of sodium carbonate and sodium hydroxide are presented in Table 1. The obtained pulp yield values range from 41.84% to 60%, while the Kappa number of pulps ranges from 35 to 70.4. The obtained yield values were in agreement with other works.[16,20,21] Kappa number of pulps are correlated with yield in general, with higher values than those obtained in soda pulping but lower than those obtained in trials with using sodium carbonate alone as pulping reagent. This can be explained by taking into account that the increases of sodium hydroxide concentration (lower R values) and temperature promote delignification but also increase the polysaccharide degradation leading to yield loses. Both yield and Kappa number of pulps are influenced by the process variables and depending on the severity of the treatment lower or higher values may be obtained. Strength properties of pulps obtained by Na_2CO_3/NaOH pulping also depend on the pulping conditions. Trials characterized by higher severity (*i.e.* high temperature, high alkali charge and low values Na_2CO_3/NaOH ratios) leaded to lower values of strength properties. The obtained pulps strength properties values are comparable with those mentioned by other studies available in literature.[20,22]

Response surface methodology may be used to explore the contribution of a given set of independent variables (process parameters or system inputs) on a set of dependent ones (process results or system outputs). Table 1 displays the experimental values that were used for the mathematical modeling. Figures 1-6 display the response surfaces and contour plot obtained by using model equations and by maintaining temperature at different constant values.





a) b)

Figure 1: Response surfaces (a), (170°C -lowest; 160°C - middle; 150°C- upper) and contour plot (b) of pulp yield as function of alkali charge and R (150°C - continuous line; 160°C -dotted line; 170°C- dash-dotted line)

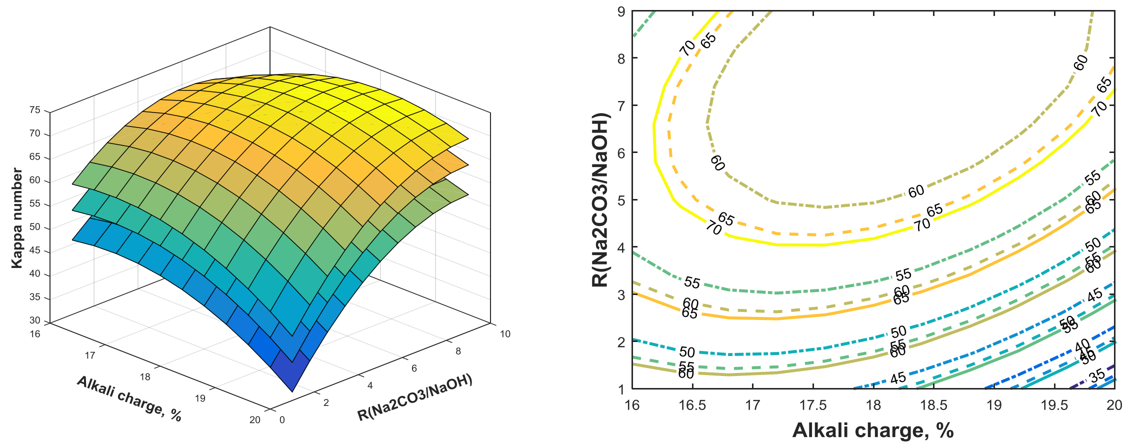
Table 1
Experimental values used in the response surface methodology study

Run	Normalized variable values X_1, X_2, X_3	Kappa number	Yield (%)	Tensile index (Nm/g)	Burst index ($kPam^2/g$)	CMT_0I (Nm^2/g)	SCTI (Nm/kg)
1	1,1,1	64.2	60.03	44.53	2.12	0.91	19.10
2	1,1,-1	61.5	46.48	24.12	1.91	1.07	23.30
3	1,-1,-1	55.5	47.60	49.17	2.41	1.64	25.90
4	-1,-1, 1	59.0	51.65	40.6	2.00	1.57	25.70
5	1,1,-1	35.5	44.58	36.95	2.51	1.27	25.00
6	-1,1,-1	35.9	51.16	39.96	2.51	1.71	32.20
7	1,-1,-1	41.8	41.91	50.26	2.33	1.56	25.90
8	-1,-1,-1	49.30	50.84	36.50	2.19	1.62	27.20
9	α,0,0	59.07	45.05	51.24	2.55	1.73	26.50
10	-α, 0,0	66.65	54.18	39.52	2.25	1.66	25.10
11	0,α,0	63.94	52.19	37.29	2.29	1.27	25.00
12	0,-α,0	69.45	50.33	50.64	2.62	1.89	33.10
13	0,0,α	71.40	50.92	33.99	2.36	1.15	21.20
14	0,0,-α	63.90	41.84	33.60	2.56	1.06	21.40
15	0,0,0	59.40	51.50	47.98	2.47	1.46	28.50
16	0,0,0	70.40	53.30	46.20	2.45	1.49	26.50
17*	0, 0.5, 0.1	65.15 (66.1)	54.63 (55.7)	46.66 (48.06)	2.58 (2.45)	1.67 (1.55)	22.8 (23.4)
18*	0, 1, 0.17	61.9 (63.99)	46.92 (47.5)	43.91 (46.66)	2.46 (2.40)	1.37 (1.44)	24.5 (25.35)

*trials 17 and 18 were use used as control experiments, the observed values are presented together with the predicted values in the brackets

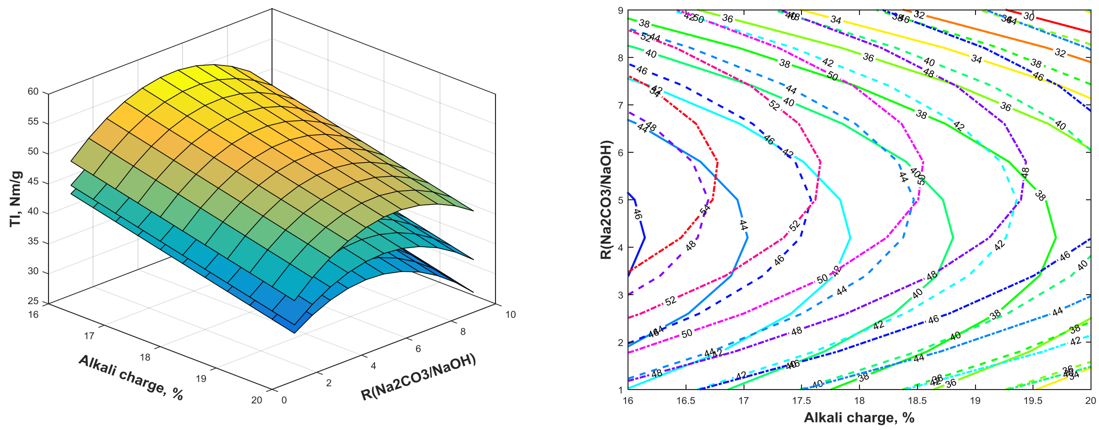
Table 2
Equations obtained for the model with coefficients scaled and centered

Dependent variable	Equation	Regression parameters	F	$F_{tab.}$ ($p<0.05$)
Pulp yield	$Y_{PY} = -0.34083X_2^2 - 2.4934X_3^2 - 3.9814X_1 - 0.3196X_2 - 3.5279X_3 + 1.3046X_2X_3 + 51.1783$	R^2=0.75; Q^2=0.52	6.15	2.99
Kappa number	$Y_{KN} = -5.7981X_1^2 - 4.039X_2^2 - 4.7062X_3^2 - 3.3334X_1 - 3.2890X_2 + 8.4667X_3 + +3.4553X_2X_3 + 71.006$	R^2=0.87; Q^2=0.87	10.44	3.01
Tensile index	$Y_{TI} = 0.8807X_1^2 - 4.81094X_3^2 + 4.2237X_1 - 3.6930X_2 - 0.3744X_3 + 1.6698X_1X_3 + 45.0939$	R^2=0.83; Q^2=0.52	7.14	3.37
Burst index	$Y_{BI} = -0.0851X_1^2 - 0.0968X_1 + 0.0152X_2 - 0.1482X_3 - 0.1123X_2X_3 + 2.4819$	R^2=0.72; Q^2=0.45	6.69	3.02
CMT_0 index	$Y_{CMT_0I} = 0.0877X_1^2 - 0.1815X_3^2 - 0.0550X_1X_2 - 0.0915X_2X_3 - 0.0423X_1 - 0.1684X_2 - 0.0744X_3 + 1.5265$	R^2=0.89; Q^2=0.6	10.1	3.29
SCT Index	$Y_{SCTI} = 1.0918X_2^2 - 1.122X_3^2 - 0.9557X_1X_2 - 1.1246X_2X_3 - 0.9395X_1 - 1.231X_2 - 1.9343X_2 + 25.7716$	R^2=0.77; Q^2=0.5	4.25	3.29



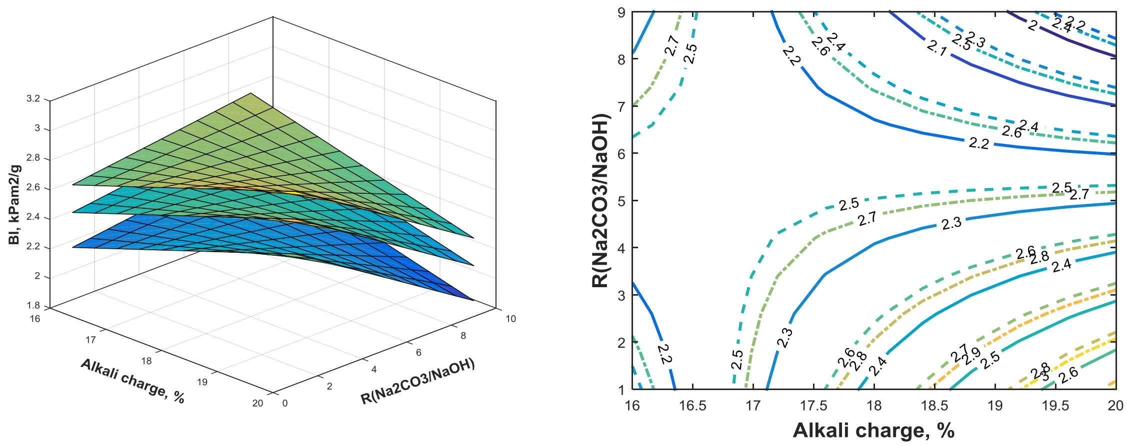
a) b)

Figure 2: Response surfaces (a) ,170°C -lowest; 160°C - middle; 150°C- upper) and contour plot (b) of Kappa number as function of alkali charge and R (150°C - continuous line; 160°C -dotted line; 170°C- dash-dotted line)



a) b)

Figure 3: Response surfaces (a) 150°C -lowest; 160°C - middle; 170°C- upper) and contour plot (b) of tensile index as function of alkali charge and R (150°C - continuous line; 160°C -dotted line; 170°C- dash-dotted line)



a) b)

Figure 4: Response surfaces (a) 150°C -lowest; 160°C - middle; 170°C- upper) and contour plot (b) of burst index as function of alkali charge and R (150°C - continuous line; 160°C -dotted line; 170°C- dash-dotted line)

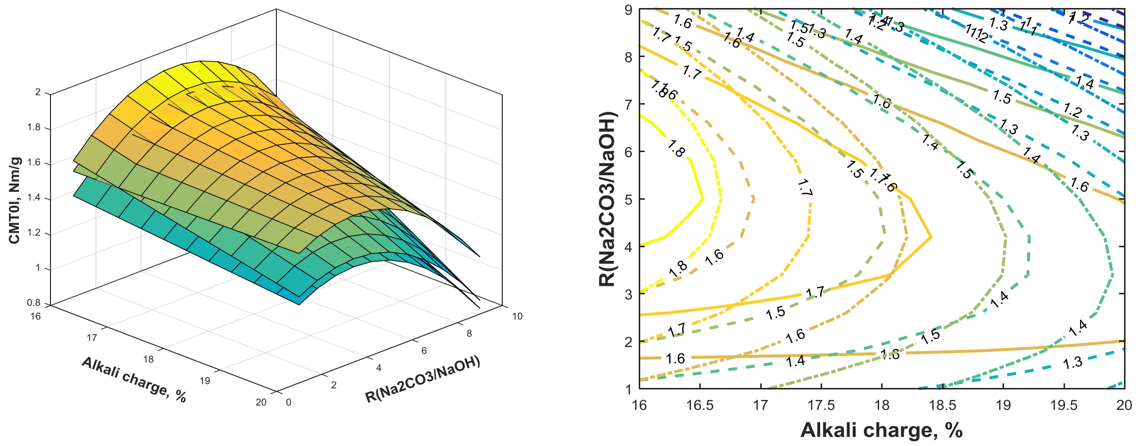
The coefficient of determination, R^2, designates the fitness between practical results and mathematical model. The model predictive power is reflected by parameter Q^2.[23] The Modde software computes the R^2 and Q^2 values (displayed in Table 2) and performs the analysis of variance (ANOVA). These coefficients value reflect the validation of prediction. Q^2 is the fraction of the variation of the response predicted by the model according to cross validation and expressed in the same units as R^2. These parameters are used together as diagnostic tool for the model. Values close to 1 are desirable, because they indicate an excellent model. In practice, an equal or higher value than 0.5 of Q^2 designates a good model.[23] The significance of the model equation for pulp yield, kappa number and mechanical strength properties at 95% confidence interval were checked by the F test which is shown in Table 2 comparatively with tabulated F values for probability $p<0.05$ and corresponding degrees of freedom. The variable importance in the projection values (VIP), computed by Modde, reflect the importance of terms in the model and the correlation of the terms to all the responses. Equations presented in Table 2 contain the significant model terms with respect to significant VIP score values. Analysis of the data from Figures 1-6 offer information regarding the influence of independent variables on the pulp characteristics.

Figure 1a displays the response surfaces of yield as function of alkali charge and pulping liquor components mass ratio for different values of temperature. The same may be observed in Figure 1b as contour plots. As a general rule, the response surfaces and contour plots have been obtained by using the proposed model equations 3-8. A general affirmation is that each pulp characteristic is influenced by a particular set of factors, as is revealed in Figure 7, which displays the variable importance in the projection (VIP).

As it may be observed from Figure 1 (a and b) the pulp yield depends both on the alkali charge which if increased, leads to lower yields, as well as on the ratio of sodium carbonate/sodium hydroxide ratio which if decrease leads to lowering of pulp yields. Pulp yield is inversely varying with the temperature. At constant alkali charge and temperature and with respect to Na_2CO_3/NaOH ratio values, two main variation domains are present – each of them converge to a Na_2CO_3/NaOH ratio around 5 at which maximum yield values are noticed. The variation of pulp yield (Y_{YIELD}) is strongly influenced by temperature, Na_2CO_3/NaOH mass ratio and interaction of temperature with Na_2CO_3/NaOH ratio. Moderate to low temperature, low alkali charge and high Na_2CO_3/NaOH ratio are needed for obtaining a satisfying good values pulp yield.

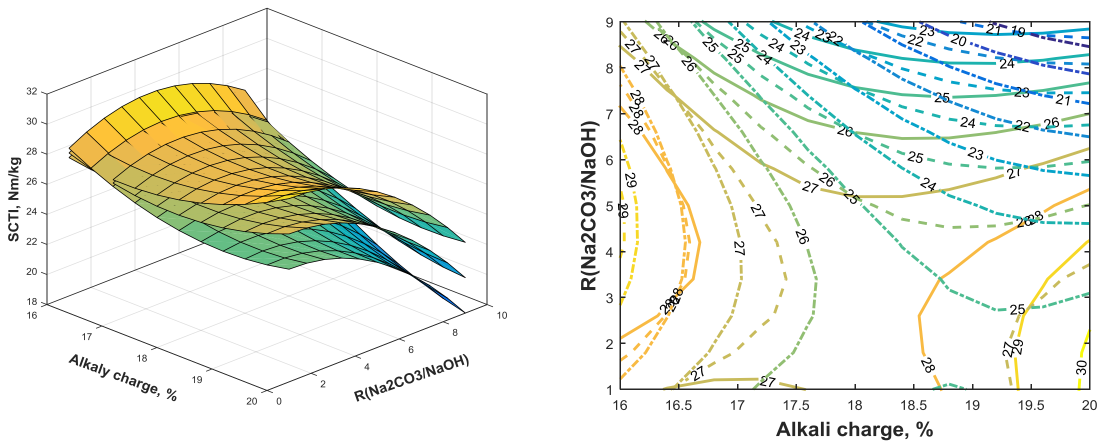
The response surface and contour plot represented in Figure 2 (a and b) displays the variation of Kappa number with respect to alkali charge and Na_2CO_3/NaOH ratio. At constant temperature and lower alkali charges, high kappa numbers are obtained, while maintaining a constant alkali charge and decreasing Na_2CO_3/NaOH ratio, the pulps' kappa numbers decrease. Increase of temperature also leads to lower values of the kappa number of the obtained pulps. Similar to yield variations, at constant alkali charge and temperature and with respect to Na_2CO_3/NaOH ratio values two main variation domains occur – each of them converge to a Na_2CO_3/NaOH ratio around 5 at which maximum Kappa number values may be observed. As reflected by Figure 7, the pulp Kappa number, Y_{KN} is significantly influenced by terms such as temperature and squared temperature, Na_2CO_3/NaOH mass ratio (and squared) and alkali charge as well as by interactions of these terms. The variations of yield and kappa number are explainable by considering the effect of the contribution of all variables to lignin removal but also to the possible polysaccharides degradation.

As regarding pulp strength properties, they are also influenced by the chosen variables but in different manners. The tensile index (TI) response surface and contour plot are displayed in Figures 3a and 3b. The TI of the obtained pulps hits a maximum for lower alkali charges and carbonate/hydroxide ratios. The temperature increase leads to increases of tensile index, but optimal values may be identified at moderate temperatures, moderate alkali charges and Na_2CO_3/NaOH ratio values. These aspects are explainable by the fact that these conditions are sufficient for lignin removal and fiber liberation. The presence of lignin in high yield pulps hinders the formation of inter-fiber bonding, which play a particular role in the development of mechanical strength.[24] On the other hand at low alkali charges, Na_2CO_3/NaOH ratios and temperature, the pulp lignin content is high and prevents the formation of inter-fibril linkages in paper structures. Figure 7 shows that Y_{TI} is strongly influenced by first order terms of temperature and alkali charge, second order term of Na_2CO_3/NaOH ratio and to a minor extent by interactions between alkali charge and temperature, second order term of alkali charge, temperature, and by first order terms of Na_2CO_3/NaOH ratio.



a) b)

Figure 5: Response surfaces (a) 150°C -lowest; 160°C - middle; 170°C- upper) and contour plot (b) of corrugating medium test index as function of alkali charge and R (150°C - continuous line; 160°C -dotted line; 170°C- dash-dotted line)



a) b)

Figure 6: Response surfaces (a) 150°C -lowest; 160°C - middle; 170°C- upper) and contour plot (b) of short span compression test index as function of alkali charge and R (150°C - continuous line; 160°C -dotted line; 170°C- dash-dotted line)

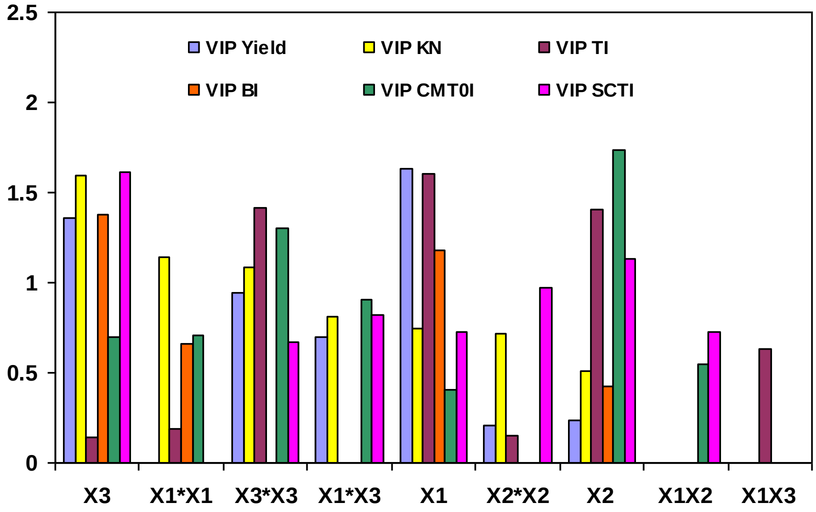


Figure 7: Plot of variables importance projection showing the contributions of the independent variables

Table 3.
Operational independent variables for optimal values of dependent variables

Response	Optimal values	Independent variable values		
		Temperature (°C)	Alkali charge (%)	Na_2CO_3/NaOH mass ratio
Yield (%)	58.8	150	20	7.8
Kappa number	31.4	170	20	1
Kappa number & Yield	40.9&50.2	150	20	1.1
Tensile index	55.7	169.9	16	5.6
Burst index	2.82	165	20	1
CMT_0 index	1.9	170	16	5.4
SCT index	30.2	150	20	1

Response surfaces and contour plot of burst index (BI) are displayed in Figures 4a and 4b. The figures show higher values of BI for higher pulping temperatures and moderate to high alkali charges and low Na_2CO_3/NaOH ratio. Burst index is strongly influenced by temperature terms (first and second order), Na_2CO_3/NaOH ratio (first order) and to a less extent by alkali charge (first order term) and alkali charge – Na_2CO_3/NaOH ratio interaction.

The SCT index and CMT_0 index are two important fluting paper characteristics which have been determined by reporting the absolute values of SCT and CMT_0 to the tested paper basis weight value (120 g/m^2). SCT index's dependence on process variables is complex. SCT is positively influenced at lower pulping temperature (*i.e.* 150 °C) and by alkali charge increase. The optimal value of alkali charge and carbonate/hydroxide ratio differs as function of temperature. Independent variables with a high influence on SCT are first order alkali charge, Na_2CO_3/NaOH ratio and temperature; second order alkali charge and Na_2CO_3/NaOH ratio and interactions such as temperature-alkali charge, temperature – Na_2CO_3/NaOH ratio. The CMT_0 seems to be less dependent on alkali charge, but shows to decrease at temperature increase. CMT_0 index significant influence factors are: first order alkali charge, temperature and Na_2CO_3/NaOH ratio; second order Na_2CO_3/NaOH ratio and temperature; interactions: temperature-Na_2CO_3/NaOH ratio and temperature-alkali charge.

Optimal conditions for pulping should be chosen according to the targeted pulp characteristics. At constant temperature, if the objective is to obtain higher strength pulps, then the alkali charge should be kept at lower values while Na_2CO_3/NaOH ratio may take higher values. If lower kappa number pulps are the target, these values are obtained at lower Na_2CO_3/NaOH ratios and higher alkali charges. In this manner, the pulp producers may choose the pulping conditions that lead to their benefits. Table 3 presents the values of operational independent variables for optimal values of dependent variables. As it may be observed from the data presented in Table 3, there is no particular set of independent variables leading to optimal values of all the responses.

CONCLUSION

The response surface methodology (RSM) with central composite design is an important instrument for the study and optimization of the processes such as pulping, which involve independent variables and response dependent variables. Second order polynomial models were established for describing the influence of pulping temperature, alkali charge and Na_2CO_3/NaOH ratio on studied pulp characteristics. The study of the interaction effects of the independent variables on pulp characteristics was also possible and the influences of each variable on different responses hierarchy have been established. The equations provided a good fit relationship between the three pulping variables in general. This would permit the pulp producer to choose the conditions that will lead to the best financial benefits. Depending on the targeted pulp proprieties and further use, optimal conditions for pulping should be chosen in agreement to the desired pulp characteristics. If the objective is to obtain higher strength pulps, moderate to low temperature pulping should be chosen, with the alkali charge at lower values (16%), while Na_2CO_3/NaOH ratio may take higher values (5-6). If lower kappa number pulps are a target, better values are obtained at lower Na_2CO_3/NaOH ratio values and higher alkali charges, but this occurs with yield losses.

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