COMPARATIVE STUDY OF PULP AND PAPER PROPERTIES OF CANOLA STALKS PREPARED BY USING DIMETHYL FORMAMIDE OR DIETHYLENE GLYCOL

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Comparision between pulping of canola stalks with dimethyl formamide and diethylene glycol was studied in order to investigate the effects of cooking temperature (190˚C, 210˚C, and 230˚C), cooking time (120 min, 150 min, and 180 min) and dimethyl formamide or diethylene glycol (50%, 60%, and 70%) on the properties of pulp and paper. SCAN viscosity was applied to estimate the extent of cellulose degradation. Responses of pulp and handsheet properties to the process were analyzed using statistical software (MINITAB 15). The results showed that DMF pulp of canola was better than DEG pulp of Canola under the same conditions of cooking and organosolv ratio. In DMF pulping and DEG pulping, cooking temperature is a significant factor affecting paper properties. Analysis of results revealed that DMF pulp canola obtained at 230 °C, 180 min, and 70% DMF had a low kappa number (25) , indicating that the desired properties of the final product dictated the optimized pulping conditions.

Keywords: Canola Stalks; Dimethyl Formamide; Diethylene Glycol; Central Composite Design; Organosolv Pulp

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INTRODUCTION

Paper consumption is continuously increasing across the world. It amounted to 52.45 Kg per person in 2004 and is expected to rise above 400 million tones by the year 2010 (Hutter and Riccio 1998; World Resources Institute).

All countries of the world do not possess suitable and sufficient quantity of wood resources to fulfill their fiber requirements. Consequently, these countries are forced to use nonwood fibers for manufacturing paper products (Hammett et al. 2001; Judt 1993). Although nonwood fibers are normally associated to developing countries, these fibers play an important role in the global pulp production. The share of nonwood fibers has been estimated to be 8-10% of the total fiber used for papermaking in the world (Atchinson 1998) and is expected to increase more in the future (Ashori 2006).

Nonwood fibers can be classified according to their origin into agricultural by-products (e.g. straw, sugar cane bagasse), industrial crops (e.g. cotton, flax, kenaf), and naturally growing plants (e.g. reed, bamboo). Besides raw material availability, especially in countries with a shortage of wood raw material, environmental issues and costs are the main driving forces behind the growing interest in nonwood pulping. Many studies have been concentrated on the different aspects of nonwood pulping for fiber production (Sain et al. 2002; Jahan et al. 2007; Conzalez et al. 2008).

Canola (*Brassica napus* L.) is one of the most important nonwood fiber sources these days because of increasing production in different countries. Vegetable oils are produced from canola seed. China, Canada, India, France, Germany and Australia are the major producers of canola. In 2003, the worldwide planted area of canola was more than 23 million hectares. The average dry biomass produced per unit area by canola depends on irrigation. It varies from 5 to 10 t/ha, and the stem portion is about 20% of the produced dry biomass. Therefore, on average about 34 million tons canola stalk are produced annually and its major portion is burned, creating environmental pollution. However, this lignocellulosic biomass can be used in various products, including pulp and paper productions.

Even though the utilization of nonwood fibers in pulp and paper production has major benefits, the production of nonwood pulp is problematic. Unfortunately the most common nonwood pulping technology, the alkaline process, has caused serious environmental problems. Due to economic reasons, the implementation of alkali recovery has not been possible in small nonwood mills. In bigger mills, the recovery of alkali has not been successful, because the dissolution of silicon into cooking liquor has resulted in scaling problems during liquor evaporation. In practice, liquors are simply discharged into the waterways and hence lead to serious environmental loads on waterways as well as increasing the consumption of both energy and chemicals (Rouso et al. 2002).

To avoid such problems and replace the classical nonwood pulping process, considerable research efforts have been carried out to introduce alternative pulping processes. Organosolv processes, using organic solvents as delignifying agents, are suitable for pulping both wood and nonwood raw materials. The most widely researched organosolv processes use alcohols (Pereira et al. 1986), organic acids (Ligero et al. 2008), phenol (Jimenez et al. 1997), formaldehyde, ethanolamine (Jimenez et al. 2004a), or ethylenenglycol (Jimenez et al. 2004b).

The quality of organosolv pulps is better than the quality of corresponding kraft pulps. Particularly in alcohol pulping, the pulp quality can be improved by adding alkali to the system. However, some new solvents such as DMF have shown interesting results, indicating that pulping by this solvent can have many advantages, such as obtaining pulp with higher hemicellulose levels, less cellulose degradation, higher yield, lower residual lignin content, higher brightness, and good strength. The pulp produced is easy to bleach and the yield after bleaching is sometimes higher than the yield of Kraft pulp (Ziaie-Shirkolaee 2007).

In order to study the potential of canola stalks for use as a fiber resource in a papermaking application, an organosolv pulping process, with two high boiling organic solvents, DMF and DEG, was used. A central composite design was used to investigate the influence of the cooking time, temperature, and organic solvent concentration on the various properties.

EXPERIMENTAL

Raw Material

The canola stalks (Brassica napus L.) used in this study were obtained from the local canola field in Karaj city. Before pulping, the raw material was cleaned, cut, sampled as pieces of approximately 3 cm length, and sundried. The chemical composition of canola stalk was determined as follows: 45% cellulose, 17.5% lignin, 72.27% holocellulose, 8.53% ash, and 2% ethanol/dichloromethane extractable, on an oven-dry weight basis (moisture content 9.8%). The deviations of these contents from their respective means were all less then 10%.

Methods of Analysis of Raw Materials and Pulp and Paper Sheets

Analyses of raw material and pulp of canola stalks were made according to TAPPI Standard Methods (TAPPI 2002) with the exception of hemicellulose, which was determined by decreasing of cellulose content from holocellulose (holocellulose determined by Wise's sodium chlorite method) (Wise and Murphy 1946), cellulose according to Kurscher and Hoffner's nitric acid method (Rowell 1984), and viscosity of pulp was measured in cupri-ethylenediamine (CED) solution according to SCAN-CM 15:88 standard and the degree of polymerization (DP) of cellulose was calculated by the equation $DP^{0.76}$ = (SCAN viscosity)/2.28 (SCAN-CM 15:88).

The freeness of pulps was measured by the method T 227 om-94. Handsheets of 60 g/m^2 were formed and their properties were evaluated in accordance with the TAPPI standard methods (TAPPI Committee 2000–2002). The handsheets were conditioned at 23 ^oC and 50% RH for at least 24 h before testing. The Burst Index of handsheets was measured by TAPPI method T 403 om-97. The Breaking length of handsheets was measured by method T 404 cm-92. The Tear index of handsheets was measured by method T 414 om-98.

For Scanning Electron Microscopy (SEM) analysis, handsheets were cut into small samples, mounted on stubs with adhesive, and then they were placed under vacuum, evacuated, and sputter-coated with gold. After preparation of samples, the samples were investigated by SEM with a ZEISS DSM 960A (Oberkochen, Germany) instrument.

Experimental Design

The tested model uses a series of points (experiments) around a central one (central experiment), and several additional points (additional experiments), to estimate the first- and second-order interaction terms of a polynomial. This design meets the general requirement that every parameter in the mathematical model can be estimated from a fairly small number of experiments (Montgomery et al. 1991).

The total number of observations (experiments) required for the three independent variables (viz. temperature (T), cooking time (time), dimethyl formamide–water mixture (DMF), and diethylene glycol–water mixture (DEG)) was calculated from the following equation (Akhnazarova and Kafarov 1982),

$$N = 2^k + 2k + 1 \qquad (1)$$

and found to be 15. The parameter k in the equation is the number of independent variables. In this work all independent variables, including temperature, organosolv (DMF or DEG) concentration, and cooking time, were normalized from -1 to +1 according to following formula (Rodriguez et al. 1998):

$$X_n = 2\frac{X - \overline{X}}{X_{\max} - X_{\min}} \qquad (2)$$

This normalization also tends to result in more accurate estimates of the regression coefficients, as it reduces the interrelationships between linear and quadratic terms (Montgomery et al. 1991). The normalized independent variables and experimental data of properties of the pulp were used for the development of empirical models, in which the dependent variables were evaluated by the following general equation,

$$Z = \mathrm{a} + \mathrm{b}X_T + \mathrm{c}X_{time} + \mathrm{d}X_{DMF}(\text{or } \mathrm{d}X_{DEG}) + \mathrm{e}X_T X_{time} + \mathrm{f}\, X_T X_{DMF} + \mathrm{g}X_{time} X_{DMF} \qquad (3)$$

where Z denotes the response variables (YI: yield, KN: Kappa number, SCAN viscosity) of the pulp, (BL: breaking length, BI: burst index, TI: tear index) of the paper handsheets, X_T, X_{time} , X_{DMF}, and X_{DEG} the normalized values of T, *time*, DMF, and DEG, and the letters a to g denote constants. The values of responses obtained allow the calculation of mathematical estimation models for each response, which were subsequently used to characterize the nature of the response surface.

Pulping and Papermaking

Pulps were made in a 21-liter batch cylindrical mini-digester (321 stainless steel). The mini-digester includes an electric heater, a motor actuator, and instruments required for measurement and control of pressure and temperature. In a typical experiment, 300 g of oven-dried canola stalks (moisture content 9.8%) was weighed and charged into the minidigester. The solid/liquor ratio was fixed (1/12 d.w.), and the dimethyl formamide–water mixture (or diethylene glycol–water mixture) in the cooking liquor was set at 50%, 60%, or 70% by weight. The maximum pressure generated was 12 atm. After the mini-digester was loaded with canola stalks and the cooking liquor, it was heated to the operating temperature, which was then maintained throughout the experiment. After cooking, the cooked pulp was then washed with warm water and finally disintegrated (with 3000 rpm and 2.5 min) in a standard disintegrator (T 205 sp-95). Afterwards, the pulps were beaten in a stainless steel PFI mill under standard conditions (T 248 sp-00) up to 350 mL CSF. The temperature, pulping time, and dimethyl formamide-water mixture (or diethylene glycol–water mixture) used in the different experiments of the CCD were 190, 210, and 230 ˚C, 120, 150, and 180 min, and 50/50 (or 50%), 60/40 (or 60%), and 70/30 (or 70%) by weight, respectively.

RESULTS AND DISCUSSION

The characteristics of the both DMF and DEG pulping, as well as papermaking from canola stalks obtained in the 15 pulping runs (each run having three repetitions) are summarized in Tables 1 and 2 (see Appendix). Data processing enabled estimation of the main effects and the interactions of the factors for the responses considered. The effect of a factor is the change in the response when it is changed from the low (-1) to the high level (+1). The main effect of each factor estimates its average effect over all possible conditions of the other variables. Each of the responses analyzed can be affected only by the main effects or by interactions among them. The main effect of a variable should be individually interpreted only if there is no evidence that the variable interacts with other variables. When there is evidence of one or more such interactions, the interacting variables should be considered jointly.

A set of four prelimnary experiments was conducted for both of DMF pulping and DEG pulping under central operating conditions, namely: 210 ˚C, 150 min, and 60% organosolv ratio (DMF or DEG). The experimental results obtained in the determination of dependent variables differed from the mean values, shown in the nineth row of Table 1 and Table 2, by less than 5-10%. Subsequent tests, corresponding to the experimental design adopted, provided the results shown in the other rows. Based on the results of preliminary experiments, the operating variables were changed over the following ranges: 190-230 ˚C, 120-180 min, and 50-70 organosolv ratio (DMF or DEG). A constant liquid / solid ratio of 12 was used in all tests in order to ensure thorough mixing in the reactor. The MINITAB 15 software suite was used to conduct a multiple liner regression analysis involving all the terms of Eq. (2), except for those with alpha-to enter 0.15 and alpha to remove 0.15, which were left out using the stepwise method (Draper and Smith 1981). Equations (4) through (11) are reduced models for each response. There are some of the statistical parameters such as: S, R-Sq, and R-Sq(adj) in front of each equation which indicate how well the model fits the data.

Equations allow the estimation of the variation of the properties of the pulp and paper with changes in each independent variable, over the range considered, while holding the other two variables constant.

Kappa Number

KN (DMF pulp of canola stalks) =

$$39.47-7.1X_T-3.6X_{DMF}-0.8X_{time}-2.13X_TX_{DMF}-0.88X_TX_{time} \quad (4)$$

S:1.22, R-Sq:98.08, R-Sq(adj):97.01

KN(DEG pulp of canola stalks): =

$$45.73-10.7X_T-3.6X_{DEG}-1X_{time}-1.75X_TX_{DEG} \quad (5)$$

S:0.997, R-Sq:99.25, R-Sq(adj):98.95

Equations (4) and (5) show that the variation of cooking temperature had the most influence on kappa number, and the variation of cooking time had the lowest influence on kappa number (Rezayati-Charani and Mohammadi-Rovshandeh 2005; Ziaie-Shirkolaee 2007). The kappa number in DEG pulping was more sensitive to changes of cooking temperature (-10.7) than DMF pulping (-7.1), but change in organosolv ratio had an effect that was equal to both of them (-3.6). The effect of cooking time in DEG pulping (-1) was a little more than in DMF pulping (-0.8).

The interaction effect of cooking temperature and DMF ratio in DMF pulping (-2.13) on kappa number was greater than the interaction effect of cooking temperature and DEG ratio in DEG pulping on kappa number. The interaction effect of cooking temperature and cooking time in DMF pulping on kappa number was very little (-0.88), but the interaction effect of cooking temperature and cooking time in DEG pulping on kappa number was not significant.

Figures 1, 2, and 3 show the individual effects of cooking temperature, organosolv ratio, and cooking time, respectively, on kappa number. Comparison between DMF pulping of canola stalks and DEG pulping in the same cooking temperature, organosolv ratio, and cooking time showed that DMF pulping resulted in lower kappa number than DEG pulping.

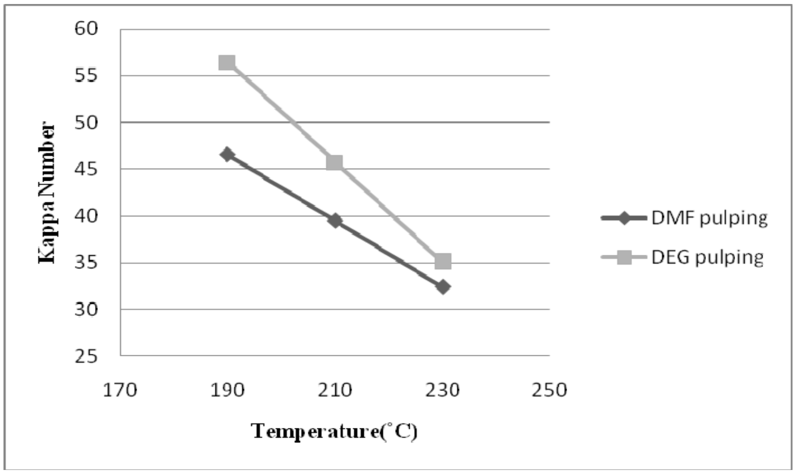

Fig. 1. Individual effect of cooking temperature on kappa number in DMF and DEG pulping of canola

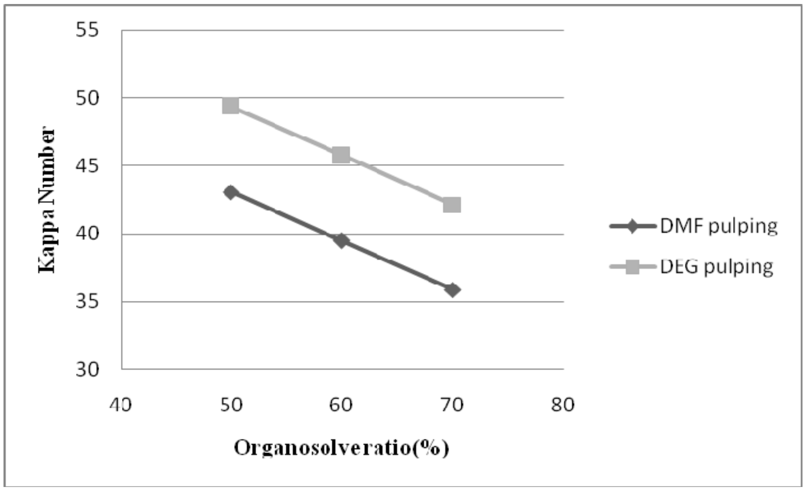

Fig. 2. Individual effect of organosolv ratio on kappa number in DMF and DEG pulping of canola

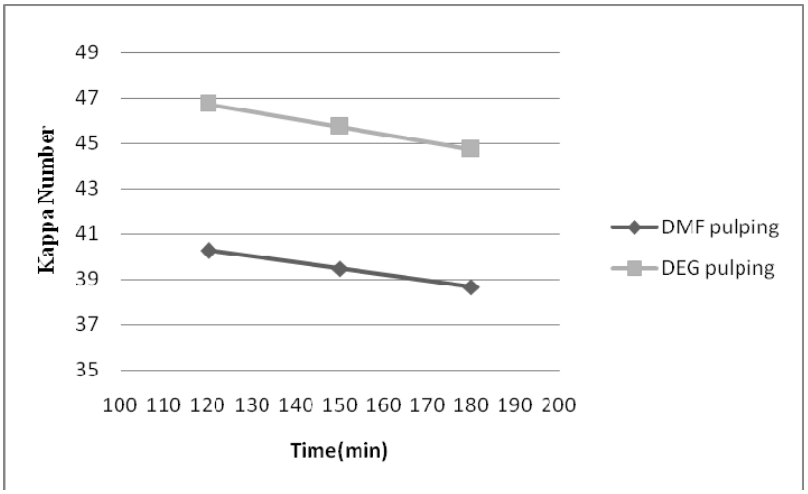

Fig. 3. Individual effect of cooking time on kappa number in DMF and DEG pulping of canola

Yield

YI(DMF pulp of canola stalks) =
$$69.40-6X_T-1.3X_{DMF}-1.1X_{time} \tag{6}$$
S:1.3, R-Sq:95.44, R-Sq(adj):94.19

YI(DEG pulp of canola stalks) =
$$63.20-5.9X_T-1.4X_{DEG}-0.8X_{time} \tag{7}$$
S:0.625, R-Sq:98.86, R-Sq(adj):98.5

Equations (6) and (7) show that variation of cooking temperature in DMF pulping (-6) had an effect that was almost equal to that of DEG pulp with respect to yield. Cooking Temperature had the greatest influence on yield. Variation in organosolv ratio in DMF pulping (-1.3) had almost equal effect with DEG pulping (-1.4) on yield. The effect of cooking time in DMF pulping (-1.1) on yield was a little more than DEG pulping(-0.8) on yield. Therefore, the yield was much more sensitive to changes of cooking temperature than organosolv ratio and cooking time, so the greatest changes on yield resulted from variation of cooking temperature (Ziaie-Shirkolaee 2007).

According to a previons study (Shatalov and Pereira 2002), the yield of organosolv pulping is expected to be higher than kraft pulping. The protective action of organosolv conditions on the noncellulosic components of nonwood against degradation under kraft pulping conditions has been mentioned as a main reason of the fairly high yield of organosolv pulps.

Figures 4, 5, and 6 show the individual effects of cooking temperature, organosolv ratio, and cooking time, respectively, on yield. Comparison between DMF pulping and DEG pulping at the same cooking temperature, organosolv ratio, and cooking time show that DMF pulping had higher yield than DEG pulping.

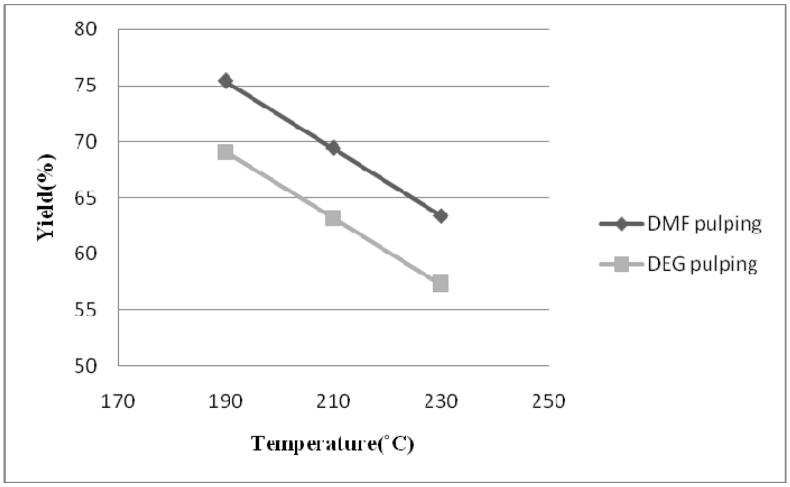

Fig. 4. Individual effect of cooking temperature on yield in DMF and DEG pulping of canola

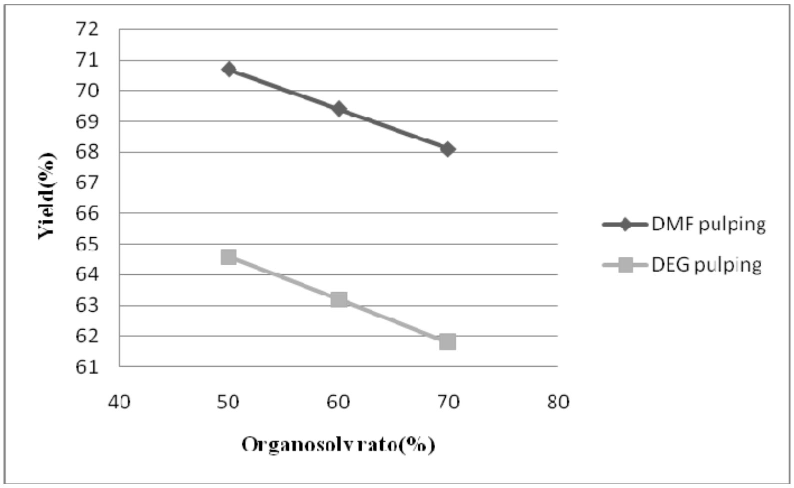

Fig. 5. Individual effect of organosolv ratio on yield in DMF and DEG pulping of canola

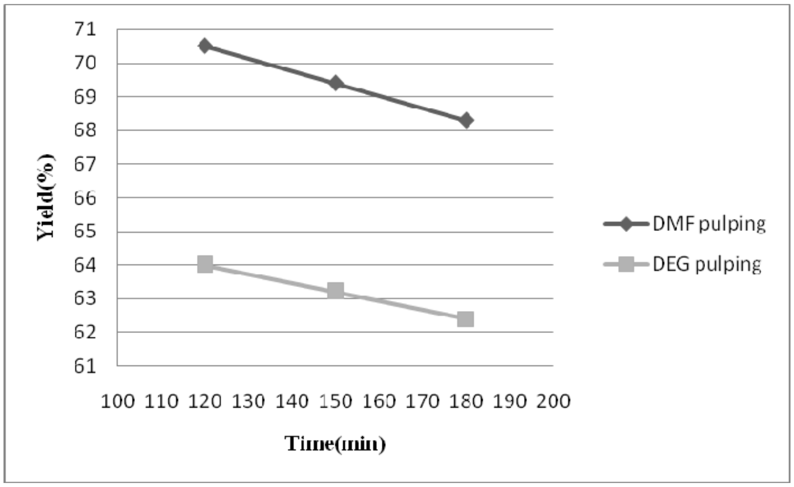

Fig. 6. Individual effect of cooking time on yield in DMF and DEG pulping of canola

Scan Viscosity and Degree of Polymerization

Scan Viscosity (DMF pulping of Canola stalks) =

$$1289-12.6X_T-6.9X_{time}+6.3X_{DMF} \quad (8)$$

S:7.57, R-sq:79.61, R-sq(adj):74.05

Scan Viscosity(DEG pulping of Canola stalks) =

$$1270-16X_T-5X_{time}+1X_{DEG} \quad (9)$$

S:0.913, R-sq:99.65, R-sq(adj):99.59

Equations (8) and (9) show that variation of cooking temperature in DEG pulping (-16) had more effect on Scan Viscosity than in the case of DMF pulping. Increasing of cooking temperature or cooking time caused a decrease of Scan viscosity, but increasing organsolv ratio caused an increase in scan viscosity, especially in DMF pulping (+6.3), but the corresponding change in the case of DEG pulping (+1) was lower than for DMF pulping.

The results of Scan viscosity can be applied in estimating the extent of cellulose degradation during the cooking process (SCAN-CM 15:88 standard (SCAN, 1998)). Use of increasing DMF ratio had a highly significant effect in reducing cellulose degradation. In other words, the viscosity of the pulp increased with increasing DMF ratio.

The viscosity is a function of cellulose fiber degradation during a pulping processes (SCAN 1998). Increasing temperature has the main effect for damaging of cellulose structure of nonwood pulps on the basis of decreasing of viscosity in comparison with the two other main factors. The advantages of this solvent in comparison with other pulping process include more retention of carbohydrates and low degradation of cellulose (Ziaie-Shirkolaee 2007).

The degree of polymerization (DP) of cellulose was calculated by the equation of $DP^{0.76}$ = (SCAN viscosity) / 2.28 (SCAN 1998; Shatalov and Pereira 2007); therefore, the principal effect of three parameters on DP were similar to the effects of viscosity variation.

Figures 7, 8, and 9 show the individual effects of cooking temperature, organosolv ratio, and cooking time, respectively, on viscosity. Comparison between DMF pulping and DEG pulping at the same cooking temperature, organosolv ratio, and cooking time showed that DMF pulping had a higher viscosity than DEG pulping.

Breaking length

Breaking length (DMF pulping of canola stalks) =

$$4535+519X_T+182X_{DMF}+103X_TX_{DMF} \quad (10)$$

S:131, R-sq:94.27, R-sq(adj):92.76

Breaking length (DEG pulping of canola stalks) =

$$4149+733X_T+218X_{DEG}+173X_TX_{DEG} \quad (11)$$

S:150, R-sq:96.08, R-sq(adj):95.01

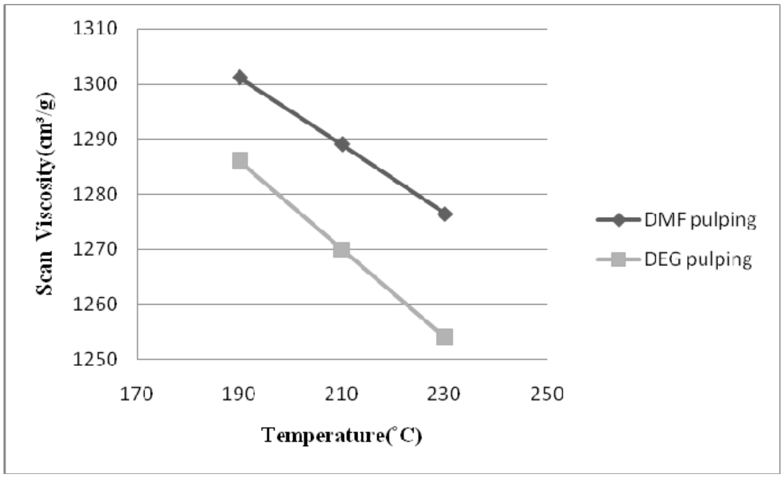

Fig. 7. Individual effect of cooking temperature on Scan viscosity in DMF and DEG pulping of canola

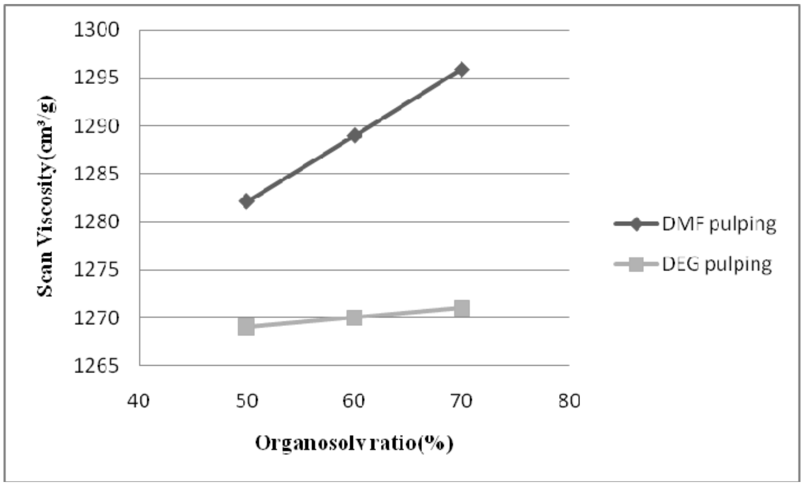

Fig. 8. Individual effect of organosolv ratio on Scan viscosity in DMF and DEG pulping of canola

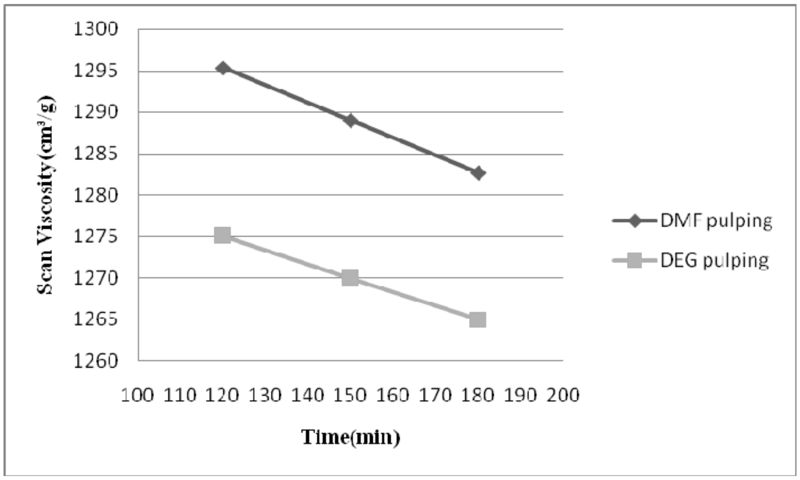

Fig. 9. Individual effect of cooking time on scan viscosity in DMF and DEG pulping of canola

As seen from Eqs. (10) and (11), the variation of cooking temperature had the most influence on the breaking length of handsheets, followed by the organosolv ratio.

Increasing of the cooking temperature resulted in increased breaking length. Variation of cooking temperature and DEG ratio in DEG pulping of canola had more influence than variation of cooking temperature and DMF ratio in DMF pulping of canola.

A lot of research has been carried out related to the strength of fibers (see, for instance, Ekhtera et al. 2008; Hubbe 2006a,b). The breaking length is principally associated with the effective number of bonding sites (hydrogen bonds) available on the fiber surface, while the tear index depends mainly on fiber length and strength. The average length of fibers of a particular raw material would remain unchanged during the course of organosolv pulping, while the degree of hydrogen bonding, which is finite in nature, may depend, to a certain extent, on the severity of hydrothermal treatment or the extent of dissolution of fiber constituents. These relationships may also be complicated by the degree of depolymerization of the cellulosic material or degradation of the inherent mechanical strength of fibers (Rezayati-Charani 2005).

Figures 10 and 11 show the individual effect of cooking temperature and organosolv ratio on breaking length.

Burst Index

Burst Index(DMF pulping of canola stalks) =

$$2.281+0.44X_T+0.13X_{DMF}+0.06X_{time}+0.063X_TX_{time} \quad (12)$$

S:0.0847, R-sq:96.8, R-sq(adj):95.52

Burst Index (DEG pulping of canola stalks) =

$$1.66+0.7X_T+0.17X_{DEG}+0.175X_TX_{DEG} \quad (13)$$

S:0.186, R-sq:93.43, R-sq(adj):91.64

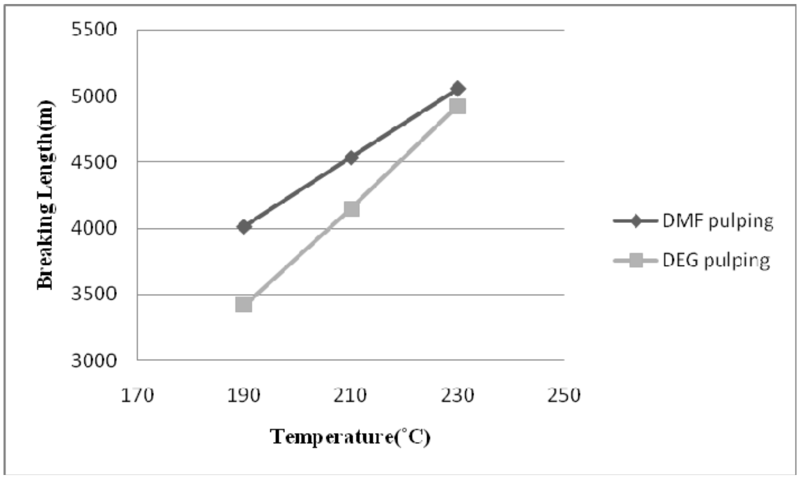

Fig.10. Individual effect of cooking temperature on breaking length in DMF and DEG pulping of canola

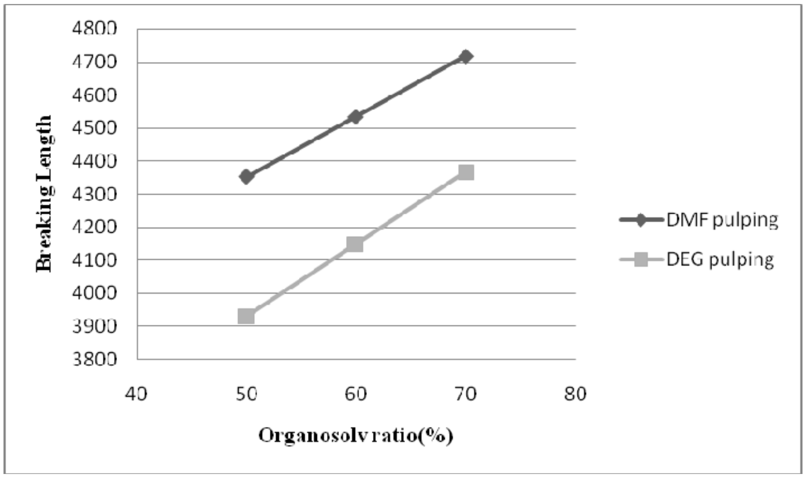

Fig.11. Individual effect of organosolv ratio on breaking length in DMF and DEG pulping of canola

As seen from Eqs. (12) and (13), the most influential factor affecting burst index was the variation of cooking temperature, following by the organosolv ratio, while the cooking time was the least. Increasing of cooking temperature, organosolv ratio, and cooking time caused increasing burst index.

Variation of cooking temperature, DEG ratio, and cooking time in DEG pulping of canola had more influence than variation of cooking temperature, DMF ratio, and cooking time in DMF pulping of canola.

Figures 12 and 13 show the individual effects of cooking temperature and organosolv ratio on burst index.

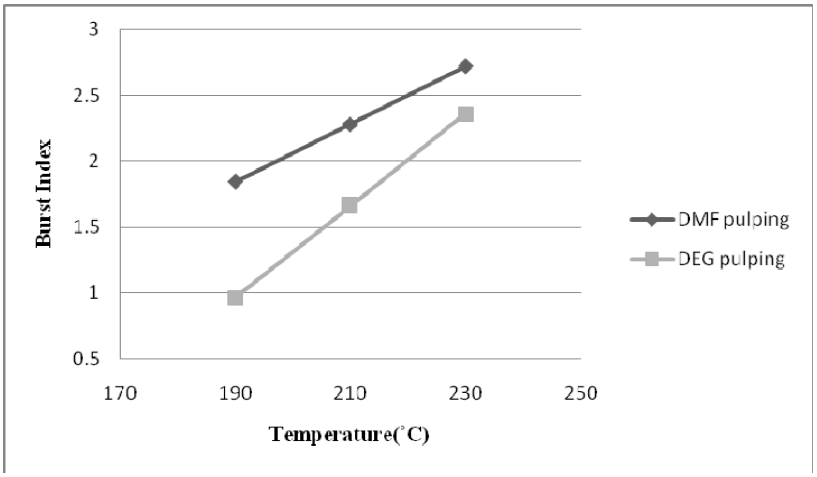

Fig.12. Individual effect of cooking temperature on burst index in DMF and DEG pulping of canola

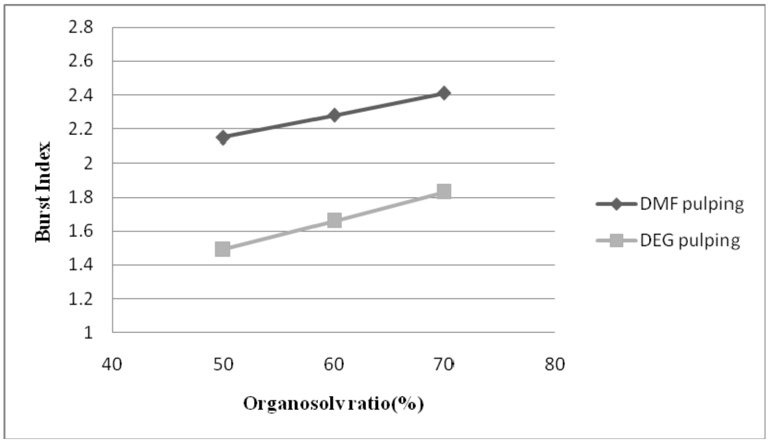

Fig.13. Individual effect of organosolv ratio on burst index in DMF and DEG pulping of canola

Tear Index

Tear Index(DEG pulping of canola stalks): =

$$4.36+0.34X_T+0.29X_{DMF}+0.25X_TX_{DMF} \quad (14)$$

S:0.252, R-sq:78.13, R-sq(adj):72.16

Tear Index(DEG pulping of canola stalks) =

$$3.893+0.49X_T+0.2X_{DEG}+0.175X_TX_{DEG} \quad (15)$$

S:0.142, R-sq:93.17, R-sq(adj):91.31

Equations (14) and (15) show that variation of the cooking temperature and organosolv ratio had the most influence on tear index. However, it has been established that tear strength is a function of both fiber strength and fiber bonding (Page and Macleod 1992; Seth and Page 1988).

Variation of cooking temperature in DEG pulping had more influence than in DMF pulping on tear index, but variation of DMF ratio in DMF pulping had more influence than in DEG pulping on tear index. Figures 14 and 15 show the individual effects of cooking time and organosolv ratio on tear index.

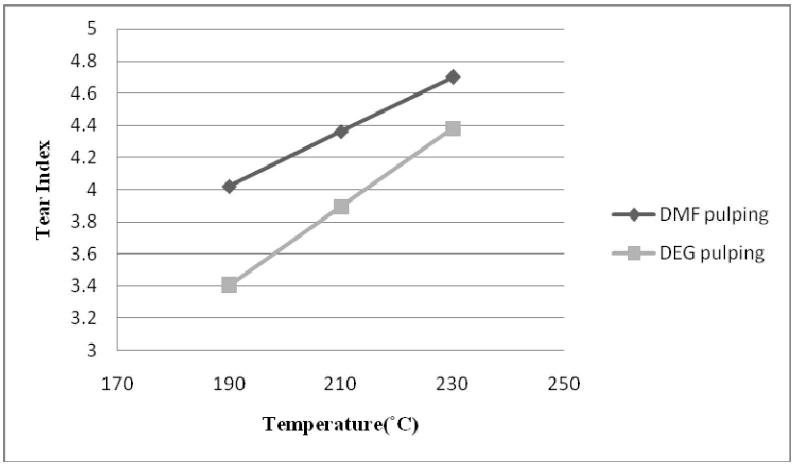

Fig.14. Individual effect of cooking temperature on tear index in DMF and DEG pulping of canola

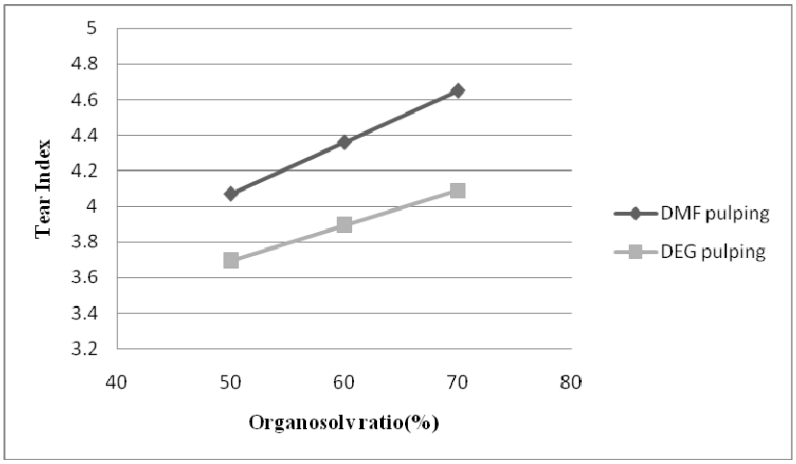

Fig.15. Individual effect of organosolv ratio on tear index in DMF and DEG pulping of canola

Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) images are used often for evaluations and analysis of paper structure (Allem 1998; Allem and Uesaka 1999; Dickson 2000; Chinga and Helle 2002; Lipponen et al. 2004; Ekhtera et al. 2008). Photographs of paper prepared from DMF and DEG pulps from canola stalks are shown in Figs. 16 and 17 (at the same kappa: 43). Comparison between Figs. 16 and 17 shows that there were a lot of pores and areas of destruction on the surfaces of fibers obtained from DEG pulping, but there were not any visible pores and areas of destruction on the surfaces of fibers produced by DMF pulping. These pores and areas of destruction can be the result of extensive degradation of holocellulose during DEG pulping, but degradation of holocellulose in during DMF pulping is very low. Therefore, pulp and paper properties of DMF were better than DEG.

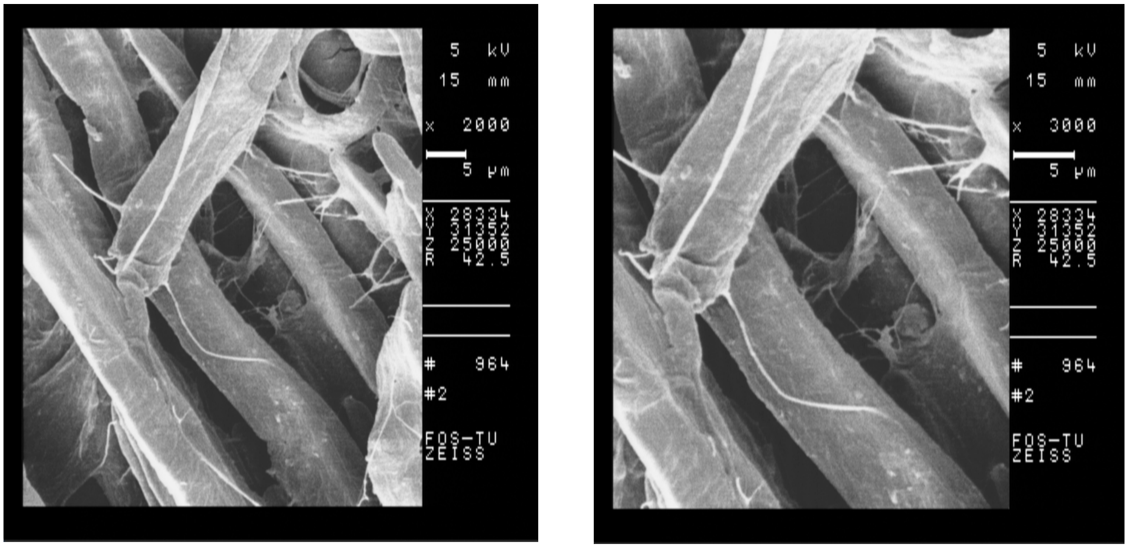

Fig.16A. SEM of canola paper at kappa: 43 with DMF pulping

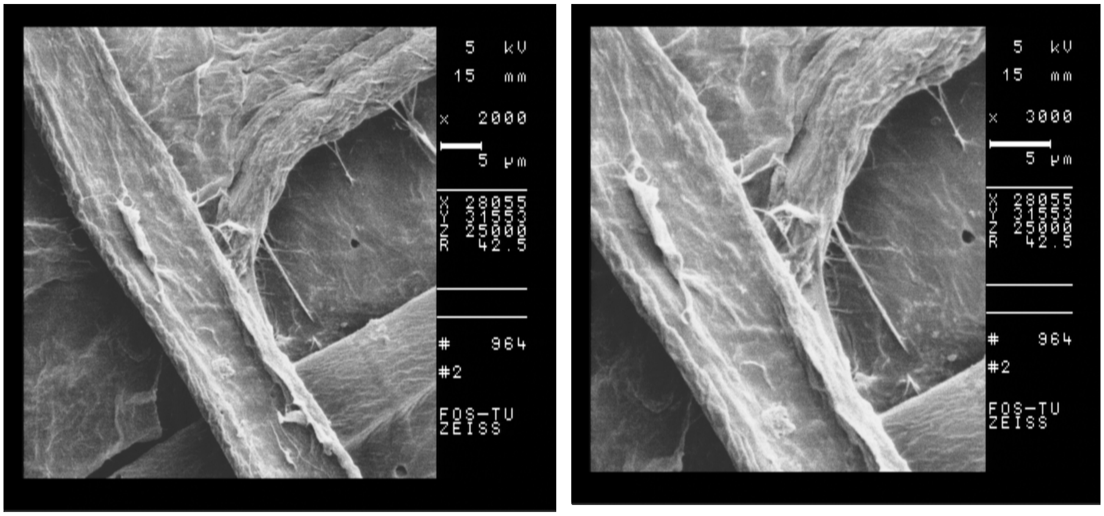

Fig.16B. SEM of canola paper at kappa: 43 with DMF pulping

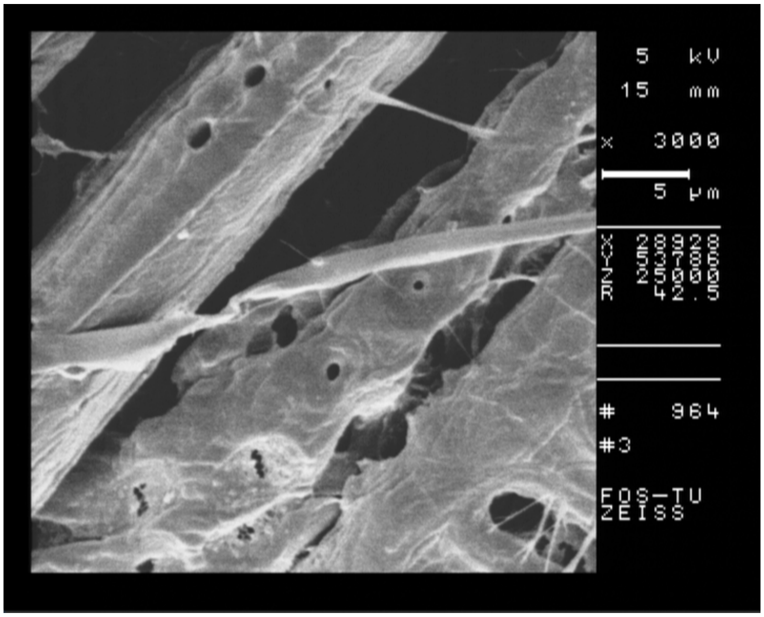

Fig.17A. SEM of canola paper at Kappa: 43 with DEG pulping

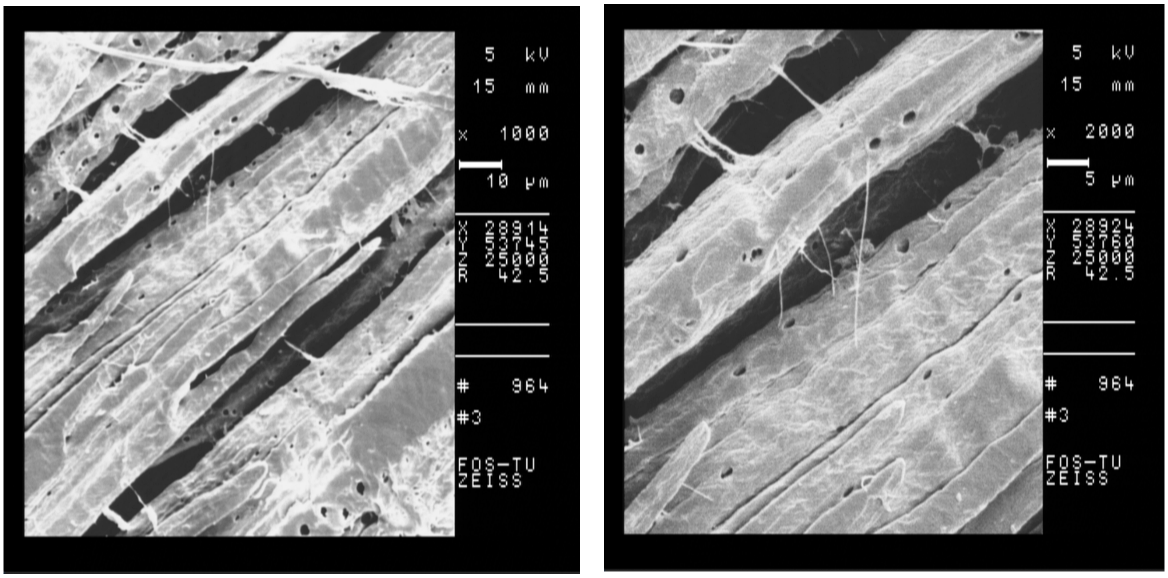

Fig.17B. SEM of canola paper at Kappa: 43 with DEG pulping

CONCLUSIONS

1. The delignification of canola can be achieved by using either dimethyl formamide or diethylene glycol, but dimethyl formamide as a solvent is preferable to diethylene glycol and has a good influence on delignification and paper properties. Dimethyl formamide has a very significant influence on reducing carbohydrates.
2. According to experimental results for DMF and DEG, we can obtain optimum pulping conditions for the production of pulp having acceptable properties.
3. Analysis of results revealed that DMF pulp canola obtained at 230 °C, 180 min, and 70% DMF had a low kappa number (25), indicating that the desired properties of the final product can be achieved under optimized pulping conditions.

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APPENDIX

Table1. Values of the Independent Variables and the Mechanical Chemical Properties of the Pulp and Paper Obtained in the Dimethyl Formamide Pulping by Using the Proposed Experimental Design and Papermaking

Cooking Number	X_T	X_t	X_{DMF}	T (°C)	t (min)	**DMF (%)**	***KN***	***YI* (%)**	**SCAN Viscosity (cm^3/g)**	***DP***	***BL* (m)**	**TI (mNm^2/g)**	***BI* (kN/g)**
1	**1**	**-1**	**1**	**230**	**120**	**70**	**28**	**63**	**1283**	**4150**	**5300**	**5.1**	**2.7**
2	**1**	**1**	**1**	**230**	**180**	**70**	**25**	**62**	**1275**	**4121**	**5480**	**5.8**	**3.1**
3	**-1**	**-1**	**1**	**190**	**120**	**70**	**44**	**75**	**1308**	**4257**	**4150**	**4.1**	**1.9**
4	**-1**	**1**	**1**	**190**	**180**	**70**	**46**	**74**	**1296**	**4208**	**4160**	**4.2**	**1.9**
5	**-1**	**1**	**-1**	**190**	**180**	**50**	**48**	**77**	**1276**	**4121**	**3980**	**4**	**1.7**
6	**1**	**1**	**-1**	**230**	**180**	**50**	**37**	**63**	**1261**	**4063**	**4900**	**4.2**	**2.6**
7	**1**	**-1**	**-1**	**230**	**120**	**50**	**40**	**67**	**1269**	**4092**	**4700**	**4.3**	**2.5**
8	**-1**	**-1**	**-1**	**190**	**120**	**50**	**49**	**78**	**1309**	**4267**	**3970**	**3.9**	**1.7**
9	**0**	**0**	**0**	**210**	**150**	**60**	**39**	**71**	**1296**	**4208**	**4640**	**4.3**	**2.3**
10	**0**	**1**	**0**	**210**	**180**	**60**	**38**	**66**	**1292**	**4189**	**4470**	**4.2**	**2.4**
11	**1**	**0**	**0**	**230**	**150**	**60**	**31**	**64**	**1278**	**4130**	**5150**	**4.4**	**2.6**
12	**0**	**-1**	**0**	**210**	**120**	**60**	**41**	**70**	**1300**	**4288**	**4330**	**4.2**	**2.3**
13	**-1**	**0**	**0**	**190**	**150**	**60**	**45**	**75**	**1303**	**4237**	**4080**	**4.2**	**1.9**
14	**0**	**0**	**1**	**210**	**150**	**70**	**38**	**67**	**1303**	**4237**	**4500**	**4.3**	**2.4**
15	**0**	**0**	**-1**	**210**	**150**	**50**	**43**	**69**	**1287**	**4169**	**4220**	**4.2**	**2.2**

X_T: normalized temperature; X_t: normalized cooking time; X_{DMF}: normalized dimethyl formamide water mixture; *YI:* yield ; *KN*: kappa number; SCAN viscosity: viscosity of pulp; *DP*: degree of polymerization; *BL*: breaking length; *TI*: tear index; *BI*: burst index

Table 2. Values of the independent variables and the mechanical chemical properties of the pulp and paper obtained in the diethylene glycol pulping by using the proposed experimental design and papermaking

Cooking Number	X_T	X_t	X_{DEG}	***T*** **(°C)**	***t*** **(min)**	**DEG (%)**	***KN***	***YI*** **(%)**	**SCAN Viscosity (cm^3/g)**	***DP***	***BL*** **(m)**	***TI*** **(mNm^2/g)**	***BI*** **(kN/g)**
1	1	-1	1	230	120	70	30	56	1260	4059	5250	4.9	2.6
2	1	1	1	230	180	70	29	55	1250	4017	5420	4.9	3
3	-1	-1	1	190	120	70	55	68	1292	4195	3550	3.5	1
4	-1	1	1	190	180	70	54	67	1282	4152	3550	3.5	1
5	-1	1	-1	190	180	50	58	70	1280	4144	3400	3.4	0.9
6	1	1	-1	230	180	50	39	58	1248	4008	4500	4	2.1
7	1	-1	-1	230	120	50	42	60	1258	4050	4500	4.1	1.9
8	-1	-1	-1	190	120	50	59	71	1290	4187	3410	3.3	0.9
9	0	0	0	210	150	60	45	63	1270	4101	4040	3.9	1.5
10	0	1	0	210	180	60	43	62	1265	4080	4100	3.8	1.6
11	1	0	0	230	150	60	35	57	1254	4034	5100	4.2	2.2
12	0	-1	0	210	120	60	47	65	1275	4123	4000	3.8	1.5
13	-1	0	0	190	150	60	56	69	1286	4170	3530	3.5	1
14	0	0	1	210	150	70	44	63	1271	4106	4050	3.8	1.8
15	0	0	-1	210	150	50	50	64	1269	4097	3830	3.8	1.9

X_T: normalized temperature; X_t: normalized cooking time; X_{DEG}: normalized diethylene glycol water mixture; *YI*: yield ; *KN*: kappa number; SCAN viscosity: viscosity of pulp; DP: degree of polymerization; *BL*: breaking length; *TI*: tear index; *BI*: burst index