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Chemical Composition and Fiber Properties of *Crambe orientalis* and *C. tataria*

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ABSTRACT

In this study, chemical composition and morphological properties of *Crambe orientalis* var. *orientalis* and *C. tataria* var. *tataria* stalks growing in Turkey were investigated. Typical chemical properties determined were the amount of holocellulose, alpha cellulose, cellulose, lignin, ash and silica. The results showed that lignin contents of *C. orientalis* and *C. tataria* were 24.5% and 20.6%, respectively. Cellulose ratio was found to be 40.1% in *C. orientalis* and 40.3% in *C. tataria*. The highest solubility with 1% NaOH was 34.9% and 33.7% for *C. orientalis* and *C. tataria*, respectively. Also the suitability of the fiber for pulp and paper manufacturing was examined and fiber length, fiber diameter, lumen diameter and cell wall thickness were measured using vizopan microscopic technique. The obtained data was utilized to calculate the felting rate, flexibility coefficient, Rigidity coefficient, Runkel index and F ratio. The effects of these properties on paper strength were evaluated. In addition, different chemical pulping procedures were applied to *Crambe* species to determine its pulping potential and the produced pulps optical and strength properties were studied. Moreover different chemical pulping procedures were applied to *Crambe* species to evaluate its pulping potential. The optical and strength properties of the paper obtained were determined. © 2010 Friends Science Publishers

Key Words: *Crambe*; Chemical composition; Fiber properties; Pulp; Paper

INTRODUCTION

Crambe is a member of the Brassicaceae family and contains oil, which is rich in erucic acid (Yaniv *et al*., 1994). The genus *Crambe* consists of about 30 species in the world (Knights, 2002) and three species in Turkey (Davis, 1982). Crambe is an erect annual herb with large pinnately lobed leaves. It has a moderately branched straight stalk. The flowers are white, clustered in racemes and show the typical Brassicaceae structure (Fontana *et al*., 1998).

Over the years, an increasing preoccupation and national use of forest and agricultural residues have occurred. This fact was mainly motivated by the increasing consumption of wood fiber-based products, such as panel, paper and boards (Cordeiro *et al*., 2004). Around 95-97% of all the raw materials used for this purpose are known collectively as 'non-wood' materials (Jimenez *et al.,* 2005). Non-wood fiber plants, with annual or biannual harvests that may be grown rapidly as agricultural crops, are receiving a renewed attention partly due to concerns on increasing wood consumption and raw-material availability for the pulp industry in some regions. Non-wood plants are important pulp fibers: they represented 6% of the world pulp production in 1991, with a 7% annual increase thousand tons in 1993, of which 92 thousand tons were imported (Gominho *et al*., 2001). Non-wood plants are an alternative to the increasingly scant forest wood as a source of pulp fiber (Jimenez *et al*., 2005).

A lot of works dealing with the use of Crambe crops as a source of fibers concerns species, which is different from our raw material, namely: *C. abyssinica* (Gastaldi *et al*., 1998). Studies of *C. abyssinica* seed as a new source of oil for food (i.e., confectionery & margarine) and industrial uses (i.e., mineral & mould lubricants in the manufacture of greases & in steel casting) have been in progress since the early 1960s (Gastaldi *et al*., 1998).

The oil extracted from Crambe plant's seeds has been using a lot of industrial sector. But it fairly confines the use of Crambe's stalk on the contrary to seed. In addition to instantaneous heat, getting burning process is a bad process, because of environment pollution. Hence Crambe stalks are an alternative solution to use for pulp production. Turkey which is an agricultural country has an important potential in agricultural residues and has about 20 million m^3 wood raw material annually. An important amount of these raw materials were used as combustion materials and also stand in competition with paper sector (lumber, fiberboard, particleboard, furniture & so on). For Turkey is imperative to use alternative raw material source to wood in pulp and paper industry.

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This study was, therefore, aimed at to determine the chemical and fiber properties of *C. orientalis* and *C. tataria* stalks were performed and investigate the suitability of the fibers for pulp and paper production.

MATERIALS AND METHODS

Collection of specimens from the native flora: *Crambe spp.* naturally grown in Kahramanmaras (Turkey) was collected in June-July 2004. *C. orientalis* var. *Orientalis* was obtained from Ahirdagi Mountain (latitude: 37.36°; longitude: 36.56°) at an altitude of 700-800 m. *C.* tataria *var. tataria* was obtained from Kahramanmaras-Elbistan (latitude: 38.132°; longitude: 37.12°) at an altitude of 1200-1300 m. It should be noted that the plants had mature seeds when they were collected. Plants were identified according to Flora of Turkey and East Aegean Islands (Davis, 1982).

Chemical analysis and morphological properties: The chemical composition and morphological properties of the stalks of both *Crambe* spp. studied here were determined according to the relevant TAPPI standard methods. In order to determine the chemical composition of the stalks of both species were first oven-dried and ground to 60 mesh by using Willey Mill (Anonymous, 1992).

The extractives content was determined after successive extraction in a soxhlet apparatus by petroleum ether (6 h). The determination of the humidity, α-cellulose, lignin, ashes, silica were performed using following standards Tappi T 264 om-88, Tappi T 203 os-71, Tappi T 222 om-88, Tappi T 211 om-85 and Tappi T 244 om-88, respectively (Anonymus, 1992).

The alcohol-benzene solubility, water solubility and 1% NaOH solubility were determined using Tappi T 207 om-88. The holocellulose and cellulose contents of *Crambe* spp. were determined according to Wise's chlorite and Kurscher-Hoffer nitric acid method, respectively (Wise, 1962; Browning, 1967).

The fiber length, fiber diameters, lumen diameters and cell wall thicknesses from morphologic properties of whole Crambe stalks were measured by using vizopan microscope. To measure fiber morphologic properties of the specimens (0.5-mm thickness & 2 cm long in parallel to fiber), chloride delignification method was applied. In this method, specimens were immersed into chloride solution until they were defibred and later, morphologic properties were measured.

Important criteria in papermaking can be determined using following five equations (Kırcı, 2006):

Felting rate: Fiber length ÷ Fiber diameter

Elasticity coefficient (%): Lumen diameter ÷ Fiber diameter×100

Rigidity coefficient (%): Cell wall thickness ÷ Fiber diameter ×100

Runkel index: Cell wall thickness ×2 ÷ Lumen Diameter.

F ratio (%): Fiber length ÷ Cell wall thickness ×100

Pulping: Cramabe stalks were cleaned and cut to a length of 6-8 cm. Experimental cooking conditions of soda-oxygen were given in Tables V. Double cooks were made and cooks were accomplished in an electrically heated laboratory rotary digester of 15 L capacity and maximum pressure of 25 kg cm^{-2}. All pulps were washed and screened on a 0.15 mm slotted screen. Screened pulps were beaten in a valley beater to 50^o SR freeness level and hand sheet were made on a Rapid Kothen machine. Pulp yield was determined as dry matter obtained on the basis of oven dried (od) raw material. Hand sheets of unbleached pulps with a grammage of ~60 g m^{-2} were prepared according to Tappi T 272 om-92. Kappa number and viscosity were determined in accordance with T 236 cm-85 and T 230 om-94, respectively.

Crambe stalks were cleaned and cut to a length of 6-8 cm. Cooking experiments were made in an electrically heated laboratory rotary digester of 15 L capacity and maximum pressure of 25 kg cm^{-2}. All pulps were washed and screened on a 0.15 mm slotted screen. Screened pulps were beaten in a valley beater to 50^o SR freeness level and hand sheets were made on a Rapid Kothen machine. Pulp yield was determined as dry matter obtained on the basis of oven dried (od) raw material. Hand sheets of unbleached pulps with a grammage of ~60 g m^{-2} were prepared according to Tappi T 272 om-92. Kappa number and viscosity were determined in accordance with T 236 cm-85 and T 230 om-94, respectively.

Statistical analysis of data: The experimental data regarding the results of chemical analysis, morphological properties and physical and optical properties of pulp and paper of both species were statistically analyzed by analysis of variance (ANOVA) techniques and the treatment means were checked by Duncan's test. All the statistical analyses were conducted by using computer program of SPSS 15.0.

RESULTS AND DISCUSSION

The papermaking potential of Crambe spp. stalks were investigated in this study. Chemical analyses (four replicates) were performed for each process under optimum conditions and minimum-maximum and average values for *C. orientalis* and *C. tataria* were summarized in Tables I and II.

The holocellulose and α-cellulose ratio of *C. orientalis* were 70.50% and 50.65%, respectively. These values for *C. tataria* were 75% and 50.42%, respectively. Cellulose and lignin ratio for *C. orientalis* and *C. tataria* were found to be 40.10% and 40.30%; and 24.50% and 20.59%, respectively. Silica content was 2.30% for *C. orientalis* and 2.99% for *C. tataria.*

The solubility of Crambe stalks were also investigated for different treatments. The alcohol-benzene solubility of *C. orientalis* and *C. tataria* stalks were 6.26% and 5.04%, respectively. Stalks of *C. orientalis* and *C. tataria* were solved 17.18% and 21.60% in cold water; 17.97% and

Table I: The results chemical analysis of *Crambe* spp.

Species	Properties	*C. orientalis*			*C. tataria*		
		Minimum Value	Maximum Value	Average	Minimum Value	Maximum Value	Average
	Humidity	5.60	5.72	5.66 ± 0.06*	4.78	4.82	4.80 ± 0.31*
Chemical Components	Ash	7.65	8.04	7.83 ± 0.11**	9.09	9.44	9.31 ± 0.12**
	Silica	2.07	2.60	2.34 ± 0.27*	2.76	3.33	2.88±0.07*
	Holocellulose	70	71	70.50 ± 0.36*	73	77	75 ± 1.91*
	α-cellulose	50.19	51.11	50.65 ± 0.46*	49.08	51.75	50.42 ± 1.34*
	cellulose	39.87	40.28	40.10 ± 0.21*	39.87	41.12	40.30 ± 0.83*
	Lignin	24.30	24.70	24.50 ± 0.20*	19.76	21.41	20.59 ± 0.83*
Solubility	Alcohol-Benzene Solubility	5.48	7.03	6.26 ± 0.78*	4.53	5.55	5.04 ± 0.51*
	Cold Water Solubility	16.71	17.67	17.18±0.28**	21.20	21.82	21.60±0.20**
	Hot Water Solubility	17.68	18.40	17.97 ± 0.22**	16.61	17.15	16.92 ± 0.16**
	1% NaOH Solubility	34.53	35.28	34.87 ± 0.22**	33.20	34.37	33.65 ± 0.36**

* $p>0.05$, statistically no significant
** $p\leq0.05$, statistically significant

Table II: The results of morphological properties of *C. orientalis and C. tataria*

Species	Morphological properties					
	Sample numbers	Fiber lengths (mm)	Fiber diameters (μ)	Lumen diameter (μ)	Cell wall thickness (μ)	Double wall thickness (μ)
C. orientalis	100	0.61*	25.75**	20.35**	2.70*	5.40*
C. tataria	100	0.62*	17.4**	12.20**	2.60*	5.20*

* $p>0.05$, statistically no significant
** $p\leq0.05$, statistically significant

Table III: Comparison of fiber properties of the stalks from the *C. orientalis* and *C. tataria* to those of same other fibers (Tutus & Eroglu, 2003; Kırcı, 1996)

Species	Felting rate	Elasticity coefficient	Rigidity coefficient	Runkel index	*F* ratio
C. orientalis	23.69	79.03	10.49	0.27	22.59
C. tataria	35.52	70.11	14.94	0.43	23.84
Wheat straw	53.13	33.04	34.02	2.23	15.19
Reed stalks	103.00	51.90	23.70	0.91	43.43
Cotton stalks	32.60	63.30	18.10	0.57	27.82
Sunflower stalks	57.90	70.60	14.90	0.42	37.79
Rye straw	37.90	60.80	19.80	0.65	21.70
Tobacco stalks	39.92	28.60	36.10	2.52	20.19

16.92% in hot water; 34.87% and 33.65% in 1% NaOH, respectively. The results showed that 1% NaOH solubility of both *Crambe* spp. was not very high and it should be cooked in alkali processes.

Analysis of variance and the treatment means show that there is no statistically difference between *C. orientalis* and *C. tataria* in humidity, silica, holocellulose, α-cellulose, cellulose and lignin contents as well as alcohol-benzene solubility. But there is statistically difference between two *Crambe* species mentioned above in ash content, cold water solubility, hot water solubility and 1% NaOH solubility at the 95% confidence level.

Annual plant stalks have important a potential to solve raw material problem for paper industry for Turkey. Annual grain stalk production of Turkey is 50 million tones and wheat stalks are to form to 57-80% of this (Tutus, 2000). When chemical properties of *Crambe* spp. were compared with wheat (*Triticum aestivum* L.), *Pinus brutia* (Usta, 1993), *Picea orientalis* (Hafizoglu & Bilgin, 1995) and *Cedrus libani* (Usta & Kara, 1997), holocellulose (77%), cellulose (52.07%), silica (5.43%) and 1% NaOH solubility (48.81%) rates of wheat straw (*T. aestivum*) had higher values *Crambe* spp., but lower lignin (18.11%) and alcohol-benzene solubility (5.52%). Compared with *P. orientalis*, *P. brutia* and *C. libani*, *Crambe* spp. had lower α-cellulose, hot water and 1% NaOH solubility but higher cellulose and lignin ratios. The highest holocellulose content was observed for *C. tataria*. *C. orientalis* had holocellulose content compared to *P. brutia*. Alcohol-benzene solubility was highest in *C. libani* and lowest in *P. orientalis.*

The results of chemical analysis of some annual plant were comparable with *Crambe* spp. Exception was only observed with wheat straw. The ash content of *C. orientalis* (7.83%) and *C. tataria* (9.3%) were higher than most annual plants and wood-based materials. The lignin content of *C. orientalis* (24.5%) and *C. tataria* (20.6%) was higher compared with other annual plants of *Oryza sativa* (12-16%), *Triticum aestivum* (16-21%), *Hordeum vulgare* (14-15%), *Avena sativa* (14-19%), *Secale celeale* (14-19%) *Hibiscus canabinus* (15-19%) and *Cannabis sativa* (9-13%) but lower than wood-based materials (Anonymous, 2006).

The holocellulose content of *Crambe* spp. was higher than 70%, (o.d. material), meaning a hemicellulose/cellulose ratio about 1:2, which is also common to other vegetal species. This ratio is important when considering the capital role of hemicelluloses in papermaking (Cordeiro *et al*., 2004).

The quantity of cellulose of *C. orientalis* and *C. tataria* were 40.0% and 40.3%, respectively. These values were approximately similar when compared with some other annual plants of *Oriza sativa* (28-48%), *Triticum aestivum*(29-51%), *Hordeum vulgare* (31-45%), Avena sativa (31-48%) and Secale celeale (33-50%). However cellulose content of wood-based materials were higher than *C. orientalis* and *C. tataria*. The amounts of silica of annual plants expect for *Secale celeale* (0.5-4%) were higher those of than *C. orientalis* (2.30%) and *C. tataria* (3%) (Anonymous, 2006).

The results of fiber lengths, fiber diameters, lumen diameter and cell wall thickness values were shown in Table II. These values were used to calculate the felting rate, elasticity coefficient, rigidity coefficient, Runkel index and F ratio of *Crambe* species.

Analysis of variance and the treatment means show that there is no statistically difference between *C. orientalis* and *C. tataria* in fiber lengths, Cell wall thickness double wall thickness. But there is statistically difference between two *Crambe* species mentioned above in fiber diameters and lumen diameter at the 95% confidence level.

The criteria, which were determined to be suitable in papermaking and calculated based-upon relationships between morphological properties of stalks, were explained. Some values of fiber dimensions compared with those of *Crambe* species and some annual plants fiber are presented in Table III.

The strength properties of the papers were found to be positively correlated with the felting rate (fiber length/fiber diameter). It is stated that if felting coefficient of a fibrous material is lower than 70, it is invaluable for quality pulp and paper production (Young, 1981; Bektas *et al*., 1999). The felting rate of *C. orientalis* and *C. tataria* fibers observed was 23.69 and 35.52, respectively. Conclusively high felting rate means lower strength properties. Some authors have a different opinion, because not only strength properties depend on felting rate, but also cell wall thickness (Eroğlu, 1998).

Results showed a strong relationship between the strengths of paper and morphologic structure of Crambe. The relationships between the physical properties of papers and of Crambe fiber properties were compared in Table IV.

It was understood that increase in fiber length and decrease in cell wall thickness had considerable effects on the physical properties of paper, presented in Table IV. It also can be seen in Table IV that the burst, tear and double folding strengths of paper were increased with increase in fiber length and increase in tear strength was due to higher cell wall thickness. On the other hand, higher burst and double folding strengths was observed for fibers having

Table IV: Relationships between the morphological properties of fiber cells and the physical properties of paper (Dadswell 1961; Bostancı, 1987)

Relationships	BS[a]	TS[b]	DFS[c]	PD[d]
with increasing the fiber length	+	++	+	–
with increasing the cell wall thickness	–	+	– –	– –
with decreasing the cell wall thickness	+	–	++	++
with increasing the fiber length/fiber diameter			+	
with increasing the spiral grain	– –	+	+	–

[a]Burst strength; [b]Tearing strength; [c]Double folding strength; [d]Paper density; [+]it had been determined that it has a positive effect; [++]There is certainly positive effect; [–]it had been determined that it has a negative effect; [– –]There is certainly negative effect

Table V: Pulping conditions of *Crambe* species and results of the characterization of unbleached pulp samples soda-oxygen methods and of paper sheets made from them

Parameter	**Soda-oxygen pulping process**	
	C. orientalis	***C. tataria***
NaOH rate (%)	16	16
O_2 pressure (kg cm^{-2})	6	6
Temperature (^oC)	140	140
Time (minute)	40	60
Liquor to straw ratio	5/1	5/1
Screened yield (%)	44.50*	45.25*
Kappa no	18.4**	19.5**
Pulp viscosity (cp)	10.50**	11.72**
Freeness (SR^o)	50±5	50±5
Breaking length (km)	4.70*	4.95*
Burst Index (kPa.m^2 g^{-1})	3.25*	3.40*
Tear index (mN.m^2 g^{-1})	4.15**	4.50**
ISO Brightness (%)	59.2**	60.8**
Printing opacity (%)	93.7*	94.0*

* $p>0.05$, statistically no significant
** $p\leq0.05$, statistically significant

lower cell wall thickness.

The fiber length and cell wall thickness of *Crambe* species are given in Table II and those of other annual plants are presented in Table III. The burst, tearing and double folding strengths of papers made from Crambe's fibers can be little strong in comparison to papers produced from other annual plants. This is because the fiber lengths of other annual plant species were longer than Crambe fibers. The cell wall thickness of Crambe was lower than those of wheat straw, reed, cotton, sunflower, tobacco stalks and rye straw. The burst strength, double folding strength and paper density of Crambe's papers may be better in comparison to those of others. But the burst and double folding strengths of *Crambe* species were much lower compared to those of wheat straw, cotton stalk and rye straw.

C. orientalis and *C. tataria* were cooked by soda-oxygen processes. Pulping conditions and results of the characterization of unbleached pulp samples obtained using soda-oxygen method and of paper sheets made from them are presented in Table V.

Table V showed that pulp yield in *C. orientalis* and *C. tataria* were as 44.50 and 45.25%, respectively and kappa numbers were little higher than other non-wood pulps. This finding could be explained with high amount of water and alkali solubility of *Crambe* species (Table I). At similar cooking conditions, wheat straw showed similar pulp yield and kappa number (Tutus & Eroglu, 2003 & 2004). Viscosity values were found for *C. orientalis* and *C. tataria* pulps as 10.50 and 11.72 cp, respectively. The strength and optical properties of *Crambe* species for unbleached alkaline pulps are also given in Table V. The breaking lengths were higher than that of paulownia and olive pulps (Ates *et al.*, 2008; Jimenez *et al*., 1992). Burst index for the soda-oxygen *Crambe* species pulps, 3.25 and 3.40 kPa·m² g^{-1}, respectively. Similar results for optimum wheat straw soda-oxygen pulp were obtained by Tutus and Eroglu (2004) as 46.2% yield, 18.7 kappa number, 56.1% ISO brightness, 5.84 km breaking length, 3.47 kPa m^2 g^{-1} burst index and 5.71 mN m^2 g^{-1} tear index.

Due to its higher content of fines and shorter average fiber length, the soda-oxygen pulp had higher breaking length and tear index than the ethanol pulp. The reason is probably the carbohydrates are being protected more effectively against hydrolysis reactions in high alcoholic environment (Akgul & Kırcı, 2002) coupled with the effect of the alkali in white liquor.

Analysis of variance and the treatment means show that there is no significant difference between *C. orientalis* and *C. tataria* in screened yield, breaking length, burst index and printing opacity. But there is statistically difference between two *Crambe* species mentioned above in kappa no, pulp viscosity, tear index and ISO brightness.

CONCLUSION

The holocellulose, cellulose α-cellulose and lignin ratios in *Crambe* spp. were lower than those of softwood, hardwood and common non-wood. *Crambe* spp. had higher water, alkali and alcohol-benzene solubility than that of soft- and hard-woods, which caused lower pulp yield. The pulp yields and viscosities are lower and kappa numbers are higher than some common wood and non-wood raw materials. *Crambe* spp. fibers had lower felting rate, elasticity coefficient, rigidity coefficient, Runkel index and F ratio than those of soft- and hard-wood. Although these kinds of fibers are considered as low quality materials, it can be used for paper production when mixed with long fibrous materials.

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