Pak J Sci Ind Res 2002 45 (1) 34-40

Catalyzed Organosolv Pulping of Sunflower *(Helianthus annus)* Stems by Lower Aliphatic Organic Acids

Tanzil Haider Usmani*, M Tahir, M Aleem Ahmed and M A Damani

PCSIR Laboratories Complex, Off University Road, Karachi-75280, Pakistan

(Received 20 October 1999; accepted 10 February 2001)

Sunflower *(Helianthus annus)* stems were subjected to organosolv delignification with acetic, formic and propionic acids. It was found that, among lower aliphatic organic acids, only acetic acid sufficiently delignified this raw material. The kinetics of delignification process was also studied and it was established that optimum acetosolv delignification was achieved with 95% acetic acid, and 0.25% hydrochloric acid as catalyst in 90 min of fractionation time. Further data on measurement and classification of fiber dimensions of this raw material showed the absence of long fibres and abundance of short fibres in the pulp.

Key words: Sunflower stems, Organosolv pulping, Delignification, Fibre dimensions.

Introduction

Kraft and Neutral Sulfite Semi Chemical (NSSC) processes are most commonly used worldwide in the pulp and paper industry over the years. However, environmental and economic limitations, associated with these processes are stimulating a search for alternatives (Goyal *et al* 1992). Organosolv pulping processes have the advantage that these conduct delignification with minimum degradation of cellulose and holocellulose with extraction of lignin in most valuable form (Pannir Selvam *et al* 1993).

Agricultural residues and biomass have a great promise as a raw material for pulp and paper industry. In Pakistan, forest resources are too meagre as per international standards. In this scenario of extreme scarcity of wood, potential agroresidues and biomass should be explored as possible alternative pulping raw materials.

The common sunflower *(Helianthus annus)*, is a member of the family Compositae. It is a native of the great plains region of the U.S. It is an annual herb with rough hairy stem 0.9144 to 4.572mm high, broad coarsely toothed rough leaves 76.2 to 304.8mm long and heads of flowers 76.2 to 152.4mm wide in wild specimens. It is also cultivated in Russia, different parts of Europe, Egypt and the Subcontinent. The seeds of the plant are normally used for extraction of oil and leaves are used as animal fodder. Pakistan imports huge quantity of sunflower and other vegetable oils for meeting its domestic requirements. Recently under a nationwide campaign, sunflower has been grown over a wide area. Local environmental conditions have been found to be quite conductive for its growth. The stem of the plant is a mere waste after use of its seeds in oil extraction. Saveleva (1971) carried out studies on the kinetics of biodegradation of sunflower hulls. Further Jimenez (1991) studied the viability of sunflower stems for pulp and paper by their alkaline pulping. No work is yet known to authors on organosolv pulping of sunflower stems.

Systematic studies on establishing appropriate pulping conditions for organosolv pulping of sunflower stems with lower aliphatic organic acids like acetic, formic and propionic were made. These acids were initially selected for this study due to the fact, that with them, pulping can be conducted at a lower temperature and atmospheric pressure. Suitable pulping conditions for each acid like percentage concentration, percent catalyst and solid-liquor ratio would be selected in the light of certain characteristics like percent yield, Kappa no. and Klason lignin of the resultant pulp products.

Materials and Methods

Sunflower stems for this study were obtained through the courtesy of the University of Agriculture, Tando Jam (Sindh). The stems were thoroughly washed with a stream of water to get rid off the dirt and foreign material and dried in an oven at 105-110 C° to constant weight. The dried sample was disintegrated in a Warner blender to particle size of 0.315-1.0 mm and stored in a dessicator. This sample was then analyzed for its alcohol-benzene extractives (ASTM 1983), Klason lignin, ash and α-cellulose contents. This analysis was carried out on the basis of initial dry weight of the raw material.

The fractionation treatments of washed, disintegrated and classified sunflower stems were carried out in 250 ml pyrex R.B. flask provided with a reflux condenser and placed inside a heating mantle. These delignification treatments were being conducted at 118, 101 & 141°C for acetic, formic and propionic

*Author for correspondence

acids respectively. Ground and classified sample (10 g) was used in each set of experiment, for respective acid, water and catalyst (hydrochloric acid), in varying proportions, as per working conditions, in that particular experiment. All these experiments were carried out for a period of 180 min established after a series of experiments. Three sets of experiments were performed for each of the three acids under study, for selection of optimum conditions for delignification of percent respective acid, percent catalyst and solid-liquor ratio. All the three variables of acid, catalyst concentration (%ww^{-1}), and solid-liquor ratio were the same *viz.* 85,90,95 percent, 0.20,0.25, 0.30 percent and 1:10, 1:12.5, 1:15 in case of acetic and propionic acids respectively. However, variables of acid and catalyst concentration in formic acid were 70, 75, 80 percent and 0.15,0.20 and 0.25 percent.

The kinetics of these fractionation treatments, performed for delignification of sunflower stems, were carried out by a series of experiments for different time periods varying from 15 to 210 min. The resultant delignified products were then analyzed and evaluated for their % yield, Klason lignin and Kappa no. (Vazquez *et al* 1992). All the fractionated products were also evaluated for their percent residual lignin (PRL), remaining in the products after delignification treatment (Parajo *et al* 1993).

Results and Discussion

The proximate chemical composition of sunflower stems has been presented in Table 1. It shows that α-cellulose in this particular raw material is around 50%, whereas Klason lignin which is rather an undesired material is not too high (15%). Moreover, ash and extractives contents are also on the lower side. All these observations signify the fact that, sunflower stems seems to be a worth investigating raw material. The three experimental variables, whose effects on certain characteristics of delignified products have been studied are percentage concentration of the acid, percent catalyst (HCl) and solid-liquor ratio. Table 2 shows the effect of percentage variation of acetic acid used in fractionation of sunflower stems on the eventual yield, Klason & residual lignins and Kappa nos. of different fractionated products (Erismann *et al* 1994). Experiments were carried out under three acetic acid concentrations (85%, 90% & 95% ww^{-1}) using 0.25% HCl at 118 °C for 180 min under reflux condenser. A review of Table 2 shows that, a comparatively better delignified product having Klason and residual lignins of 4.7 and 17.3% respectively was obtained by fractionation with 90% acetic acid. Still a better fractionated product having Klason lignin of 3.9% was obtained by delignification with 95% acid, but at the cost of 5% yield. Henceforth, the working conditions of fractionation with 90% acetic acid was selected as being optimum for sunflower stem and used in further studies. Moreover, this fractionated product had a Kappa no. of 30, which according to certain standards is bleachable grade pulp (Dong *et al* 1991). Additional studies were performed to provide further insight on the chemical fractionation of sunflower stems by variation of catalyst concentration, using 90% acetic acid solution, as established in the study described earlier. The minimum catalyst concentration for the most efficient delignification of this raw material was established from this study. The concentration of catalyst was varied in the range of 0.2, 0.25 & 0.3% and the time utilized in each case was 180 min. A review of Table 3 shows that, optimum delignification to the extent of 4.7% was achieved at 0.25% catalyst concentration. A lower catalyst concentration (0.2%), although gave fractionated product in quite higher yield of 62%, having Klason lignin 5.4%, but its Kappa no. was slightly higher than that of desired standards. Moreover, the use of 0.3% catalyst concentration reduced the yield to around 50% with quite a nominal reduction in its Klason lignin. This study therefore shows that, variation in catalyst concentration in case of acetosolv fractionation of sunflower stems had a pronounced effect on the eventual yield than that of Klason lignin of the finished products.

The effect of variation of charge ratio on different characteristics of fractionated products was also studied. The data presented in Table 4 shows that, the product obtained by using solid-liquor ratio of 1:12.5 had the optimum delignification, as evident by its Kappa no., whereas a lower ratio of 1:10 totally failed to delignify this raw material. Its Klason lignin reduced only by 4% (11.6%), probaby due to quite insufficient volume of liquor to react with the raw material. The use of higher ratio (1:15), seems not to be justified, as its Klason lignin just reduced nominally at the expense of yield. Therefore, charge ratio of 1:12.5 was selected, being optimum, for delignification of sunflower stems.

As a result of above studies, the base line data for acetosolv delignification of sunflower stems was established as 90% acetic acid, 0.2% HCl as catalyst, and solid-liquor ratio of 1:12.5. The kinetics of delignification under the established

Table 1
Proximate chemical composition of sunflower stems

Constituents determined	% (W W^{-1})
Ash content	4.35
Alcohol-benzene extractives	3.15
α-Cellulose	49.83
Klason lignin	15.20
Pentosans	23.20

conditions of this particular raw material was also studied, by carrying out a series of fractionation treatments for time periods varying from 15-180 min. The results of these kinetic studies have been presented in Table 5. It may be seen that rate of delignification is rather slow in the initial fractionation time of 60 min. Thereafter, the rate is enhanced and delignification reaction reaches at an optimum level in fractionation time of 90 min. Afterwards, delignification proceeds at a very slow rate. This behaviour has further been highlighted in Fig 1 which shows gradual reduction of the percentage residual lignin (PRL), remaining in the delignified products against different periods of fractionation. It is quite clear that a sharp slope, as observed in Fig 1 is obtained in the first 90 min of fractionation time. Afterwards, this decrease in PRL is less pronounced.

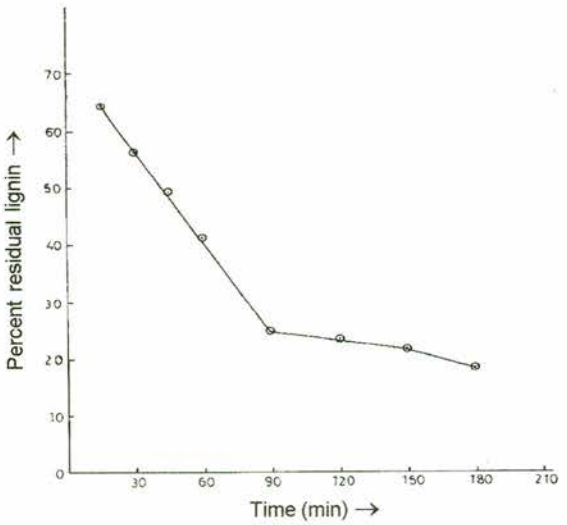

Fig 1. Dependence of % residual lignin on time.

Different characteristics like Klason and resdual lignins and Kappa no. with yield of various delignified products obtained in different periods of fractionation, have also been shown in Table 5 (Ahmed *et al* 1998). It is quite apparent in Figs 1-2 that the product eventually obtained in 90 min of fractionation time has a good yield of above 62% having Klason lignin 6% and Kappa no. 28, which meets the desired standard (Dong *et al* 1991). Henceforth, working conditions for delignification of sunflower stems, using acetic acid as a medium are 90% acid, 0.25% catalyst, solid-liquor ratio 1:12.5 and fractionation time of 90 min. Further, studies on organosolv delignification of sunflower stems were also made using formic and propionic acids as medium. Separate set of experiments were designed for the two acids, using 70, 75 and 80% acid, 0.15, 0.20 and 0.25% catalyst, 1:10, 1:12.5 and 1:15 solid-liquor ratio in case of formic acid (Baeza *et al* 1991). In case of propionic

Table 2
Establishment of acetic acid percentage

Solid-Liquor ratio	CH_3COOH %	HCl %	Time (min)	Yield %	Klason lignin %	Residual lignin%	Kappa no
01:12.5	85	0.25	180	60.09	7.83	30.79	36.8
01:12.5	90	0.25	180	56.03	4.73	17.34	30.1
01:12.5	95	0.25	180	50.80	3.91	13.00	23.7

Table 3
Establishment of catalyst (HCl) percentage

Solid-Liquor ratio	CH_3COOH %	HCl %	Time (min)	Yield %	Klason lignin %	Residual lignin%	Kappa no
01:12.5	90	0.20	180	62.66	5.44	22.31	33.2
01:12.5	90	0.25	180	56.03	4.73	17.34	30.1
01:12.5	90	0.30	180	49.92	3.64	11.89	28.4

Table 4
Establishment of solid liquor-ratio

Solid-Liquor ratio	CH_3COOH %	HCl %	Time (min)	Yield %	Klason lignin %	Residual lignin%	Kappa no
01:10.0	90	0.25	180	62.66	11.61	47.27	43.2
01:12.5	90	0.25	180	56.03	4.73	17.34	30.1
01:15.0	90	0.25	180	55.22	4.59	16.59	29.9

acid, the delignification conditions in respect of concentration of acid, catalyst and solid-liquor ratio utilized were 85,90,95% 0.20, 0.25, 0.30% and 1:10 1:12.5, 1:15 respectively (Ahmed *et al* 2000). The results of these studies were presented in Tables 6-11. A review of these Tables shows clearly that, both of these acids, *viz* formic and propionic, were found to be quite incapable to sufficiently delignify this raw material. Extreme delignification conditions like 80% formic acid and 0.25% catalyst and 90% propionic acid and 0.30% catalyst, as given in Tables 7 and 10 show that, delignification in these two utmost cases reached upto Klason lignin content, remaining in the fractionated product, of 8.2 and 8.5% respectively, having Kappa Nos. 33.5 and 36.2, which are not at all bleachable (Dong *et al* 1991). Moreover, it may also be seen in Tables 6-11, that although formic and propionic acids completely fail to delignify sunflower stems to desired level, but yield in both these cases is also most adversely affected.

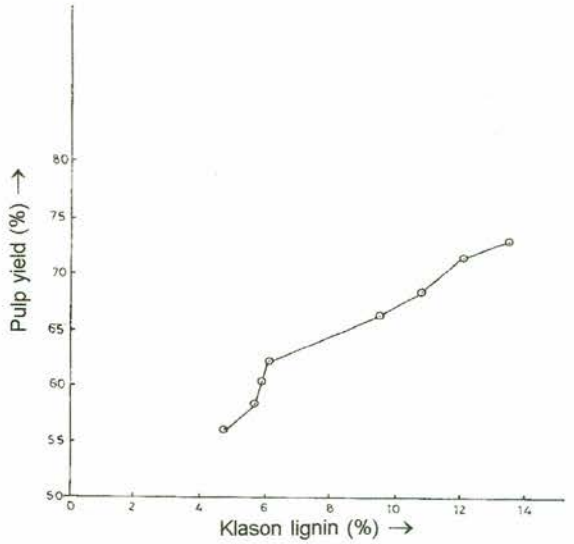

Fig 2. Relationship between pulp yield and klason lignin.

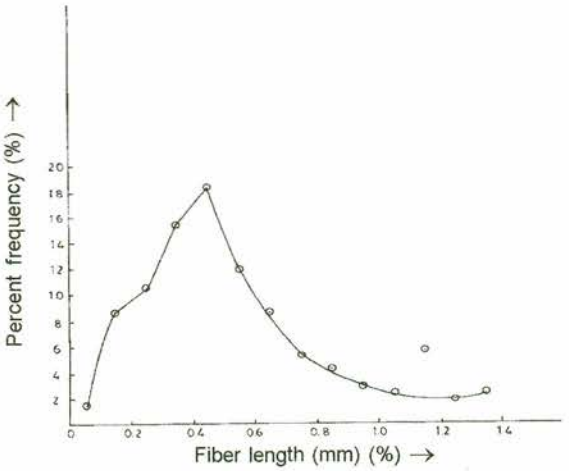

Fig 3. Fiber length distribution curve of sunflower stems.

Table 5
Kinetic studies of the established operational conditions of delignification with acetic acid

Time (min)	Yield %	Klason lignin %	Residual lignin %	Kappa no
15	72.77	13.52	64.39	38.9
30	71.27	12.09	56.39	37.3
45	68.22	10.81	48.26	36.1
60	66.22	9.5	41.17	33.2
90	62.34	6.11	24.93	28.0
120	60.4	5.91	23.36	27.4
150	58.41	5.69	21.75	25.0
180	56.01	4.73	17.34	22.7

Acetic acid: 90%; Catalyst (HCl):0.25%; Solid-liquor ratio:1:12.5

Table 6
Establishment of formic acid percentage

Solid-Liquor ratio	H.COOH %	HCl %	Time (Min)	Yield %	Klason lignin %	Residual lignin%	Kappa no
01:12.5	70	0.20	180	60.39	12.58	49.72	48.1
01:12.5	75	0.20	180	53.16	10.06	35.00	41.0
01:12.5	80	0.20	180	46.06	8.50	25.62	35.6

Table 7
Establishment of catalyst (HCl) percentage

Solid-Liquor ratio	H.COOH %	HCl %	Time (min)	Yield %	Klason lignin %	Residual lignin%	Kappa no
01:12.5	80	0.15	180	47.60	9.90	30.84	40.8
01:12.5	80	0.20	180	46.06	8.50	25.62	35.6
01:12.5	80	0.25	180	45.9	8.20	24.63	33.5

indicating an undue attack on cellulosic content of the raw material.

The length and width of fibres of unbleached acetosolv pulp of sunflower stems have been shown in Table 12-13 presents the fibre dimensions of some common agroresidues (Rydholm 1965: Ahmed *et al* 1998). A review of data in these two tables clearly indicates that, although slenderness ratio of the fibres of sunflower stems is quite low, but average length as well as width of fibres of this particular raw material, which are of course recommended factors for any good pulping raw material (Britt 1970), are comparatively on the lower side (0.550 and 0.016 mm respectively), as compared to woods and other

Table 8
Establishment of solid-liquor ratio

Solid-Liquor ratio	H.COOH %	HCl %	Time (min)	Yield %	Klason lignin %	Residual lignin%	Kappa no
01:10.0	80	0.20	180	48.25	8.90	28.1	38.9
01:12.5	80	0.20	180	46.06	8.50	25.62	35.6
01:15.0	80	0.2	180	44.05	8.35	24.07	32.9

Table 9
Establishment of propionic acid percentage

Solid-Liquor ratio	C_2H_6. COOH %	HCl %	Time (min)	Yield %	Klason lignin %	Residual lignin%	Kappa no
01:12.5	85	0.25	180	63.25	10.02	41.48	42.1
01:12.5	90	0.25	180	60.19	9.97	39.27	41.0
01:12.5	95	0.25	180	56.62	9.19	34.05	38.1

Table 10
Establishment of catalyst (HCl) percentage

Solid-Liquor ratio	C_2H_5. COOH %	HCl %	Time (min)	Yield %	Klason lignin %	Residual lignin%	Kappa no
01:12.5	90	0.2	180	69.4	12.72	57.77	55.6
01:12.5	90	0.25	180	60.19	9.97	39.27	41.0
01:12.5	90	0.3	180	40.8	8.47	22.62	36.2

Table 11
Establishment of solid-liquor ratio

Solid-Liquor ratio	C_2H_5. COOH %	HCl %	Time (min)	Yield %	Klason lignin %	Residual lignin%	Kappa no
01:10.0	90	0.25	180	67.2	10.5	46.18	45.3
01:12.5	90	0.25	180	60.19	9.97	39.27	41.0
01:15.0	90	0.25	180	58.92	9.91	38.21	40.9

Table 12
Fibre dimensions of sunflower stems

Long Fiber (L.F) (2.0-3.0 mm)		Medium fiber (M.F.) (1.0-2.0 mm)		Short fiber (S.F.) (0.1-1.0 mm)		Relation of S.F. to M.F.	Diameter (25-40μ)		(10-25μ)		(2-10U)		Mean length	Mean dia	Slender-ness
% Freq	Mean length (mm)	% Freq	Mean length (mm)	% Freq	Mean length (mm)		% Freq	Mean dia (μ)	% Freq	Mean dia (μ)	% Freq	Mean dia (μ)	(l) (mm)	(d) (mm)	Ratio l/d
NIL	NIL	12.49	1.18	87.51	0.47	1.0.143	13.15	29.10	77.33	18.52	9.52	9.70	0.55	0.016	34.37

Table 13
Fibre dimensions of some common agroresidues

Agroresidues	Fiber length (mm)			Diameter (μ)			Slenderness ratio (l / d)
	Max	Min	Average	Max	Min	Average	
Wheat straw	3.1	0.7	1.5	27	7	13	110
Rice Straw	3.5	0.6	1.5	14	5	9	170
Bagasse	2.8	0.8	1.7	34	10	20	85
Corn Stalk	2.9	0.5	1.5	24	14	18	85
Cotton Stalk	2.7	0.38	1.03	23	8	13	79
Esparto	1.6	0.5	1.1	14	7	9	120
Kenaf	2.5	0.8	1.5	50	25	29.5	51

common agroresidues. Statistical analysis of the data on fibre dimensions, collected during the study, was also carried out to determine the percentage frequencies and mean length of the long, medium and short fibres categorized on the basis of Klemm classification (Casey 1960, 1981). The data presented in Table 12 further reveals that long fibres are totally absent in acetosolv pulp of sunflower stems. Moreover, the percentage frequencies and mean length of medium and short fibres present in these raw materials have also been shown and it is quite evident therein, that overall short fibres are totally dominant as compared to medium, as far as their percentage frequencies are concerned, and are in the ratio 1:0.143. However, diameters of these fibres are mostly in the medium class (10-25μ). The fibre length data has further been enlightened by fibre distribution curve (Fig 3), based on percentage of length of bires plotted against their respective percentage frequencies. It is quite apparent from the scenario of the fibre dimensions of unbleached acetosolv pulp of sunflower stems that, it is not a superior class of pulp, with absence of long and abundance of short fibres. This observation further corresponds with a UNIDO report, confirming the use of sunflower stems as raw material for only liner board grades and corrugating medium (UNIDO Monographs 1979).

Conclusion

It has therefore been concluded from these studies that among lower aliphatic organic acids, only acetic acid in 95% concentration delignifies sunflower stems, having catalyst (HCl) concentration and solid-liquor ratio of 0.25% and 1:12.5 respectively. As for fibre dimension, it has been established that, it is a short length fibrous material having medium width and low slenderness ratio.

References

Ahmed T W, Usmani T H, Motan M T, Damani M A, Askari S H A 1998 Delignification of Kenaf *(Hibiscus sabdariffa)* by organosolv process-Part 1. Acetic acid. *Pak J Sci Ind Res* **41** (5) 235-239.

Ahmed T W, Usmani T H, Motan M T, Damani M A 2000 Delignification of Kenaf *(Hibiscus sabdariffa)* by organosolv pulping process-Part 2. Formic and propionic acids. *Pak J Sci Ind Res.* **43** (2) 103-107.

ASTM 1983. *Standard Test Method for Alcohol-benzene Soluble Matter in Cellulose,* D-1794, Vol 15.04 American Society for Testing Material, Philadelphia P.A., U.S.A.

Baeza J, Urizar S, Erismann N M, Freer J, Schmidt E, Duran N 1991 Organosolv pulping-V: Formic acid, Delignification of *Eucalyptus globulus* and *Eucalyptus grandis. Bioresource Technology* **37** 1-6.

Britt K W 1970 *Pulp and Paper Technology.* Van Nostrand Reinhold Co., N Y, USA, 2nd ed pp 670-673

Casey J P 1960 *Pulp and Paper.* John Wiley & Sons, N Y, USA, Vol 1, 2nd ed p 647.

Casey J P 1981 *Pulp and Paper.* John Wiley & Sons, USA, 3rd ed pp 497, 831.

Dong H K, Hyon P K, Chin H K 1991 Acetosolv pulp at atmospheric pressure for the reduction of pollution and energy. *Palpu, Chongi Gisul* **23** (2) 21-32.

Erismann N M, Freer J, Baeza J, Duran N 1994 Organosolv pulping-VII: Delignification selectivity of formic acid pulping of *Eucalyptus grandis. Bioresource Technology* **47** 247-256.

Goyal G C, Lora J H, Pye E K 1992 Autocatalysed organosolv pulping of hardwoods. *Tappi J* **75** 110-116.

Jimenez A L 1991 The manufacture of pulp from sunflower stems. *Pap. Carton Cellul* **40** (7-8) 63-69.

Pannir Selvam P V, Ghose T K, Ghosh P 1993 Catalytic solvent delignification of agricultural residues: Inorganic Catalysts. Process Biochemistry 13-15.

Parajo J C, Alonso J L, Vazquez D 1993 On the behaviour of lignin and hemicellulose during the acetosolv processing of wood. *Bioresource Technology* **46** 233-240.

Rydholm S A 1965 *Pulping Processes.* Interscience Publishers, N.Y. USA, p 680.

Saveleva T G 1971 Degradation products of sunflower hull polysaccharides studied during mechanico chemical treatment. *Khim Dev* **8** 119-125.

UNIDO 1979 Monographs on Appropriate Industrial Technolgy for Paper Products and Small Paper Mills, UNO, N Y, USA, No.3 p 96.

Vazqueq D, Lage M A, Parajo J C, Vazquez G 1992 Fractionation of Eucalyptus wood in acetic acid media. *Bioresource Technology* **40** 131-136.