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LIQUEFACTION OF COTTON STALKS (*GOSSYPIUM HIRSUTUM* L.) WITH PHENOL

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ABSTRACT

In this study, we aimed to synthesize resol type wood adhesive from resinification of cotton stalk liquefied into phenol in the presence of sulfuric acid as catalyst. The biomass was first liquefied with phenol in the presence of sulfuric acid as a catalyst at various reaction conditions.

It was detected that increasing acid concentration, temperature and time resulted in a great decrease on the amount of unliquefied cotton stalks and a significant increase in the percentage of combined phenol in the produced resin.

It was also found out that the resin produced from cotton stalks can be perfectly used in the production of wood composite materials.

KEY WORDS: cotton stalk, phenol, liquefaction, sulfuric acid

INTRODUCTION

Many attemps have been done on the liquefaction of wood into phenol, alcohols, tannin, bisphenol, carboxymethylated with acidic catalyst at moderate temperature and without catalyst at elevated temperatures to produce phenol formaldehyde type molding resins (Lin et al. 1994, Alma et al. 1995, Marcos et al. 1995, Santana et al. 1995, Alma et al. 1996a, Alma et al. 1996b, Alma and Acemioglu 2002, Alma and Basturk 2005), adhesives (Kishi and Shiraishi 1986, Pu 1994), recently. The ingredients used in the production of synthetic adhesives are essentially petrochemicals or their derivatives. The synthetic adhesives are the most expensive components in the production of wood-based composite materials such as plywood, particleboard, fiberboard, etc. because of the oil prices increased recently.

A number of investigations have been done to prepare the adhesives from a variety of lignocellulosic materials such as lignin, spent sulphite liquor, untreated wood, wood chemically modifed by esterification, etherification etc., tannin, tree barks to find out replacements for phenol largely consumed in the production of phenol-formaldehyde resins

Ono and Sudo 1993, Shiraishi et al. 1993, Alma 1996c, Alma et al. 1997, Trosa and Pizzi 1998, Alma and Kelley 2000). Numerous investigations have been done on preparing lignin and tannin-based resol resin adhesives and their mechanisms. However, very few studies have been done on the making of resol-type aqueous phenol resin adhesives from the whole untreated wood or the modified wood wastes.

About 600 000 tones of cotton stalks and about 10 million tones are annually produced in Turkey and in the world, which are considered as a waste and used only as a source of energy (Eroglu 1988). Recently, large amounts of the agricultural wastes have became very attractive natural sources for the investigators to increase their values. In one of our previous studies, the cotton stalk wastes were successfully evaluated in the production novolak-type molding materials (Indonesia paper). On the other hand, it is known that resol type cotton stalk adhesives (phenol-formaldehyde resin) have been prepared by the reaction of phenol with formaldehyde in the presence of NaOH. Recently, this type of adhesive has been prepared from cotton stalk, barks and tannins (Ayla 1984, Gama 1984, Pizzi 1994) used as replacement for phenol. However, no one has used cotton stalks as replacement of phenol in the production of resol-type adhesives so far.

Therefore, in this study, the cotton stalks are liquefied with phenol at different acid concentration, temperature and times.

MATERIAL AND METHODS

Liquefaction of cotton stalks with phenol

The powders of cotton stalk (*Gossypium hirsutum* L.) (150 mμ). "Guaranteed reagent grade" phenol (organic solvent), 98 % sulfuric acid and 40 % aqueous NaOH (catalysts for liquefaction and resinification of cotton stalk, respectively) and methanol (solvent) were purchased from Carlo Erba Reagenti Chemical Co. on the other hand, walnut and wheat flour were used as filler in the adhesives.

A mixture of oven-dried powders 10 g of cotton stalks, phenol 20 g and 98 % H_2SO_4 (3 %, 5 % and 7 % based on the total amounts of phenol) were first heated in a-three-necked round bottom flask placed in an oil bath at 130 °C, 150 °C and 170 °C for 1/2, 1, 2 and 3 h and then the reaction temperature (Tab. 1-3) was decreased to about 100 °C under ambient conditions.

Tab. 1: Reaction conditions and chemical amounts used at 130 °C

Number	CS/ P[1]	H_2SO_4[2] (g)	CS[3] (g)	P[4] (g)	t[5] (min)	T[6] (°C)
C_{13}	1:2	0.612 (3%)	10	20	30	130
C_{14}	1:2	0.612 (3%)	10	20	60	130
C_{15}	1:2	0.612 (3%)	10	20	120	130
C_{16}	1:2	0.612 (3%)	10	20	180	130
C_{17}	1:2	1.020 (5%)	10	20	30	130
C_{18}	1:2	1.020 (5%)	10	20	60	130
C_{19}	1:2	1.020 (5%)	10	20	120	130
C_{20}	1:2	1.020 (5%)	10	20	180	130
C_{21}	1:2	1.428 (7%)	10	20	60	130
C_{22}	1:2	1.428 (7%)	10	20	120	130
C_{23}	1:2	1.428 (7%)	10	20	180	130

[1]CS/P: Cotton Stalk/Phenol Ratio, [2]H_2SO_4: Quantity of Phenol Devoted to % Weight, [3]CS: Quantity of Cotton Stalk, [4]F: Quantity of Phenol, [5]t: Time, [6]T: Temperature.

Tab. 2: Reaction conditions and chemical amounts used at 150 °C

Number	CS/ P[1]	H_2SO_4[2] (g)	CS[3] (g)	P[4] (g)	t[5] (min)	T[6] (°C)
C_8	1:2	0.612 (3%)	10	20	30	150
C_{10}	1:2	1.020 (5%)	10	20	30	150
C_{12}	1:2	1.428 (5%)	10	20	30	150
C_6	1:2	1.428 (7%)	10	20	60	150
C_7	1:2	1.020 (5%)	10	20	60	150
C_1	1:2	0.625 (3%)	10	20	60	150
C_4	1:2	1.020 (5%)	10	20	60	150
C_2	1:2	0.612 (3%)	10	20	120	150
C_3	1:2	1.020 (5%)	10	20	120	150
C_5	1:2	1.428 (7%)	10	20	120	150
C_9	1:2	0.612 (3%)	10	20	180	150
C_{11}	1:2	1.020 (5%)	10	20	180	150

[1]CS/P: Cotton Stalk/Phenol Ratio, [2]H_2SO_4: Quantity of Phenol Devoted to % Weight, [3]CS: Quantity of Cotton Stalk, [4]F: Quantity of Phenol, [5]t: Time, [6]T: Temperature.

Tab. 3: Reaction conditions and chemical amounts used at 170 °C

Number	CS/ P[1]	H_2SO_4[2] (g)	CS[3] (g)	P[4] (g)	t[5] (min)	T[6] (°C)
C_{24}	1:2	0.612 (3%)	10	20	30	170
C_{25}	1:2	0.612 (3%)	10	20	60	170
C_{26}	1:2	0.612 (3%)	10	20	120	170
C_{27}	1:2	1.020 (5%)	10	20	30	170

[1]CS/P: Cotton Stalk/Phenol Ratio, [2]H_2SO_4: Quantity of Phenol Devoted to % Weight, [3]CS: Quantity of Cotton Stalk, [4]F: Quantity of Phenol, [5]t: Time, [6]T: Temperature.

The resulting reaction mixture was dissolved with methanol and filtrated with a glass-fiber filter (filter paper (Selecta filter, 589 Weiβband, Germany). While the methanol-insoluble parts, the so-called "unliquefied cotton stalk", were mainly discarded, the methanol-soluble parts were evaporated at 50 °C under vacuum in order to remove the methanol.

Determination of percent unliquefied cotton stalks

In order to determine the percent unliquefied cotton stalk residue, mixtures obtained at the end of cotton stalk-phenolation stage were diluted with methanol and filtered as described above. The remaining residue was oven-dried at 103±2 °C in an oven and weighed. Finally, percent unliquefied cotton stalk residue (UC_r) was determined by the following equation (1):

$$UC_r = \frac{C_r}{C_0} x\,100 \qquad (\%) \tag{1}$$

where, C_0 is the oven-dry amount of starting cotton stalk material (g) and C_r is the oven-dry amount of unliquefied cotton stalk residues determined after the stage (g).

Determination of percent combined phenol

In order to determine the percentage of combined phenol in resultant resin, (i.e., percent phenol reacted, essentially, with various degraded components of the cane along with sulfuric acid and phenol itself), the amounts of free phenol remaining in the methanol-soluble part were first measured by using high performance liquid chromatography (HPLC) (Cecil 1100 series) equipped with a SPD-10A UV-vis detector (254 nm) and Zorbax ODS column (4,6 x 25 cm). Measurements were done at 40 °C and a flow rate of 3 mL/min using a methanol/water solution (1/2, v/v) as

the mobile phase. Moreover, phenol was used as a standard solution. For the measurements, the methanol-soluble part (10 mL) having a concentration of 0.1 % was injected into the HPLC apparatus. And then, the amount of combined phenol so-called "percent combined phenol" was determined as follows:

$$\chi_A = \frac{w_{A0} - w_A}{w_{A0}} x\,100 \qquad (\%) \tag{2}$$

where w_{A0} and w_A are the amounts of starting phenol (g) and phenol remained after the liquefaction (g), respectively.

RESULTS AND DISCUSSION

Figs. 1-2. shows depending on 130 ˚C and 150 ˚C temperature the relationship between 3 %, 5 % and 7 % acid concentration and percentage of unliquefied cotton stalk. As shown in this figure, the percentage of unliquefied cotton stalks slightly decreases. The percent combined phenol, mainly, with degraded wood components, somewhat phenol and sulfuric acid is demonstrated. As depicted in this figure, the percentage of combined phenol linearly increases with increasing the acid concentration from 3 %, 5 % and 7 % and become almost constant.

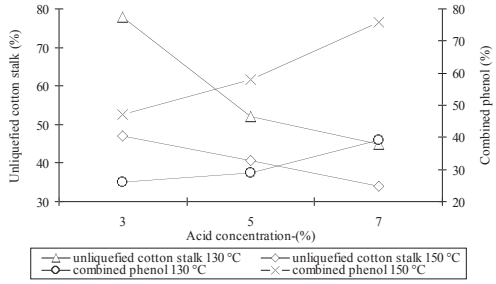

Fig. 1: Relationship between acid (H_2SO_4) concentration (based on phenol, w/w) and the percentage of unliquefied cotton stalk and the combined phenol. Time: 60 min. Phenol/cotton stalk (w/w): 2. Cotton number studied: 130 °C: C_{14}-C_{18}-C_{21}, 150 °C: C_1-C_4-C_6

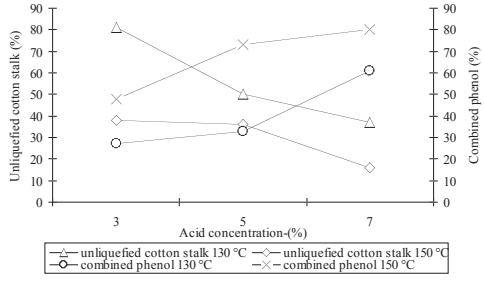

Fig. 2: Relationship between acid (H_2SO_4) concentration (based on phenol, w/w) and the percentage of unliquefied cotton stalk and the combined phenol. Time: 120 min. Phenol/cotton stalk (w/w): 2. Cotton number studied: 130 °C: C_{15}-C_{19}-C_{22}, 150 °C: C_2-C_3-C_5

Fig. 3 shows depending on 130 °C and 150 °C temperature the relationship between 1/2, 1, 2 and 3 h time and percentage unliquefied cotton stalk. As shown in this figure, the percentage unliquefied cotton stalks slightly decreases. The percentage of phenol combined, mainly, with degraded wood components, somewhat phenol and sulfuric acid is demonstrated. As depicted in this figure, the percentage combined phenol linearly increases with increasing the time from 1/2, 1, 2 and 3 h and become almost constant.

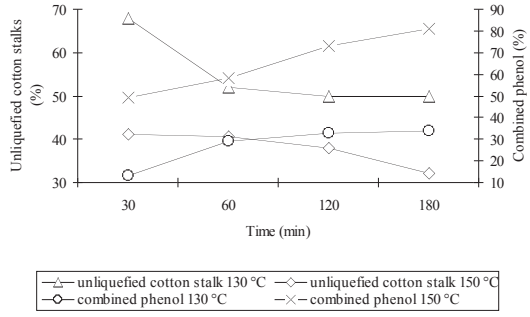

Fig. 3: Relationship between time and the percentage unliquefied cotton stalk and the combined phenol. Acid concentration: 5 %. Phenol/cotton stalk (w/w): 2. Cotton number studied: 130 °C: C_{17}-C_{18}-C_{19}-C_{20}, 150 °C: C_{12}-C_4-C_3-C_{11}

Fig. 4 shows depending on 1, 2 and 3 h time the relationship between 3 %, 5 % and 7 % acid concentration and percentage unliquefied cotton stalk. As shown in this figure, the percentage of unliquefied cotton stalks slightly decreases. The percentage phenol combined, mainly, with degraded wood components, somewhat phenol and sulfuric acid is demonstrated. As depicted in this figure, the percentage combined phenol linearly increases with increasing the acid concentration from 3 %, 5 % and 7 % and become almost constant.

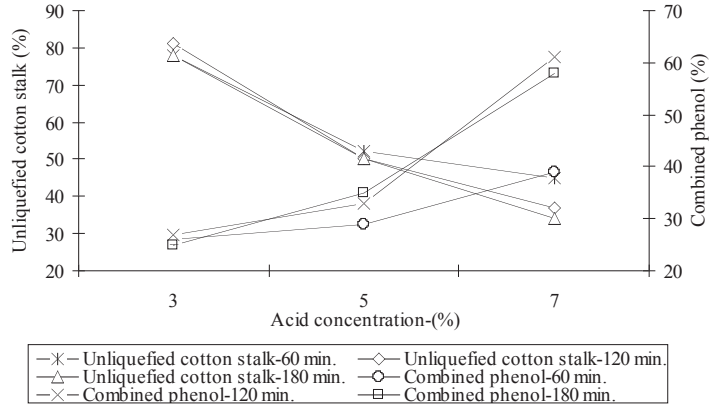

Fig. 4: Relationship between acid (H_2SO_4) concentration (based on phenol, w/w) and the percentage unliquefied cotton stalk and the combined phenol. Temperature: 130 °C. Phenol/cotton stalk (w/w): 2. Cotton number studied: 60 min: C_{14}-C_{18}-C_{21}, 120 min: C_{15}-C_{19}-C_{22}, 180 min: C_{16}-C_{20}-C_{23}

Fig. 5 shows depending on 1 and 2 h time the relationship between 3 %, 5 % and 7 % acid concentration and percentage unliquefied cotton stalk. As shown in this figure, the percentage unliquefied cotton stalks slightly decreases. The percentage phenol combined, mainly, with degraded wood components, somewhat phenol and sulfuric acid is demonstrated. As depicted in this figure, the percentage combined phenol linearly increases with increasing the acid concentration from 3 %, 5 % and 7 % and become almost constant.

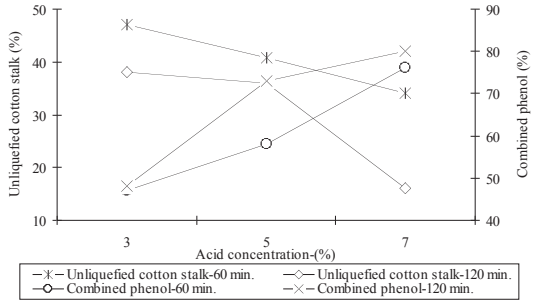

Fig. 5: Relationship between acid (H_2SO_4) concentration (based on phenol, w/w) and the percentage unliquefied cotton stalk and the combined phenol. Temperature: 150 °C. Phenol/cotton stalk (w/w): 2. Cotton number studied: 60 min: C_1-C_4-C_6, 120 min: C_2-C_3-C_5

Fig. 6 shows depending on 1/2 and 3 h time the relationship between 3 % and 5 % acid concentration and percentage unliquefied cotton stalk. As shown in this figure, the percentage unliquefied cotton stalks slightly decreases. The percentage phenol combined, mainly, with degraded wood components, somewhat phenol and sulfuric acid is demonstrated. As depicted in this figure, the percentage of combined phenol linearly increases with increasing the acid concentration from 3 % and 5 % and become almost constant.

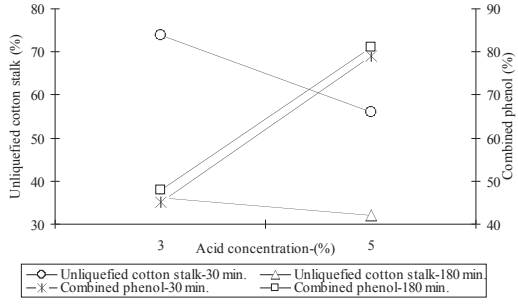

Fig. 6: Relationship between acid (H_2SO_4) concentration (based on phenol, w/w) and the percentage unliquefied cotton stalk and the combined phenol. Temperature: 150 °C. Phenol/cotton stalk (w/w): 2. Cotton number studied: 30 min: C_8-C_{10}, 180 min: C_9-C_{11}

Fig. 7 shows depending on 1/2 h time the relationship between 3 % and 5 % acid concentration and percentage unliquefied cotton stalk. As shown in this figure, the percentage unliquefied cotton stalks slightly decreases. The percentage phenol combined, mainly, with degraded wood

components, somewhat phenol and sulfuric acid is demonstrated. As depicted in this figure, the percentage of combined phenol linearly increases with increasing the acid concentration from 3 % and 5 % and become almost constant.

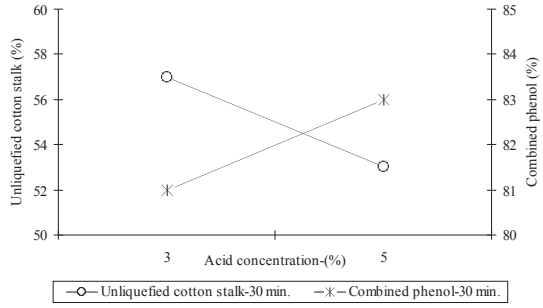

Fig. 7: Relationship between acid (H_2SO_4) concentration (based on phenol, w/w) and the percentage unliquefied cotton stalk and the combined phenol. Temperature: 170 °C. Phenol/cotton stalk (w/w): 2. Cotton number studied: 30 min: C_{24}-C_{27}

Fig. 8: shows depending on 1/2, 1 and 2 time the relationship between 130, 150 and 170 °C temperature and percentage unliquefied cotton stalk. As shown in this figure, the percentage unliquefied cotton stalks slightly decreases. The percentage phenol combined, mainly, with degraded wood components, somewhat phenol and sulfuric acid is demonstrated. As depicted in this figure, the percentage of combined phenol linearly increases with increasing the acid concentration from 130, 150 and 170 °C and become almost constant.

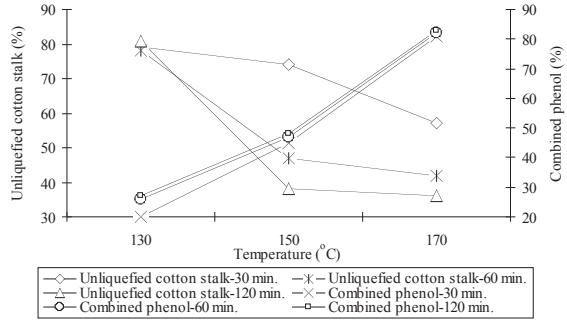

Fig. 8: Relationship between temperature and the percentage unliquefied cotton stalk and the combined phenol. Acid concentration: 3 %. Phenol/cotton stalk (w/w): 2. Cotton number studied: 30 min: C_{13}-C_8-C_{24}, 60 min: C_{14}-C_1-C_{25}, 120 min: C_{15}-C_2-C_{26}

Fig. 9 shows depending on 1, 2 and 3 time the relationship between 130 and 150 °C temperature and percentage unliquefied cotton stalk. As shown in this figure, the percentage unliquefied cotton stalks slightly decreases. The percentage phenol combined, mainly, with degraded wood components, somewhat phenol and sulfuric acid is demonstrated. As depicted in this figure, the percentage combined phenol linearly increases with increasing the acid concentration from 130 and 150 °C and become almost constant.

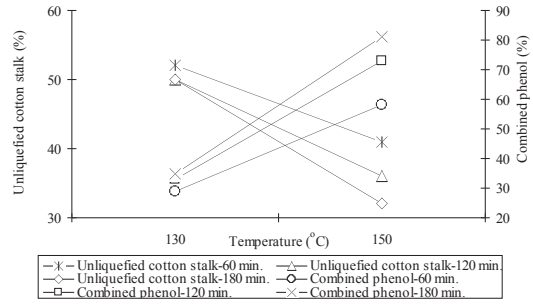

Fig. 9: Relationship between temperature and the percentage unliquefied cotton stalk and the combined phenol. Acid concentration: 5 %. Phenol/cotton stalk (w/w): 2. Cotton number studied: 30 min: C_{18}-C_4, 60 min: C_{19}-C_3, 120 min: C_{20}-C_{11}

Fig.10 shows depending on 1 and 2 time the relationship between 130 and 150 ˚C temperature and percentage unliquefied cotton stalk. As shown in this figure, the percentage of unliquefied cotton stalks slightly decreases. The percentage of combined phenol, mainly, with degraded wood components, somewhat phenol and sulfuric acid is demonstrated. As depicted in this figure, the percentage of combined phenol linearly increases with increasing the acid concentration from 130 and 150 ˚C and become almost constant.

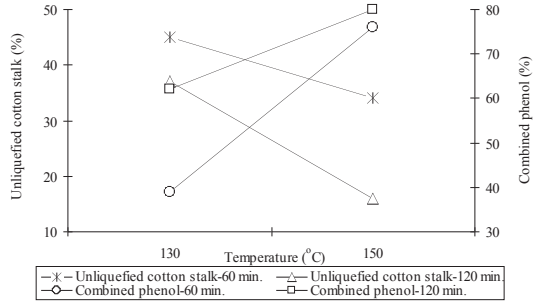

Fig. 10: Relationship between temperature and the percentage unliquefied cotton stalk and the combined phenol. Acid concentration: 7 %. Phenol/cotton stalk (w/w): 2. Cotton number studied: 60 min: C_{21}-C_6, 120 min: C_{22}-C_5

In the present study, cotton stalk wastes were successfully liquefied with phenol in the presence of H_2SO_4 as catalyst at 130, 150 and 170 ˚C. About 90 % of cotton stalk was found to dissolve into phenol at the studied conditions.

CONCLUSION

In the present study, cotton stalks wastes were successfully liquefied with constant amount of phenol, at various concentration of H_2SO_4 as catalyst at different reaction times. It shows that the reactions with 7 % percent H_2SO_4 for 2 hours gave the best result as the smaller amount of unliquefied cotton stalks were left and the highest amount of combined phenol in the produced resin were obtain.

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