

# Effect of temperature on the surface free energy and its polar component of corn stover fibers

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The contact angles of three probe liquids on the surface of corn stover fibers treated at different temperatures were tested by capillary rise method. Based on Washburn equation and the method suggested by Owens-wendt-Kaelble, the surface free energy and the corresponding polar and dispersive components were calculated. The results demonstrated that the contact angles of distilled water on corn stover fibers treated at elevated temperatures increased and that of formamide decreased, the surface free energy and the corresponding dispersive component of corn stover fibers were 28.88 mN/m and 6.68 mN/m, respectively. When the heat treatment time was 1 h, as the elevated treated temperature, the surface free energy of corn stover fibers decreased, its dispersive component increased, and its polar component decreased. The reasons for these results were discussed as well in this paper. The results confirm that this method of calculating the surface free energy and its components of cellulosic biomass is a useful and low-cost semi-quantitative measure of the surface characteristics of cellulosic biomass.

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## 1. Introduction

Cellulosic biomass is a natural polymer composite, made up mainly of 38%-50% cellulose, 23%-32% hemicellulose, 15%-25% lignin, and a small amount of extractives [1]. The adhesion between polar hydrophilic cellulosic biomass and non-polar hydrophobic materials is very poor. In order to improve the interfacial adhesion, a number of studies have been carried out [2-8]. Some methods are based on cellulosic biomass modification (physical or chemical) and others are based on the addition of a coupling agent for interfacial adhesion improvement. But very few studies about the surface characteristics of cellulosic biomass have been made and the purpose of this study was to investigate the effect of temperature on the surface free energy and its polar component of corn stover. The contact angles of different probe liquids on the surface of corn stover treated at different temperatures were tested by capillary rise methods. Based on Washburn equation and the method suggested by Owens-wendt-Kaelble, the surface free energy and the corresponding dispersive and polar components were calculated.

## 2. Experimental

### 2.1 Materials

The corn stover fibers used in this study were collected from a local sawmill and manually screened. 60-80 mesh wood particles were stored in sealed plastic bags and were classified into three fractions, then were treated at 100°C, 140°C, 180°C for 1 h prior to experiment, respectively.

Methanol, formamide were provided by Xi'an Sanpu Chemical Plant, and distilled water was prepared in the laboratory by myself.

### 2.2 Contact angle measurement

According to Washburn equation [9]:

$$h^2 = \frac{\gamma_L R t \cos \theta}{2 \eta} \quad (1)$$

Where h is the height of liquid penetration into the capillary at time t;  $\gamma_L$  is the surface free energy of liquid;  $\eta$  is the viscosity of liquid;  $\theta$  is the contact angle of the liquid against a solid; R is the average effective radius of capillary.

If make

$$K = \frac{\gamma_L R \cos \theta}{2 \eta} \quad (2)$$

The equation (1) will be transformed into

$$h^2 = K t \quad (3)$$

K can be obtained from the coefficient of the equation of  $h^2$ -t based on the experiment.

Then

$$R = \frac{2 K \eta}{\gamma_L \cos \theta} \quad (4)$$

And

$$\cos \theta = \frac{2 K \eta}{\gamma_L R} \quad (5)$$

The contact angles of different liquids against a solid can be determined by the equation of  $h^2$ -t. The corn stover fibers system can be considered as a capillary system, and the average effective radius of capillary can be considered as a constant when the filled conditions (the filled speed, height and weight) of corn stover fibers in the glass tube are identical, it can be calculated as per the liquid whose contact angle against corn stover fibers is zero. Then the contact angles of other liquids against corn stover fibers can be obtained according to equation (5).

The corn stover fibers were filled in the glass tube under the same condition (the same speed, height and weight), then the filled glass tubes were fixed upon the liquid for 2 h to reach adsorption balance of liquid molecules on the surface of corn stover fibers. After that, the height of glass tube was adjusted to make sure the glass tube was in the liquid for 2 mm. When the liquid rose to the 2 mm scale line, the stopwatch began to work, and the height (h) of liquid in the glass tube and the time (t) of rising were recorded at a certain interval. Six replicates were tested for a certain liquid and the mean was used.

### 2.3 Calculation of surface free energy and its polar component

The principle of calculating the surface free energy of a solid and its polar component through the contact angles of liquids against the solid is the equation of Young [10-12]:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (6)$$

Where  $\gamma_{SV}$  is the surface free energy of the solid against its saturated vapor;  $\gamma_{SL}$  is the free energy of the interface between liquid and solid;  $\gamma_{LV}$  is the surface free energy of the liquid against its saturated vapor;  $\theta$  is the contact angle of a liquid against the solid.

According to the viewpoint of Owens-wendt-Kaelble [13, 14], the surface free energy of a solid can be divided into dispersion and polar components and the sum of the components is approximately equal to the surface free energy of the solid ( $\gamma_S^0 = \gamma_S^d + \gamma_S^p$ ). If there exist interactions of dispersion and polar forces between a solid and a liquid, the free energy of the interface between the liquid and the solid can be determined by the following equation:

$$\gamma_{SL} = \gamma_{LV} + \gamma_S^0 - 2(\gamma_S^d \times \gamma_{LV}^d)^{1/2} - 2(\gamma_S^p \times \gamma_{LV}^p)^{1/2} \quad (7)$$

Where  $\gamma_{SL}$  is the free energy of the interface between liquid and solid;  $\gamma_{LV}$  is the surface free energy of the liquid;  $\gamma_S^0$  is the surface free energy of the solid;  $\gamma_S^d$  is the dispersion component of the surface free energy of the solid;  $\gamma_S^p$  is the polar component of the surface free energy of the solid;  $\gamma_{LV}^d$  is the dispersion component of the surface free energy of the liquid;  $\gamma_{LV}^p$  is the polar component of the surface free energy of the liquid.

Then combine equation (7) into (6), and the difference between  $\gamma_S^0$  and  $\gamma_{SV}$  was ignored[14], the following equation can be obtained:

$$\gamma_{LV}(1 + \cos \theta) = 2(\gamma_S^d \times \gamma_{LV}^d)^{1/2} + 2(\gamma_S^p \times \gamma_{LV}^p)^{1/2} \quad (8)$$

In equation (8), only  $\gamma_S^d$  and  $\gamma_S^p$  are unknown, if we can find two liquids whose  $\gamma_{LV}^d$  and  $\gamma_{LV}^p$  are known,  $\gamma_S^d$  and  $\gamma_S^p$  can be calculated through the contact angles of the two liquids against the solid.

Here methanol was chosen as the liquid whose contact angle against the poplar wood-flour is zero because of its low surface free energy (22.5 mN/m). Therefore, the average effective radius of capillary R can be calculated as per the equation (4). Then the contact angles of distilled water and formamide against the corn stover fibers can be obtained from equation (5). The  $\gamma_S^d$  and  $\gamma_S^p$  of corn stover fibers can be calculated by equation (8). The dispersive and polar components of the surface free energies and viscosities of probe liquids in the experiment were given in Table 1 [15].

Table 1. The surface free energies, corresponding components and viscosities of probe liquids.

Items Probe liquids	$\gamma_{LV}$ mN/m	$\gamma_{LV}^d$ mN/m	$\gamma_{LV}^p$ mN/m	$\eta^*$ mN·s/m <sup>2</sup>
Distilled water	72.8	21.8	51	1.175
Formamide	57.9	34.4	23.5	4.641
Methanol	22.5	22.5	0	0.619

$\eta^*$  was the viscosity of probe liquids at the ambient temperature which was measured by Ubbelohde viscometer.

## 3. Results and discussion

### 3.1 The contact angles of three probe liquids on corn stover fibers

Fig.1 to Fig.3 show the curves of  $h^2$  (mm<sup>2</sup>)-t (s) of three probe liquids on corn stover fibers which were treated at 100 °C, 140 °C, 180 °C for 1 h, respectively. The values of K and cosine of contact angles of probe liquids on corn stover fibers which were treated at

100 °C, 140 °C, 180 °C for 1 h, respectively, were listed in Table 2.

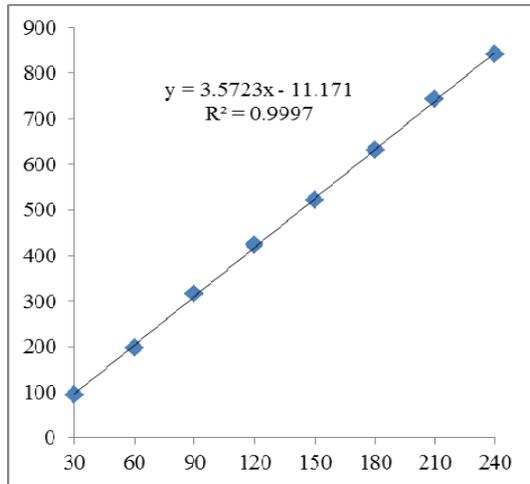


Fig.1A. The curve of  $h^2$  ( $mm^2$ )- $t$  (s) of methanol on corn stover fibers which were treated at 100 °C for 1 h.

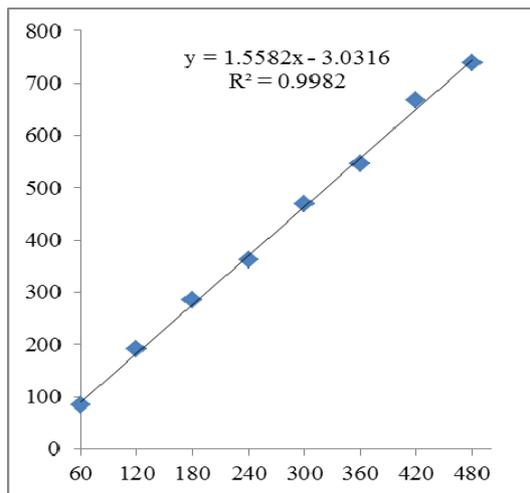


Fig.1B. The curve of  $h^2$  ( $mm^2$ )- $t$  (s) of distilled water on corn stover fibers which were treated at 100 °C for 1 h

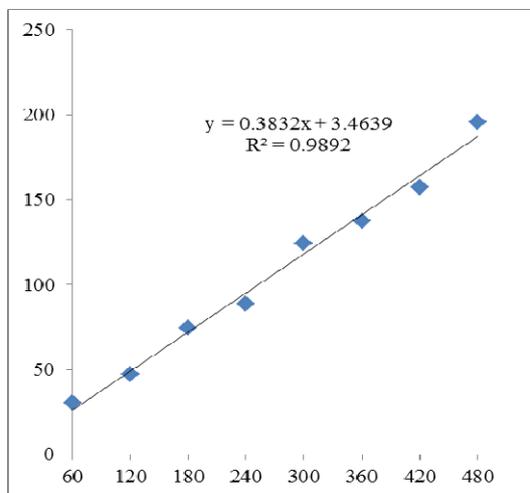


Fig.1C. The curve of  $h^2$  ( $mm^2$ )- $t$  (s) of formamide on corn stover fibers which were treated at 100 °C for 1h

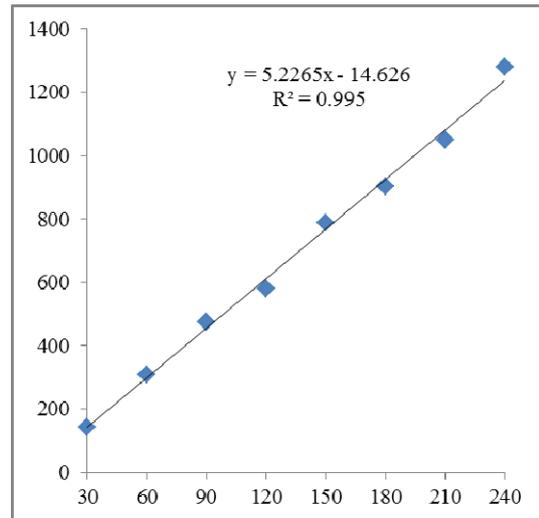


Fig.2A. The curve of  $h^2$  ( $mm^2$ )- $t$  (s) of methanol on corn stover fibers which were treated at 140 °C for 1 h

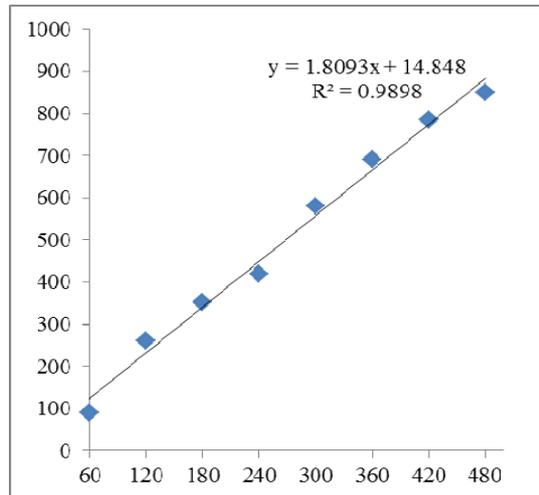


Fig.2B. The curve of  $h^2$  ( $mm^2$ )- $t$  (s) of distilled water on corn stover fibers which were treated at 140 °C for 1 h

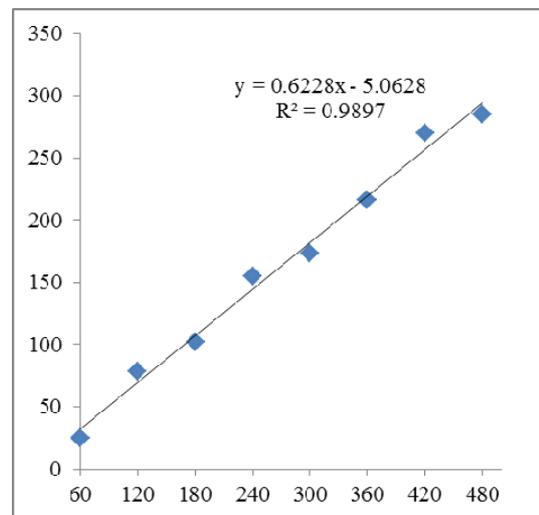


Fig.2C. The curve of  $h^2$  ( $mm^2$ )- $t$  (s) of formamide on corn stover fibers which were treated at 140 °C for 1 h

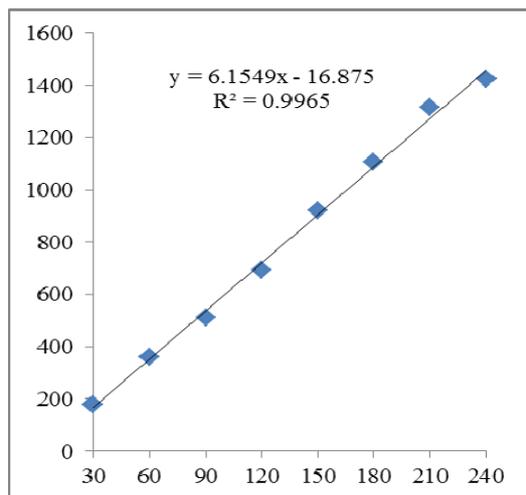


Fig.3A. The curve of  $h^2$  ( $\text{mm}^2$ )- $t$  (s) of methanol on corn stover fibers which were treated at 180 °C for 1 h

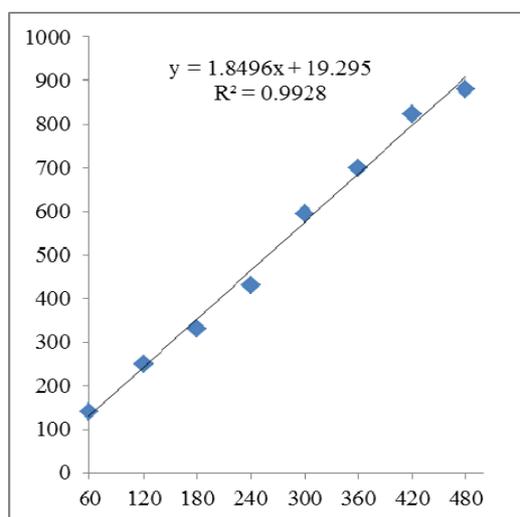


Fig.3B. The curve of  $h^2$  ( $\text{mm}^2$ )- $t$  (s) of distilled water on corn stover fibers which were treated at 180 °C for 1 h

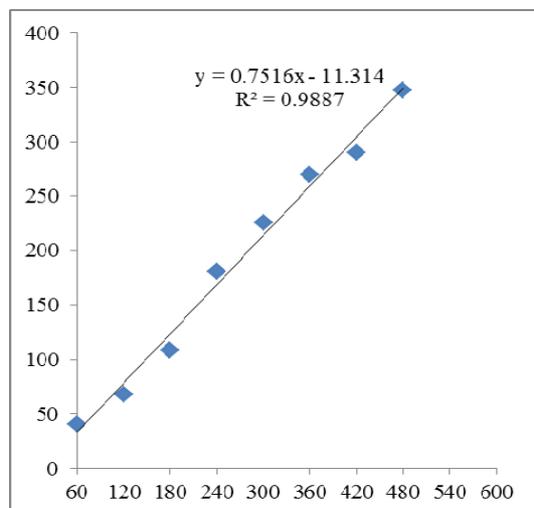


Fig.3C. The curve of  $h^2$  ( $\text{mm}^2$ )- $t$  (s) of formamide on corn stover fibers which were treated at 180 °C for 1 h

Table 2. The values of  $K$  and cosine of contact angles of probe liquids on corn stover fibers which was treated at 100 °C, 140 °C, 180 °C for 1 h, respectively

Temperatures Probe liquids	100 °C		140 °C		180 °C	
	K	cos $\theta$	K	cos $\theta$	K	cos $\theta$
Methanol	3.572	1.000	5.226	1.000	6.154	1.000
Distilled water	3	0	5	0	9	0
Formamide	1.558	0.255	1.809	0.203	1.849	0.176
	2	9	3	1	6	3
	0.383	0.312	0.622	0.347	0.751	0.355
	2	5	8	2	6	8

As can be seen from Table 2, the values of cosine of contact angles of distilled water on corn stover fibers decreased as elevated temperature; however, the values of cosine of contact angles of formamide on corn stover fibers increased as elevated temperature. The reasons for these were as following: the polarity of distilled water was strong and the polarity of formamide was weaker than distilled water, the surface polarity of corn stover fibers decreased as elevated temperature, so distilled water spread on the surface of corn stover fibers more difficultly and formamide spread on the surface of corn stover fibers more easily.

### 3.2 The surface free energies and its components of corn stover fibers

The surface free energies and its components of poplar corn stover fibers treated at different temperatures were derived from plugging the values of  $\cos\theta$ ,  $\gamma_{LV}^d$  and  $\gamma_{LV}^p$  of distilled water and formamide into the equation (8) and listed in Table 3. Table 3 shows that as the elevated treated temperature, the surface free energy of corn stover fibers decreased, its dispersive component which reflected the dispersion force increased, and its polar component which reflected the surface polarity decreased. These should be due to the dehydration and the hydrogen bonds association of hydroxyl of corn stover fibers, and the formation of ether linkage among hydroxyls at high temperature which led to the decrease of hydroxyl and the increase of non-polar functional groups on the surface of corn stover fibers.

Table 3. The surface free energies and its components of corn stover fibers after 1 h treatment at different temperatures

Items	$\gamma_s$	$\gamma_s^d$	$\gamma_s^p$
Temperatures	(mN/m)	(mN/m)	(mN/m)
100 °C	28.88	6.68	22.20
140 °C	26.92	11.84	15.08
180 °C	26.71	14.28	12.43

#### 4. Conclusion

The contact angles of three probe liquids on the surface of corn stover fibers treated at different temperatures were tested by capillary rise method. Based on Washburn equation and the method suggested by Owens-wendt- Kaelble, the surface free energy and the corresponding dispersive and polar components were calculated. The surface free energies and the corresponding dispersive components and polar components of the corn stover fibers treated for 1 h were 28.88 mN/m, 6.68 mN/m and 22.20 mN/m at 100 °C, 26.92 mN/m, 11.84 mN/m and 15.08 mN/m at 140 °C, 26.71 mN/m, 14.28 mN/m and 12.43 mN/m at 180 °C, respectively. As the elevated treated temperature, the surface free energy of corn stover fibers decreased, its dispersive component which reflected the dispersion force increased, and its polar component which reflected the surface polarity decreased. These indicated that high temperature treatment can make the surface polarity of corn stover fibers decrease to improve the compatibility between corn stover fibers and non-polar hydrophobic materials.

The results confirm that this method of calculating the surface free energy and its components of cellulosic biomass is a useful and low-cost semi-quantitative measure of the surface characteristics of cellulosic biomass.

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