DVS Application Note 57

Characterisation of Wheat Straw for Bio-fuel Application

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Biomass, such as wheat straw is an abundant and inexpensive natural biopolymer rich in cellulose and hemicellulose [1] which can be converted into bio-fuel. The bio-fuel has been attracting attention due to the future potential shortages of fossil fuel [2,3]. One of the crucial steps of producing bio-ethanol from wheat straw is its pre-treatment which should facilitate the economic feasibility and yield efficient conversion into biofuel. This pre-treatment is expected to increase the accessible chemical sites of the straw to increase convertibility in subsequent hydrolysis and fermentation steps. Dynamic Vapour Sorption (DVS) [4] and UV were used to assess the wheat straw pre-treatment and sugar yield, respectively.

Introduction

Bio-fuel production is shown schematically in Figure 1, and in general includes the following steps: biomass handling, biomass pre-treatment, cellulose hydrolysis, glucose fermentation and finally ethanol recovery. Pentose from hemicelluloses after pre-treatment can be also used for ethanol production without hydrolysis. A common feature of the enzymatic hydrolysis step is the need for pre-treatment of the lignocellulosic biomass resulting in a more efficient reaction, which is a crucial step as it has direct impact on the subsequent yield of enzymatic hydrolysis to produce glucose and alcohol fermentation process in the production of bio-fuel. This pre-treatment is intended to disrupt the crystalline structure of microfibrils to release the polymer chains of cellulose and hemicellulose, and modify amorphous content and open up pores in the biomass to increase accessible site of straw to enzymatic activity, which could be indicated by increase in sorption uptake, specific surface area and hydrophilicity etc. The function of the pre-treatment is shown is Figure 2. These surface modifications can be quantitatively characterised in terms of the sorption and desorption behaviour using Dynamic Vapour Sorption technique.

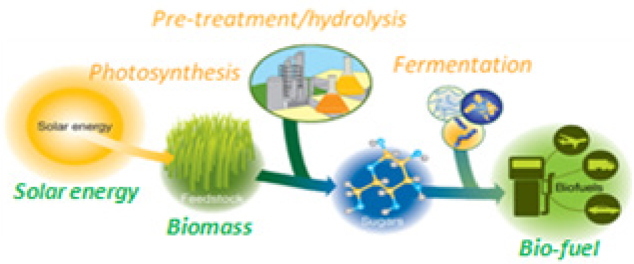

Figure 1. Schematic of bio-fuel production

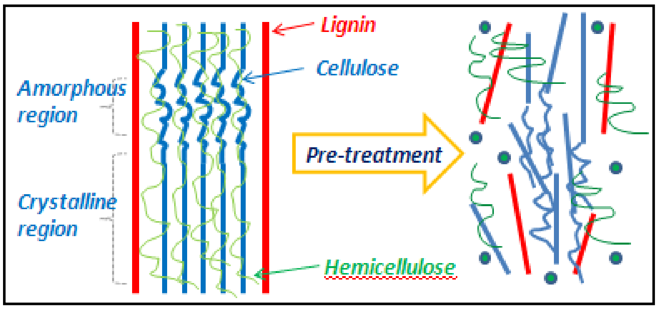

Figure 2. Schematic of pre-treatment

Method

Raw wheat straw (RWS) was pre-treated using a novel twin-strew extrusion technology which was recently reported with good potential for pre-treatment of lignocelluloses biomass [5,6,7,8] and has ability to provide high shear, rapid heat transfer, effective and rapid mixing and feasibility to combine with other pre-treatment – all in a continuous process. Detail of pre-treatment conditions and the illustration of the extruder are summarised in Table 1 and shown in Figure 3, respectively.

Table 1. Pre-treatment conditions of wheat straw

Sample	Pre-treatment conditions
Raw wheat straw RWS	Wheat straw as received without pre-treatment
Pre-treated straw WCB10009	Extruded at 100 rpm and 50°C with 4% NaOH (alkaline), Straw : H_2O = 1:2

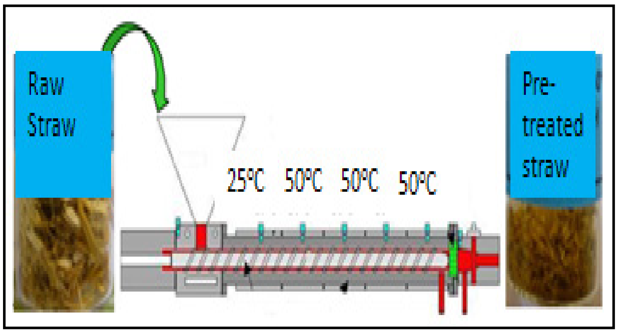

Figure 3. Illustration of the twin-screw extruder

Sample RWS is raw wheat straw without any pre-treatment. It is used for comparison with pre-treated sample (WCB10009). The pre-treated sample was extruded using a co-rotating twin-screw extruder with H_2O and alkaline (NaOH) at 50°C.

All water sorption measurements on the samples were performed using SMS dynamic vapour sorption instrument, DVS . During the measurements, the instrument was run in dm/dt mode (mass variation over time variation) to decide when equilibrium is reached. A fixed dm/dt value was selected at each RH segment. This criterion permits the DVS software to automatically determine when equilibrium has been reached and complete a relative humidity step. When the rate of change of mass falls below this threshold over a determined period of time, the relative humidity set point will proceed to the next programmed level. All analyses were carried out using the SMS DVS Analysis Suite version 6.1.1.2 and SMS DVS Analysis Suite version 6.1.1.2 (Advanced) macros.

Results

Figure 4 shows the dynamic water sorption behaviour on raw wheat straw sample (RWS) at 25°C. It can be seen that at lower relative humidity (RH < 50%), the equilibrium is established faster than the equilibrium at higher RH values. The low uptake at the lower RH is the contribution of surface sorption and the sorption is gradually developing from the surface into the bulk at higher RH, hence high uptake.

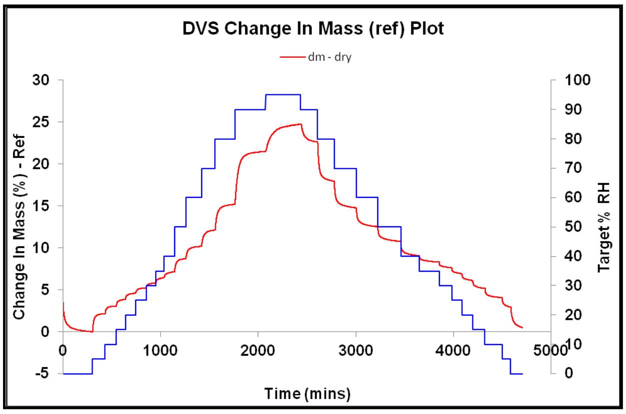

Figure 4. Dynamics of water sorption in raw wheat straw at 25ºC

The corresponding isotherms plotted in Figure 5 show a mixed Type II/III behaviour, indicated by low initial sorption and substantial uptake at higher RH. The Type II behaviour indicates a more or less surface monolayer sorption mechanism which makes BET surface calculation feasible via the water sorption measurement (organic solvents, e.g. octane, are usually used for BET surface area measurements by DVS). Since biomass pre-treament is, generally speaking, an aqueous thermal process, water sorption is therefore preferable. The hysteresis of the desorption further verifies the bulk sorption. The BET plot is shown in Figure 6, which indicates a specific surface area of 173.45 m^2/g.

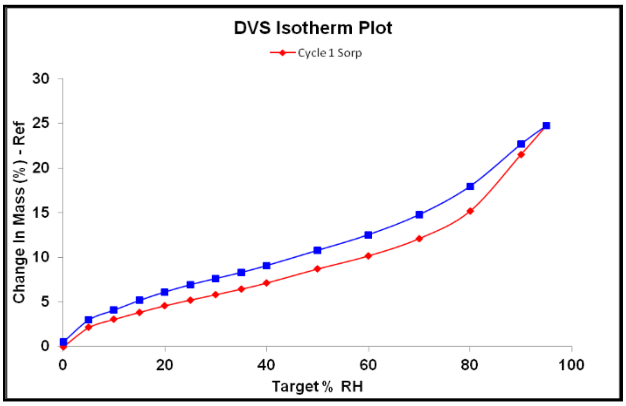

Figure 5. Isotherm of water sorption on raw wheat straw at 25 ºC

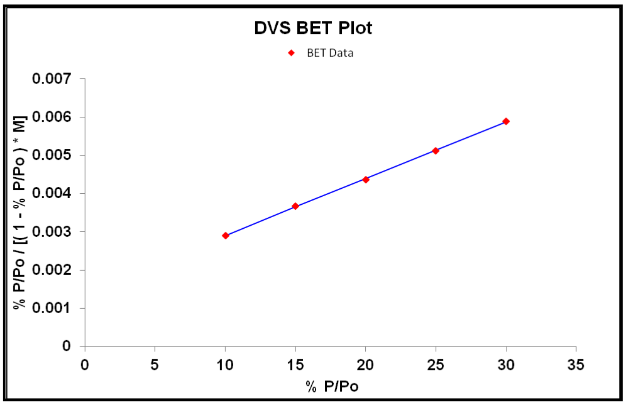

Figure 6. BET plot of water sorption on raw wheat straw at 25ºC

The water sotption measurement was also performed on the pre-treated sample (WCB10009) with the same experimental conditions. A superimposed plot of the isotherms of the two samples is shown in Figure 7. All isotherms show a mixed Type II/III behaviour.

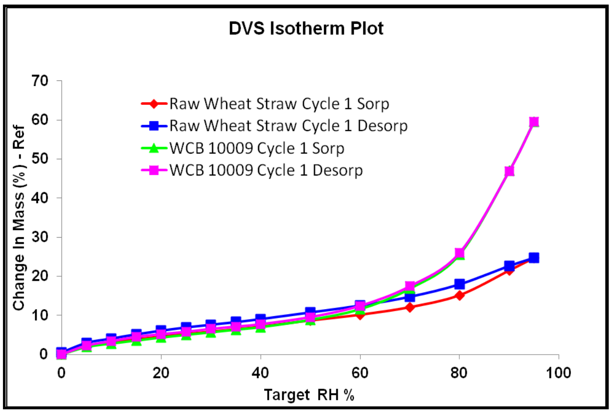

Figure 7. A superimposed plot of the isotherms of the pre-treated and untreated samples

In terms of total uptake at 95% RH, the pre-treated sample (WCB10009) has an uptake of 59.62% which is much higher than 24.76% of the untreated sample (RWS), indicating an open-up of more accessible sites to water molecules, which will be beneficial to subsequent hydrolysis process. One of the strategies employed in increasing enzymatic convertibility for fermentable sugars for bioethanol production is to decrease cellulose crystallinity [9] because amorphous region of the cellulose has faster hydrolysis rate than its crystalline region. Since most reactants, including water can mainly penetrate amorphous region and the surface of crystalline cellulose, so the uptake of water is also an indication of amorphous content of the biomass, i.e. the higher uptake, the higher amorphous content. Unlike the untreated sample, the water sorption behaviour on the pre-treated sample (WCB10009) does not show hysteresis. This is probably due to the swelling of the pores in the biomass, mainly in amorphous region of the cellulose and hemicellulose, hence less capillary force.

The results of BET specific surface measurements on the two samples are summarised in Table 2. It can be seen that the pre-treatment increases the specific surface area slightly, hence presents more accessible sites to hydrolytic reaction.

UV spectrum study on the pre-treated and the raw wheat straws shows that after pre-treatment, there is an increase by at least 30 times in glucose recovery in straw. The comparison of glucose yield of the raw wheat straw and the pre-treated wheat straw is shown in Figure 8.

Table 2. Summary of BET specific surface area of the two samples

Sample ID	BET specific surface area (m2/g)	Total uptake (%) at 95% RH
RWS	173.45	24.76
WCB10009	174.79	59.62

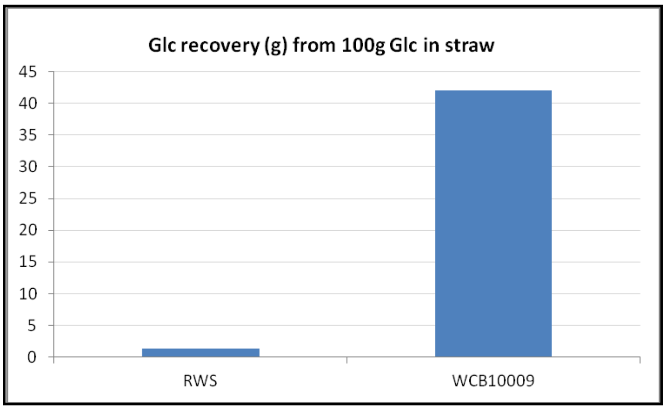

Figure 8. Yield of glucose recovery after enzymatic hydrolysis

Although the BET equation can be applied to any adsorption system where there are no adsorbate-adsorbate interactions, highly polar adsorbates such as water tend to have very strong adsorbate-adsorbate interactions and may adsorb preferentially at specific adsorption sites. In order to further support the surface area data on the straw samples, the isotherms have been fitted to the Young and Nelson isotherm model using the SMS Isotherm Suite, which contains a wide range of theoretical and semi-empirical equations to fit sorption isotherms. By deconvoluting the isotherms to monolayer and multilayer, the Young and Nelson model produces a term related to the strength of vapour interaction with the surface (E term), amount of vapor on the surface (A term) and amount of vapor in the bulk (B term).

Figures 9 and 10 show the Young and Nelson component plots for samples RWS and WCB10009, respectively. The Young and Nelson parameters for the samples are given in Table 3 and show that the surface interactions between the treated sample WCB 10009 and water molecules are significantly higher than the interactions of water and the untreated RWS sample. As a result of the enzymatic pre-treatment of sample WCB 10009 the water adsorption is considered to take place on the surface of the inner pores/cracks rather than on the exterior surface of the material. Therefore, the increase in the accessible site of straw to enzymatic activity is indicated by the increase in sorption properties, Young and Nelson constant E and specific surface area. The slight increase in the Young and Nelson parameter A for sample *WCB 10009* is consistent with the increase in the BET surface area value.

Table 3. BET specific surface area and Young and Nelson parameters for samples RWS and WCB 10009

Sample ID	BET specific surface area (m^2/g)	Young & Nelson Parameter Constant E	Young & Nelson Parameter A (mol/g)	Young & Nelson Parameter B (mol/g)
RWS	173.45	0.22	0.00246	0.002
WCB10009	174.79	5.25	0.00247	3.18×10^{-10}

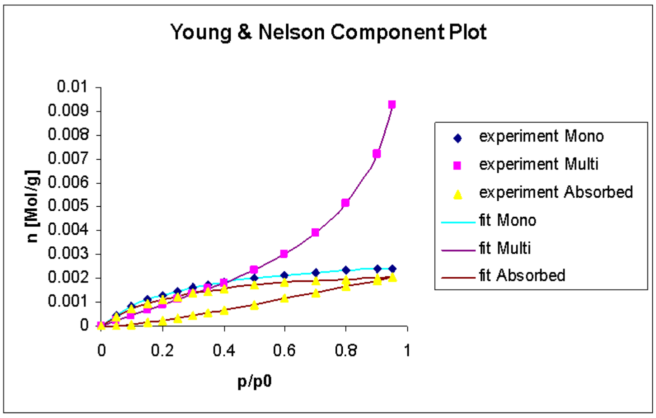

Figure 9. Young and Nelson component plots for the untreated RWS sample

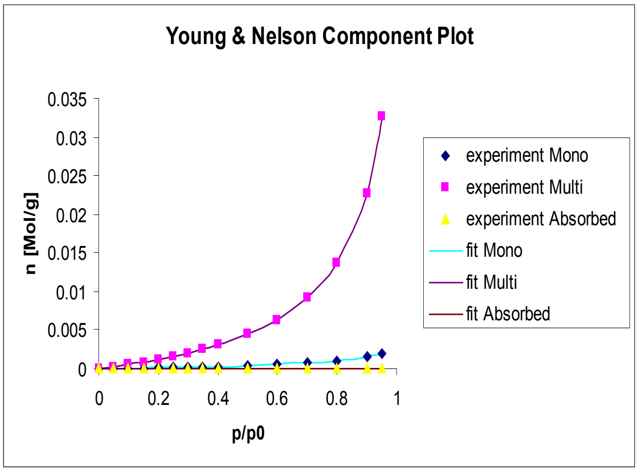

Figure 10. Young and Nelson component plots for the treated WCB 10009 sample

Conclusion

Two wheat straw samples were characterised with dynamic sorption technique using SMS DVS instrument. Results showed that the uptake of the water sorption, specific surface area, the strength of vapour interaction with the surface, and amorphous content of the pre-treated sample are higher than those of the untreated raw wheat straw sample, indicating that the sample pre-treated with the twin screw extrusion technique has more accessible sites for subsequent enzymatic hydrolysis process. This has a crucial impact on the yield of the biofuel production. HPLC study shows that there is an increase by at least 30 times in glucose recovery in straw.

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