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# HOT COMPRESSED WATER TREATMENT OF SOLID WASTE MATERIAL FROM THE SUGAR INDUSTRY FOR VALUABLE CHEMICAL PRODUCTION

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## ABSTRACT

Sugarcane bagasse, the solid waste material produced in the sugar industry, was subjected to treatment in hot compressed water. The experiments were performed in a batch-type reactor containing slurry of 10 ml of water and 1.2 g of solids. The reactor was heated to temperatures ranging between 200°C and 300°C for reaction times of 3 to 30 min. The product was separated into liquid and solid fractions. Each fraction was analyzed to investigate the alteration of the main lignocellulosic polymers by hot compressed water. Results for the liquid fractions showed that increased temperatures and reaction times completely dissolved hemicellulose and cellulose in the water, leaving lignin in the solid product. During treatment, hemicellulose and cellulose gradually decomposed into simple sugars, which were then degraded and decomposed into furfural, 5-(hydroxymethyl)furfural (5-HMF) and organic acids. However, the yield of furans and some organic acids decreased and became undetectable at 300°C and with increasing reaction time. *The solid fraction was also characterized before and after treatment. Results*

*showed that the* hydrogen and oxygen content of the solids decreased with increased reaction

conditions, due to dehydration and decarboxylation reactions. The reactions also increased the carbon content of the treatment products by 1.2–1.6 times that in the raw material, *suggesting*

*that the hot compressed water treatment of sugarcane bagasse can be considered for the provision of valuable chemicals for biofuel and high-carbon-content material (biochar).*

**Keywords:** Agricultural waste, sugarcane bagasse, hot compressed water, lignocellulosic biomass, biofuel

## INTRODUCTION

Today, many researches are focusing on ways of biomass utilization from agricultural waste as an alternative source of raw material for chemical industries and biofuel production. The utilization of biomass has many advantages compared with fossil fuel; biomass is carbon oxide neutral, low content of sulfur, nitrogen and ash, sustainable and relative environmentally benign source of green energy (Demirbas 2001; Balat 2008; Zhang 2010).

Among of biomass from agricultural waste, sugarcane bagasse is one of an abundant agricultural waste with great potential for transformation into energy and chemical feedstock (Ju et al. 2010). Generally, during the extraction process in sugar factories, about 280 kg or about 30% of wet bagasse are produced from 1 ton of sugarcane (Rodrigues et al. 2003; Sun et al. 2004). Currently, often 50% of the waste is used as a primary fuel source for sugar mills to generate heat and power and to run the sugar milling process, while the remainder is stockpiled (Lavarack et al. 2002). The stockpiled bagasse is of low economic value and constitutes an environmental

problem for sugar mills and surrounding districts, especially if stockpiled for extended periods, due to the risk of spontaneous combustion (Lavarack et al. 2002).

In order to utilize and increase the economic value of sugarcane bagasse, several conversion methods have been proposed and carried out. The conversion methods are either biochemical/biotechnology methods or thermo-chemical methods, such as pyrolysis (Garcia-Pérez et al. 2001; Tsai et al. 2006) and hydrothermal methods (Sasaki et al. 2003; Boussarsar et al. 2009) of producing energy, pulp and paper, chemicals and fermentation-based products (Pandey et al. 2000).

Recently, hydrothermal treatment has attracted more interest than other thermo-chemical conversion processes. Comparing with other methods, the required temperature range of hydrothermal treatment is lower than for gasification and pyrolysis (Zhang et al. 2010). Hydrothermal treatment, particularly using hot compressed water, is suitable for material with high moisture content (Inoue et al. 2002). Hot compressed water has unique properties of density, dielectric constant, ion product, viscosity, diffusivity, electric conductance, and solvent ability. Hot compressed water has an ion product ( $K_w$ ) about three orders of magnitude higher than that of ambient liquid water; in this condition, water acts as an acid-base catalyst precursor (Kruse and Dinjus, 2007).

Furthermore, it enhances hydrolysis reactions and decomposes lignocellulosic polymer into useful chemicals that are dissolved into the liquid product (Kumagai et al. 2004; Yan et al. 2009; Yin et al. 2011; Yuliansyah et al. 2010) and remained a solid product with high caloric value (Hirajima et al. 2003; Yuliansyah et al. 2010; Inoue et al. 2002).

A search of the literature reveals only a few reports on the hydrothermal conversion of sugarcane bagasse, especially using hot compressed water. Most of those were focused only on pre-treatment of the material for fractionation of the three main lignocellulosic polymers (Allen et al. 1996; Sasaki et al. 2003), for bioethanol feedstock (Ju et al. 2010; Cardona et al. 2010) and for sugar production (Laser et al. 2002). Allen et al. (1996) and Sasaki et al. (2003) determined the decomposition temperature of sugarcane bagasse using a percolator-type reactor. From these studies, they reported that hemicelluloses and lignin were mainly extracted as a water-soluble fraction in the temperature range 200–230°C, while the cellulose fraction was either hydrolyzed at higher temperatures in the range 230–280°C, or was recovered as solid residue. These treatments were focused on decomposition of the main lignocellulosic polymers.

The decomposition reaction of cellulose and hemicellulose for production of other chemicals such as furans and organic acids from sugarcane bagasse has not previously been investigated and described in detail, probably because previous treatments were conducted at lower temperatures and for fixed reaction times. Thus, in the present study, we explored the possibility of producing valuable chemicals from sugarcane bagasse, particularly the decomposition products of cellulose and hemicelluloses. The decomposition products from cellulose and hemicelluloses such as glucose and furans compounds (such as furfural and 5-HMF) are important chemicals for bioethanol and for alkane biooil production. Therefore, the hot compressed water treatment was performed in order to understand the specific condition for chemicals production. The treatment was conducted by varying the temperature and reaction time in the ranges 200–300°C and 3–30 min. This study emphasized the effect of treatment conditions on the composition and yield recovery of compounds in the liquid product, and the

characteristics of the solid products were also examined in order to understand the decomposition mechanism occurring during the hot compressed water treatment.

## MATERIALS AND METHODS

### Raw material

Sugarcane bagasse provided by the sugar industry was ground using a cutting mill to form a powder with maximum 1.0 mm particle size, which was dried in oven at 60°C before commencing treatment. The composition of sugarcane bagasse was determined using procedure recommended by US National Renewable Energy Laboratory (NREL) (Sluiter et al. 2005).

Prior to analyzing the composition of the raw material, a sample was extracted using ethyl alcohol to determine wax content using a soxhlet extractor for 8 h at 80°C. Afterward, 0.15 g of de-waxed sample was dried and treated using 1.5 ml of 72 wt% H<sub>2</sub>SO<sub>4</sub> at 30°C for 1 hour. Subsequently, 42 ml of water was added to the treated sample and hydrolyzed for 1 hour in an autoclave at 121°C. The hydrolyzed sample was cooled, then filtered using a GP 16 glass filter under vacuum conditions with washed several times using hot water. The residue was then dried at 105°C overnight, and was noted as a Klason lignin (i.e. acid-insoluble lignin). At the same time, the concentration of sugars such as xylose, arabinose and glucose, as well as other chemicals in the filtrate, were analyzed by a high-performance liquid chromatography (HPLC). The chromatograph was equipped with a KC-811 column (JASCO) and refractive index (RI) detector (RI-2031, JASCO). The HPLC operated under the following conditions: oven

temperature 50°C, using 2 mM HClO<sub>4</sub> as the mobile phase, delivered at a flow rate of 0.7 ml/min.

Therefore, cellulose and hemicellulose were determined with the correlations:

$$\text{Cellulose (wt \%)} = \text{glucose (wt \%)} \times 0.9 \quad (1)$$

$$\text{Hemicellulose (wt \%)} = (\text{xylose} + \text{arabinose}) \text{ (wt \%)} \times 0.88 \quad (2)$$

In addition, the ash content was determined by measuring the weight of residue before and after heating of 1.0 g the sample at 575°C for 5 h. The analysis showed that the raw material compositions were: cellulose 43.4 wt%, hemicellulose 21.7 wt%, lignin 20.3 wt%, wax 2.3 wt%, and ash 5.6 wt% on a dry basis.

### Method of treatment

The hydrothermal experiments were conducted in a batch-type reactor (SUS 316, 14 ml) and equipped with K-thermocouple to measure temperature of reaction. A slurry consisting of 10 ml water and 1.2 g sugarcane bagasse was placed in the reactor. A stream of N<sub>2</sub> gas was used to purge air in the reactor and to regulate initial internal pressure of 0.5 MPa. The reactor was immersed into a preheated salt bath at the desired temperature and a given reaction time. The reactor was then removed from the salt bath and the reaction was quickly quenched by immersion of the reactor into a water bath to room temperature. The treated slurry was collected and filtered with a GP 16 glass filter under vacuum to separate solid residue and liquid filtrate for further analysis. The liquid product was analyzed by HPLC and the yield of each chemical was determined as:

$$\text{Yield (wt \%)} = \frac{\text{Liquid volume (mL)} \times \text{Concentration (mg/mL)}}{\text{Feed material, dry basis (mg)}} \times 100\%$$



At the same time, 10 g of filtrate and solid residue were dried at 105°C until the weight was constant, yielding water-soluble (WS) and water-insoluble (WI) fractions. The gas yield fraction and the weight loss during filtration were calculated based on mass balance:

$$\text{Yield of gas} + \text{weight loss} = 100 - \text{WS} - \text{WI} \quad (4)$$

The elemental composition of the WI fraction or solid product was measured using a Yanaco CHN Corder MT-5 elemental analyzer. The elemental value was then used to calculate the gross caloric value. The gross caloric value (GCV) was calculated according to Dulong's equation:

$$\text{GCV (MJ kg}^{-1}\text{)} = 0.3383\text{C} + 1.442 (\text{H} - \text{O}/8) \quad (5)$$

Where C, H, and O are percentage of carbon, hydrogen, and oxygen, respectively. A Fourier transform infrared (FTIR) spectrometer (JASCO 670 Plus) using the KBr disk technique was applied to identify chemical structures and functional groups. In addition, cellulose, hemicelluloses and lignin content in the solid product were also determined to assist in interpreting the decomposition mechanism during the treatment. The scheme of experimental procedure is shown in Figure 1.

**Figure 1**

**RESULTS AND DISCUSSIONS****Distribution of products of hot compressed water treatment**

Figure 2 shows the product distribution following treatment, represented as percentages of WI, WS and gas + loss fractions for different temperatures and reaction times. (The loss fraction is the small amount of unrecovered material following filtration and drying). As can be seen in Figure 2, the WI fraction gradually decreased with increases in both temperature and time. However, at elevated temperatures (e.g. 300°C) the WI fraction was observed to be comparatively constant. In case of the WS fraction, at temperatures around 200°C and 240°C (< 10 min) the yield of WS increased with increased of reaction time. This occurred only under lower reaction conditions, however; at elevated conditions the WS yield decreased, as did the WI fraction. In addition, increasing treatment temperatures caused a progressive increase in decomposition into gas.

Gas formed when the organic compounds dissolved in the WS fraction decomposed during the treatment. Low gas yield was observed at lower temperatures and shorter treatment times. However, in contrast to the other fractions, gas yield increased with longer treatment times. Finally, the decomposition reaction reached equilibrium at 300°C as evidenced by the constant yield of all fractions.

The distribution results suggest that hot compressed water accelerates biomass de-polymerization by a hydrolysis reaction that occurs when hydronium ions generated by water autoionization act as an acid/base catalyst precursor (Garrote et al. 1999; Kruse and Dinjus, 2007). ‘Hydrolysis’

describes the break-up of complex polymers such as hemicellulose and cellulose into small organic fragments, some of which dissolve in the water, some are released as gas, and the residue forms chars.

### Figure 2

The above results were in agreement with the characterization results for the solid product. As can be seen in Figure 3, the cellulose and hemicellulose content in the solid product gradually decreased with increasing temperature and reaction time. Hemicellulose is more susceptible to hydrolysis than other polymers because of its branched structure and lower degree of polymerization (DP) (Bobleter, 1994). Hemicellulose started to degrade at 200°C (3 min) and was completely decomposed and undetectable at 200°C (20 min) and 240°C (5 min). By contrast, cellulose is a long glucose polymer without branches, linked by strong  $\beta$ -(1,4)-glycoside bonds, its regular structure giving it a greater thermal stability than hemicellulose; it is therefore reasonable that the cellulose would require more severe treatment conditions than hemicellulose for it to decompose. Cellulose started to decompose at 240°C (5 min) and was completely degraded at 270°C (20 min) and 300°C (10 min), with no cellulose being detected in the solid residue product after treatment at those conditions.

### Figure 3

The recovery ratio of lignin exceeded 100 wt% (Figure 4) at temperatures above 240°C and reaction times >5 min. This was mainly caused when sugar (or sugar degradation products) from the decomposition reaction of cellulose and hemicellulose reacted with lignin, increasing the Klason lignin (acid-insoluble) content in the solid residues. This implied that the lignin did not

decompose as readily as cellulose and hemicellulose; however, Garrote et al. (1999) has reported that lignin undergoes degradation and repolymerization in aqueous media, the dissolved fraction depending on the operational conditions.

**Figure 4**

### **FTIR analysis of functional group of solid product**

An FTIR analysis was conducted to investigate the effect of the hot compressed water treatment reaction conditions in more detail. Figure 5 shows the spectral data obtained from the analyzer for different temperatures and 30 min reaction time (data for other treatment conditions omitted here), showing a straightforward comparison between raw material and hot compressed water treatment product. All of the peaks in the diagram agree with data in the literature (e.g. Kobayashi et al. 2009; Proeniewicz et al. 2001; Sun et al. 2004; Wang et al. 2010; Yang et al. 2007). The peak attributed to –OH groups recorded at approximately  $3300\text{ cm}^{-1}$  decreased with rising temperature, indicating that water molecules within the solids were gradually released and the feed material was dehydrating. The peak in the range  $2928\text{--}2940\text{ cm}^{-1}$  attributed to aliphatic  $\text{CH}_n$  groups also weakened, which indicated that polymer chains fragmented and decomposed with increase in temperature. The peak in the range  $1721\text{--}1745\text{ cm}^{-1}$  represents carbonyl (C=O) stretching vibrations which is identify the hemicellulose components become weaker with increasing reaction temperature. The peak around  $1049\text{ cm}^{-1}$  represent of C-O stretching vibrations in cellulose and hemicellulose. This result suggested that the large portion of hemicellulose and cellulose decomposed with increasing temperature and reaction time. This

feature clearly observed at temperature  $>240^{\circ}\text{C}$  (30 min); Where the hemicellulose and cellulose were undetected at this temperature.

The peak of C-O-C aryl-alkyl ether linkage was detected around  $1247\text{ cm}^{-1}$ , and the peak of  $\beta$ -glycosidic linkages between glucose in cellulose observed in the range  $897\text{ cm}^{-1}$  indicated the weakening presence of cellulose, which was completely undetected at temperatures above  $270^{\circ}\text{C}$ . The peaks around  $1500\text{ cm}^{-1}$  corresponding to lignin and aromatic compounds suggest that the lignin in the feed materials was almost stable throughout the treatment, although at  $270^{\circ}\text{C}$  and above the spectral data became slightly weaker, perhaps indicating a slight degradation of the lignin at high temperatures.

**Figure 5**

### **Elemental composition of solid product**

Ultimate analysis data for the solid residue produced at different temperatures and reaction times is given in Table 1. The hot compressed water treatment progressively changed both the physical and chemical properties of the material. Table 1 shows that the reaction conditions significantly affected the characteristics of the solid product. Both hydrogen and oxygen content of the solids tended to decrease with increased temperatures and reaction times that is, the hot compressed water treatments led to dehydration and decarboxylation. At the same time, carbon content tended to increase with longer treatment times, with the product having a higher carbon content than the raw material. For instance, the product obtained at  $300^{\circ}\text{C}$  (30 min) had 69.9 wt% carbon content and 24.5 wt% oxygen content, compared to 44.1 wt% carbon and 49.7 wt% oxygen for the raw material. In the other hand, the high carbon content showed that the treatment was able

to increase the gross caloric value of material. As presented in Table 1, the gross caloric value of solid product increased with increasing temperature and reaction time. Compared with untreated sample of 14.4 MJ/kg-dry feed base, the gross caloric value of the bulk product increased up to 26.6 MJ/dry-kg base feed. This result suggests that the solid product from hydrothermal treatment has favorable properties for application as a fuel for thermal conversion processes.

**Table 1**

### **Yield of chemicals in liquid fraction**

Hemicelluloses and celluloses are both natural polymers built up from sugar units, but with significant differences. The analysis of the liquid fraction suggested that the sugars from hemicelluloses were produced at lower temperatures. The hot compressed water treatment decomposed hemicellulose into xylose and arabinose, whereas cellulose decomposed into glucose. Figure 6 shows the highest arabinose reading at 200°C (3 min), with a maximum yield of 1.4 wt%, while the highest xylose and glucose values were 8.6 wt% (200°C, 20 min), and 1.9 wt% (270°C, 3 min), respectively. However, at elevated temperatures and longer reaction times, the yield of sugars decreased due to the formation of secondary products such as furans and organic acids.

**Figure 6**

Figure 7 shows that furfural was firstly detected at 200°C (10 min), when degradation of xylose and arabinose occurred in the following reaction:



The highest yield of furfural was detected at 200°C (30 min), then gradually decreased under elevated conditions, and finally was undetected at 300°C (20 min) due to the formation of organic acids. At the same time, glucose further decomposed to form secondary products such as 5-(hydroxymethyl)furfural (5-HMF) by the dehydration reaction:



5-HMF was obtained as glucose yield decreased. The highest yield of 5-HMF was obtained at 270°C (10 min) and was undetected at 300°C (> 10 min). This suggests that elevated temperatures with longer reaction times had negative effects on 5-HMF production, mainly because of the heightened decomposition and polymerization of 5-HMF to organic acids and char, respectively (Yin et al. 2011).

As can be seen in Figure 7, acetic acid was the dominant organic acid recovered during the treatment. First detected at 200°C (5 min), the yield of acetic acid tended to rise with increasing treatment temperature and reaction time. Garrote et al. (1999) reported that presence of hydronium ions generated by water autoionization and it was splitting of the acetyl groups of hemicellulosic in raw material. In further reactions, hydronium ions from acetic acid also act as a catalyst in degradation of polysaccharides into oligomeric or monomeric sugars. However, acetic acid is not solely generated by detachment of the acetyl group from hemicelluloses but also from sugars such as glucose and xylose decomposition reaction (Yoshida et al. 2005).

It was also observed that the yield of acetic acid was higher than that of formic acid, with the maximum of yield is 6.6 wt% at 300°C (5 min) and leveled off somewhat at longer residence times. The highest yield of formic acid was detected at 240°C (10 min) and 300°C (3 min), then decreased with extended treatment time and was undetected beyond 300°C (20 min). According to Yu et al. (1998), formic acid readily decomposes at elevated temperature into CO<sub>2</sub> and H<sub>2</sub>. Compared to formic acid, acetic acid did not easily degrade at elevated reaction conditions due to its stability.

To summarize, hot compressed water enhances the hydrolysis reaction, and decomposes hemicelluloses and cellulose into sugars which are then mainly dehydrated, initially producing furfural and 5-HMF. Further fragmentation and dehydration produces a range of low-molecular-weight compounds such as formic acid and acetic acid.

### Figure 7

## CONCLUSIONS

Based on the characterization results of hot compressed water treatment of sugarcane bagasse, it was concluded that the decomposition reaction was influenced both by temperature and reaction time. Degradation of hemicellulose began at 200°C (3 min) and was complete at 200°C (20 min) and 240°C (5 min). The hemicellulose decomposed to form arabinose and xylose, which further decomposed into furfural and organic acids. Cellulose started to decompose at 240°C (5 min) and was completely degraded after 20 minutes at 270°C, and after 10 minutes at 300°C. The cellulose decomposed to form glucose, which further decomposed to form 5-HMF and organic acids. Of these, both acetic acid and formic acid content firstly increased with increasing

treatment temperature and reaction time. However, after extended treatment time, formic acid content decreased and was undetected at 300°C (20 min). All of these chemical products of sugarcane bagasse conversion are valuable and important products for chemical industries and for biofuel feedstock.

Characterization of the solid product showed that the dehydration and decarboxylation reaction rates increased with increasing reaction times and temperatures. These reactions significantly reduced the oxygen and hydrogen content of the original material. Furthermore, the carbon content of the solid product increased to 1.2–1.6 times that of the raw material. This result shows that the treatment converted the low-carbon biomass into a high-carbon content and high caloric value material that is useful as carbon source materials or biochar and solid biofuel.

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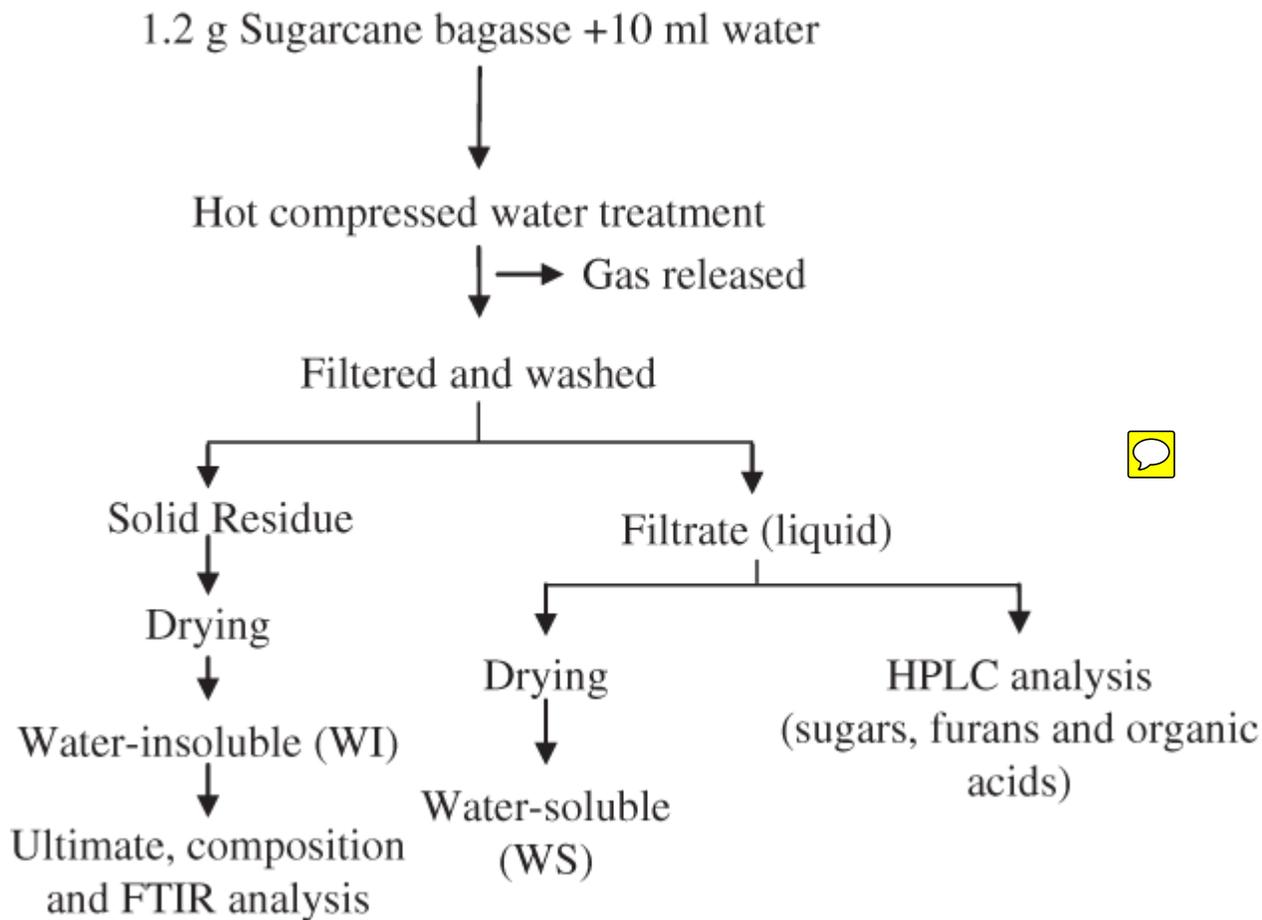
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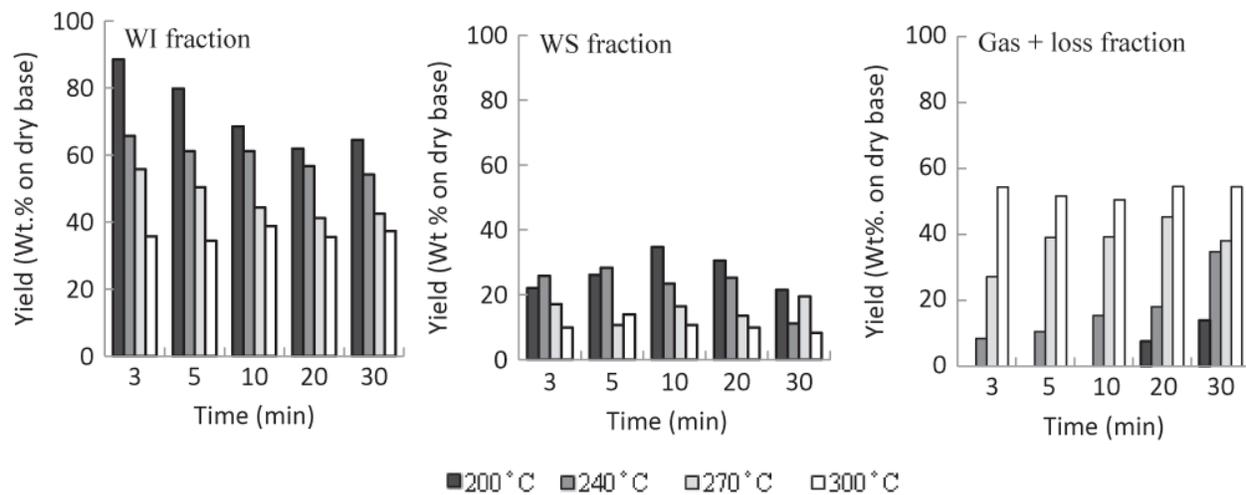
**Table 1** Elemental composition and gross caloric value of raw material and solid product from hot compressed water treatment of sugarcane bagasse for 30 minutes at various temperatures.

Treatment condition	Percentage component (wt%, daf)				GCV (MJ/dry-kg)
	C	H	O (diff)	N	
200 °C, 30 min	48.6	5.8	45.4	0.2	16.6
270 °C, 30	67.8	5.1	26.6	0.5	25.4

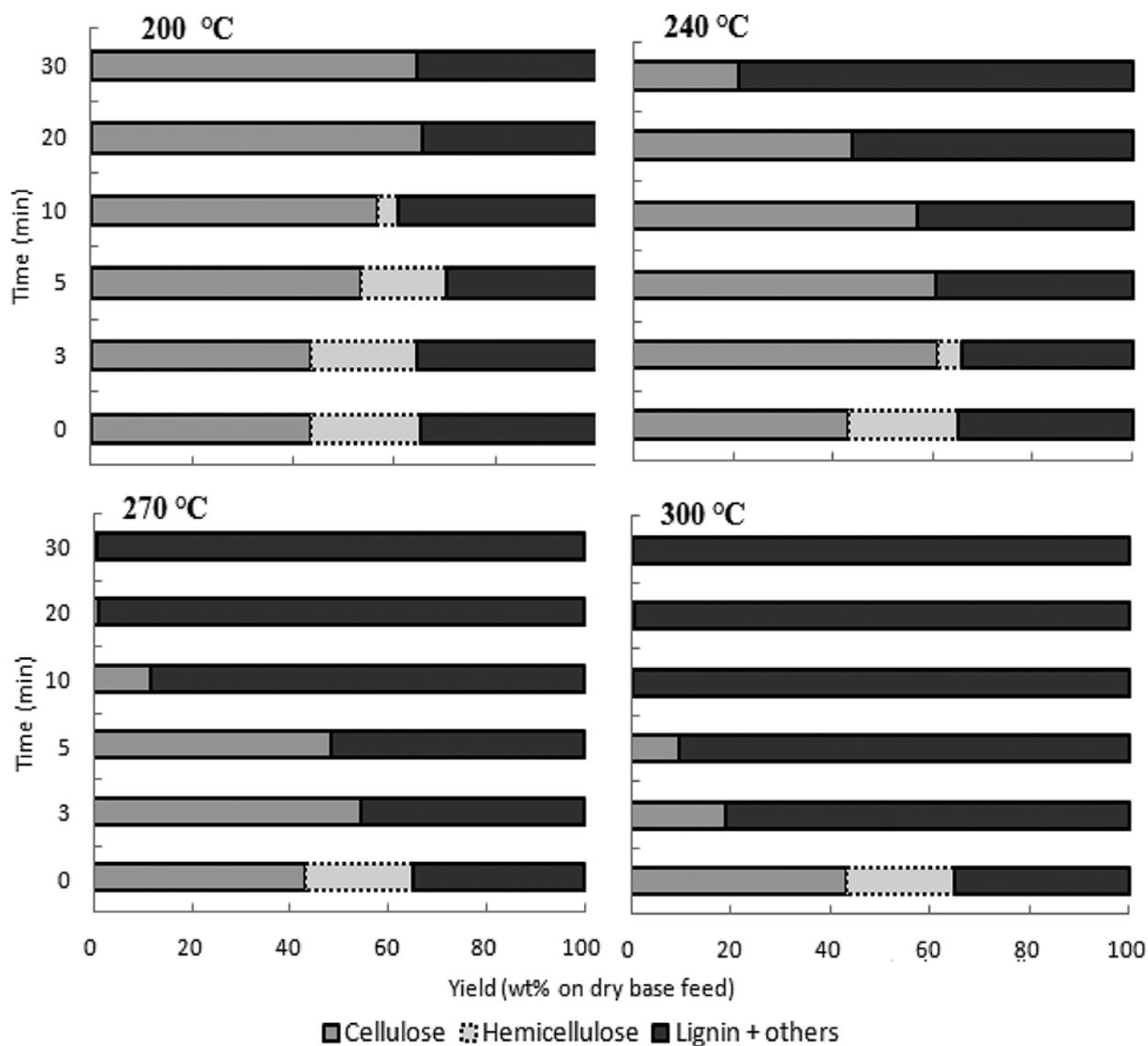
diff = differences daf = dry ash free base

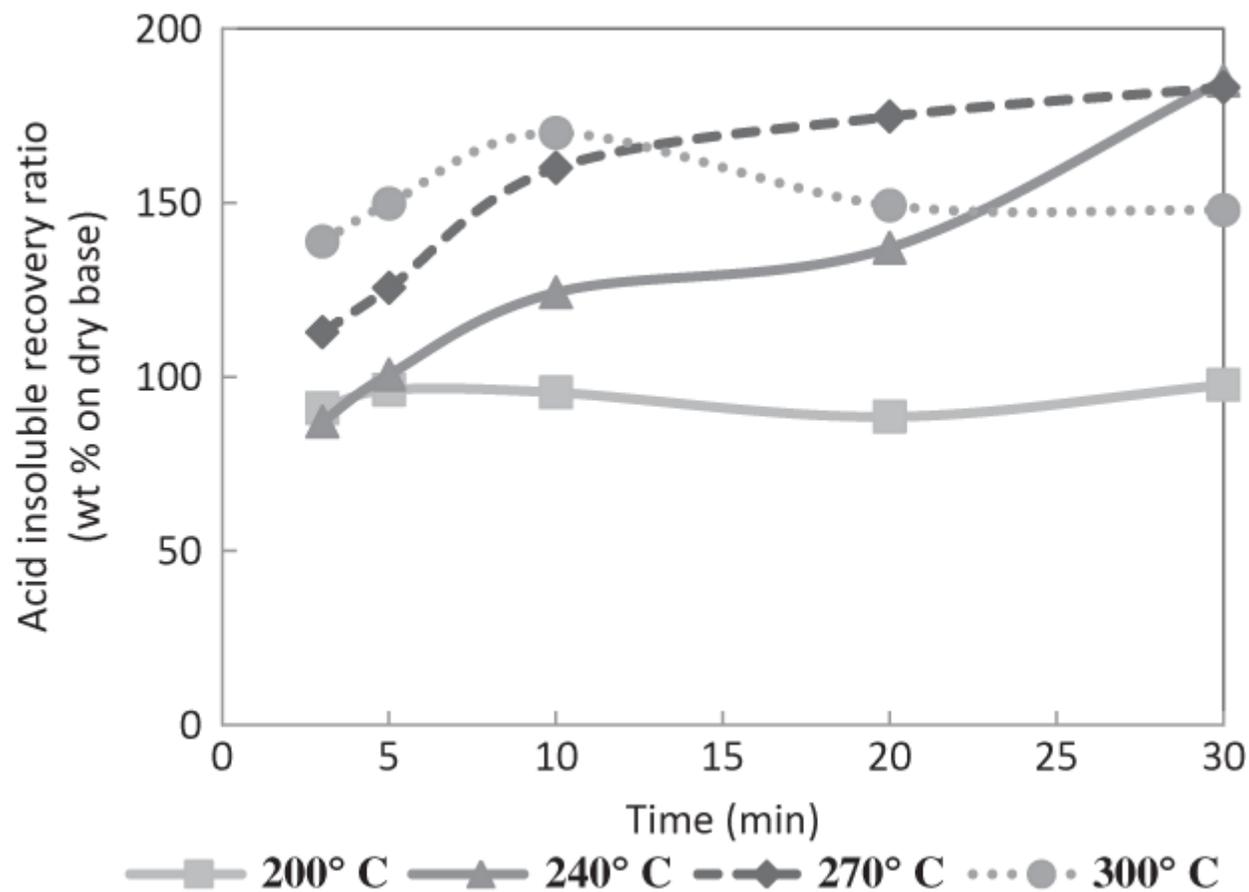
**Figure 1** Scheme of the experimental procedure.

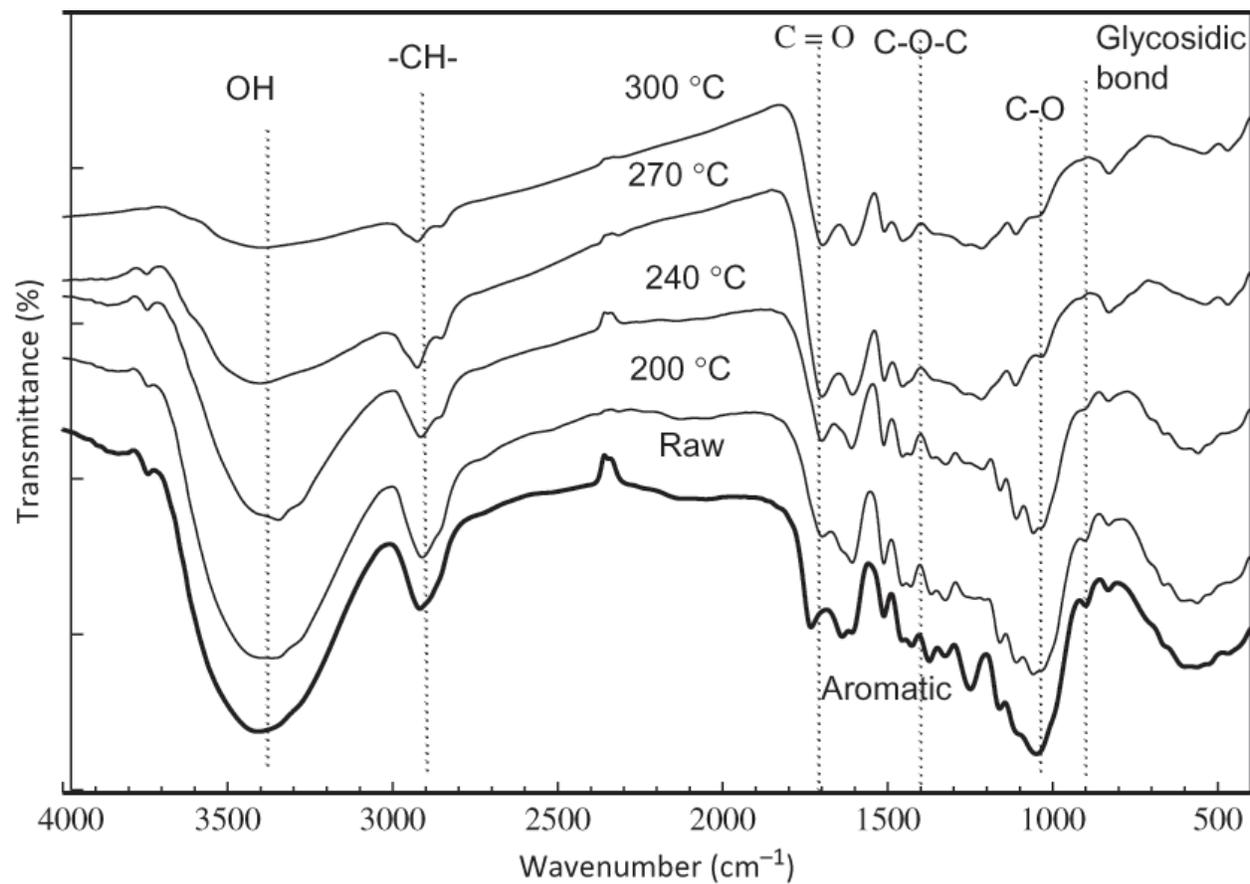
**Figure 2** Product yield distribution for WI, WS and gas+loss fractions for varied reaction time and temperatures.



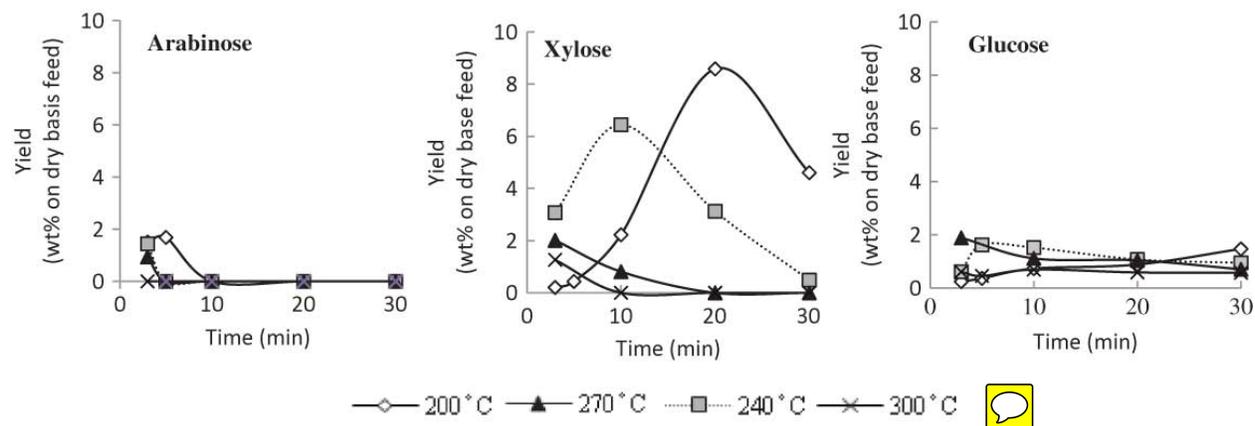
**Figure 3** Decomposition characteristics of sugarcane bagasse for varied conditions of hot compressed water treatment.



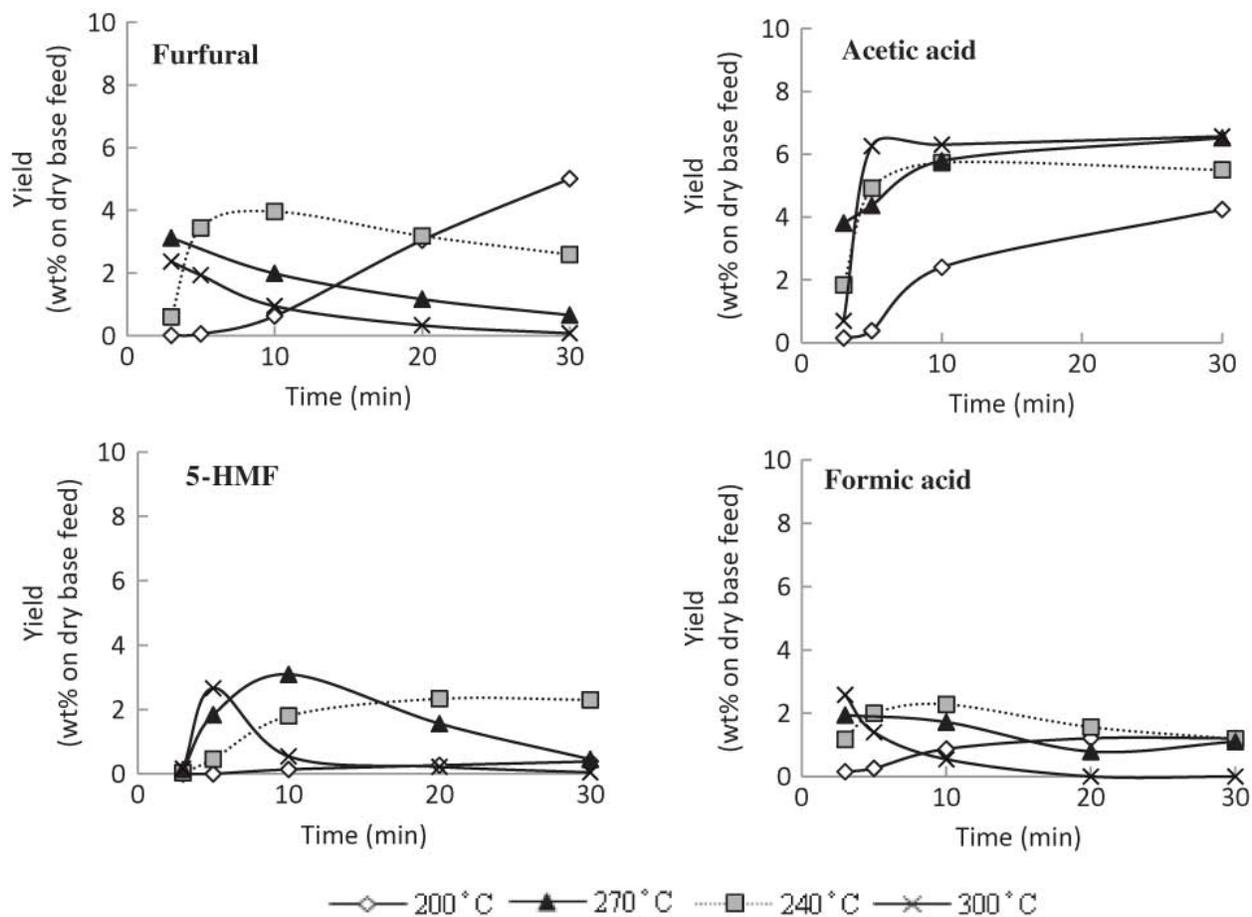
**Figure 4** Acid insoluble ratios in the solid product at different conditions of treatment.

**Figure 5** FTIR spectra of raw and solid products treated for 30 minutes at various temperatures.

**Figure 6** Yield of sugars by hot compressed water treatment at various reaction time and temperatures.



- 1 **Figure 7** Yield of chemicals from hot compressed water treatment for various reaction times and  
 2 temperatures.



3