# CHEMICAL CHARACTERISATION AND DILUTE-ACID HYDROLYSIS OF RICE HULLS FROM AN ARTISAN MILL

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The chemical composition of rice hulls produced in an artisan mill and its conversion to fermentable sugars was investigated. The carbohydrate fraction represented 59.2% (w/w) of the dry hulls. Cellulose, with 36.6%, was the main component, followed by xylan with 13.9%. An important contribution of starch (8.7%) was also detected. The content of ash (19.6%) and lignin (15.5%) was comparable with that of rice hulls obtained in industrial mills. Dilute-sulphuric acid hydrolysis at different temperatures, from 160 to 210°C, was evaluated for production of fermentable sugars. Due to starch hydrolysis, the concentration of glucose in the hydrolysates produced at 160°C was higher than the values that have previously been reported for industrial sorts of rice hulls under comparable conditions. The xylan-to-xylose conversion increased steadily with increase of the temperature and reached a maximum (67.7%) at 190°C. Further increases of the hydrolysis temperature decreased the yield of sugars due to their dehydration to furfural and HMF.

*Keywords: Lignocellulosics; Rice hulls; Dilute-acid hydrolysis; Ethanol production*

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## INTRODUCTION

Lignocellulosic materials are the world's most widely available low-cost renewable resources to be considered for the production of fuel ethanol and platform chemicals. Rice hulls, which are generated during dehulling of rough rice (*Oryza sativa*), are among the most important lignocellulosic materials available in tropical countries. That is due to the high use of rice, which supplies 20% of the world's nutritional energy, and nearly one billion households in Asia, Africa, and Latin America depend on rice for employment and nutrition (Saha *et al.* 2005). It is estimated that world production of rice was about 696 million tons in 2009 (FAO Food Outlook, 2009). Since the hulls represent 20% of the weight of harvested rice (Kim and Dale 2004), the global potential of rice hulls is around 139 million tons per year.

Potential applications for rice hulls include production of activated charcoal, heat and power generation, and silica applications (Govindarao 1980; Sánchez and Cardona

2008). However, most of the generated rice hulls are generally landfilled or burnt just to get rid of them (Koopmans and Koppejan 1997), which, undoubtedly, negatively influences the global environment. The availability of rice hulls varies from country to country and from location to location, and depends on the type and size of the rice mills. Large rice mills located in or close to urban areas generate higher amounts of hulls, and have higher disposal problems than small village-type "artisan" mills located in rural areas. On the other hand, often the artisan mills lack a good control on the milling of the rough rice, which results in grain loss due to breakage. As a result, the hulls generated in those mills contain grain fragments and bran.

Due to their carbohydrate content and to the ease of collection from rice processing sites, rice hulls are of interest as feedstocks for ethanol production (Moniruzzaman and Ingram 1998; Saha *et al.* 2005; Martín *et al.* 2006; Martín *et al.* 2007a). However, cost-intensive hydrolysis processes, either acid-catalysed or enzymatically-catalysed, are required to obtain fermentable sugars (Sun and Cheng 2002; Taherzadeh and Karimi 2007a). In order to facilitate the enzymatic hydrolysis of cellulose different kinds of chemical, physical, and physico-chemical pretreatment methods have been proposed. The pretreatment is essential in order to remove lignin and hemicelluloses, reduce cellulose crystallinity, increase the porosity of the materials and enhance the hydrolysability of cellulose (Taherzadeh and Karimi 2007b). Dilute-acid hydrolysis has been successfully developed for pretreatment of lignocellulosic materials, and it has been used for rice hulls (Saha *et al.* 2005; Martín *et al.* 2007b; Wei *et al.* 2009). However, the reports found in the literature are generally devoted to rice hulls from industrial mills, whereas the hulls produced in small-scale artisan mills, which are qualitatively different to those produced in industrial mills, have been underestimated. The presence of starch in artisan rice hulls poses additional difficulties in the hydrolytic processing of that bioresource. Due to the different hydrolysability of the polysaccharides contained in the raw material the glucose resulting from starch hydrolysis is sensitive to be destroyed under the hydrolysis conditions applied for hemicelluloses and cellulose.

In this work, the chemical composition of artisan rice hulls was investigated and the formation of glucose and xylose under different dilute-acid hydrolysis conditions was evaluated.

## EXPERIMENTAL

### Raw Material

Rice hulls used in all the experiments were obtained from an artisan mill (Finca Santa Rosa, Pedro Betancourt, Matanzas, Cuba). The material was dried at 60ºC until a dry matter (DM) content of 90-92%. A portion of the hulls was milled to 1-mm particle size, sieved and stored in plastic bags at room temperature until analysis.

## Dilute-Acid Hydrolysis

Ten g of rice hulls were soaked in 100 mL of a 0.5% sulphuric acid solution for 24 h. Cylindrical vessels made of a corrosion-resistant alloy (Stainless steel 316L) with a total volume of 140 mL (Swagelok®, Solon, Ohio, USA) were used as reaction vessels. The reactors were immersed during 10 min in a previously heated oil bath to achieve the desired temperature. Duplicate experiments at 160, 180, 190, 200, and 210ºC were carried out.

## Analytical Methods

All the hydrolysates were analyzed by high-performance liquid chromatography (Waters, Milford, USA). Glucose and xylose were separated on an Aminex HPX-87P column (Bio-Rad, Richmond, CA, USA) at 80±1ºC. Deionised water was used as eluent at a flow rate of 0.6 mL/min. Furfural and HMF were separated on an Aminex HPX-87H column (Bio-Rad) at 60±1 ºC with 0.005 M sulphuric acid as mobile phase at a flow rate of 0.6 mL/min. Glucose and xylose were detected with an RI-detector (Waters 2414), while furfural and 5-hydroxymethylfurfural (hereafter referred to as HMF) were detected with a UV-detector (Waters 2487) at 210 nm. Data acquisition software, Empower 2, was used as interface to perform analysis, retrieve data, and control the entire system.

The content of moisture, mineral components, extractives, structural carbohydrates, and lignin in the raw material was determined according to NREL analytical procedures. Moisture was determined gravimetrically after drying the materials at 105$^{o}$C (Sluiter *et al.* 2008a). Mineral components were determined as ash after incineration of an aliquot of the material at 575$^{o}$C (Sluiter *et al.* 2008b). Extractives were determined by ethanol extraction in a Soxhlet apparatus (Sluiter *et al.* 2008d).

Cellulose, hemicelluloses, and lignin were determined by analytical acid hydrolysis of the extractive-free material followed by chromatographic quantification of sugars and degradation products contained in the hydrolysate and by the gravimetric determination of acid-insoluble lignin (Sluiter *et al.* 2008c). Starch was determined by chemical solubilisation and enzymatic digestion (Ehrman 1996).

# RESULTS AND DISCUSSION

## Characterization of the Rice Hulls

The composition of the raw material is shown in Table 1. For comparison, a brief survey of the reported composition of different sorts of rice hulls and by-products of other gramineous plants is given in Table 2. Cellulose, which accounted for 36.6% of the mass, was the main component of the material used in this work. Its content was comparable with that reported in the literature for industrial rice hulls and for other materials (Table 2). Other important carbohydrate components were xylan (13.9%) and starch (8.7%). While xylan content is within the range given in other reports on rice hulls of different origin, starch has not been reported previously as a component of this bioresource. It should be noted, however, that the high glucan content found formerly by this group for other sorts of rice hulls from artisan mills (Table 2; Martín *et al.* 2007a) matches rather well with the sum of the cellulose and starch contents revealed in the current work.

**Table 1.** Composition of Rice Hulls from an Artisan Rice Mill

| Component | Content (% (w/w)) | SD | CV (%) | RPD (%) |
|---|---|---|---|---|
| Starch | 8.71 | 0.41 | 3.23 | 5.63 |
| Extractives | 8.30 | 0.47 | 5.39 | 7.62 |
| Ash | 19.61 | 0.17 | 0.87 | 1.22 |
| Cellulose | 36.60 | 1.76 | 3.39 | 4.80 |
| Xylan | 13.87 | 0.25 | 2.41 | 3.43 |
| Lignin | 15.45 | 0.16 | 1.42 | 2.01 |
| SD, standard deviation; CV, coefficient of variation; RPD: relative percent difference | | | | |

The detection of starch is a consequence of the presence of residual grain fragments remaining in artisan rice hulls. The starch content, which is usually insignificant, and consequently not reported, in industrial-mill rice hulls, is a specific feature of the hulls produced in artisan mills. This makes the artisan-mill hulls close in their composition to starch-containing agricultural bioresources, such as corn fiber and silage (Table 2). Since starch can easily be converted to glucose, artisan rice hulls, as well as the above mentioned materials, have an additional attraction, compared with industrial rice hulls and other agricultural residues, for production of ethanol and other glucose-derived chemicals.

**Table 2.** Reported Composition of Rice Hulls and other Agricultural Residues

| Material | Cellulose | Xylan | Starch | Lignin | Extractives | Ash | Reference |
|---|---|---|---|---|---|---|---|
| Rice hulls (artisan) | 49.7[1] | 9.1 | N.R. | 13.5 | 5.9 | 15.7 | Martín *et al.* 2006 |
| Rice hulls (industrial) | 39.8[1] | 13.2 | N.R. | 20.8 | 4.1 | 17.6 | Martín *et al.* 2006 |
| Rice hulls (industrial) | 35.6 | 12.0[2] | N.R. | 15.4 | N.R. | 18.7 | Saha *et al.* 2005 |
| Rice hulls (industrial) | 36.7 | 15.6 | N.R. | 21.3 | N.R. | 14.3 | Vila *et al.* 2002 |
| Rice straw | 39.0 | 20.6 | N.R. | 12.0 | N.R. | 11.0 | Karimi *et al.* 2006 |
| Wheat straw | 35.0 | 19.6 | N.R. | 15.6 | N.R. | 6.5 | Petersen *et al.* 2009 |
| Barley husks | 21.4 | 26.0 | N.R. | 19.2 | N.R. | 15.5 | Parajó *et al.* 2004 |
| Sugarcane bagasse | 39.5[1] | 22.1 | N.R. | 18.1 | 5.3 | 2.3 | Martín *et al.* 2006 |
| Corn cobs | 34.4 | 31.3 | N.R. | 18.8 | N.R. | 1.3 | Parajó *et al.* 2004 |
| Corn fiber | 15.0 | 35.0[2] | 20.0 | 8.0 | N.R. | N.R. | Saha *et al.* 1998 |
| Corn silage | 51.7[1] | 19.5[2] | 15.5[3] | 16.6 | N.R. | N.R. | Thomsen *et al.* 2009 |
| N.R., Not reported; [1]Reported as glucan; [2]Reported as hemicellulose; [3]Estimated as 30% of glucan content | | | | | | | |

Ash and lignin contents were, respectively, 19.6 and 15.5% (Table 1). These contents are comparable with those reported in the literature for industrial rice hulls (Table 2). The high ash content is known to be characteristic for rice hulls (Skrifvars *et al.* 2005). The relative percent difference (RPD) in all the analyses was below the allowed value for all determinations.

## Dilute-acid Hydrolysis

The hydrolysis conditions used were selected based on literature results on acid pretreatment of rice hulls (Saha *et al.* 2005) and on our previous experience with industrial hulls (Martín *et al.* 2007b). The experimental results revealed that the applied conditions were effective for the hydrolysis of the polysaccharides. Even at the lowest temperature, the formation of monosaccharides was remarkable (Fig. 1). Glucose was the main sugar in the hydrolysates obtained at 160˚C and also in those obtained at 200-210°C, whereas xylose was predominant at 180 to 190°C.

At 160°C, the glucose concentration was 5.5 g/L (Fig. 1), which corresponds to approximately 11% of the theoretically expected glucose from the hydrolysis of the whole glucan fraction in the raw material. The relatively high glucose formation at 160°C differs from literature reports on acid pretreatment of rice hulls under comparable conditions. In a 15 min-lasting pretreatment of industrial rice hulls at 160°C using 1.0% sulphuric acid, Saha *et al.* (2005) obtained a hydrolysate with a xylose concentration doubling that of glucose. For the current experiment, which was performed at the same temperature, but at lower sulphuric acid concentration and shorter reaction time than the above mentioned work, one could expect similar or slightly lower glucose formation if the process parameters would be the only factors affecting the results. Therefore, the higher than expected glucose formation can only be attributed to qualitative particularities of the used rice hulls, which were obtained from an artisan mill. It can, indeed, be suggested that the high glucose formation at 160°C in this work are a result of the hydrolysis of starch contained in the hulls. The hydrolytic release of glucose is comparable with the behaviour of whole-crop corn silage, a starch-rich bioresource, under mild wet oxidation conditions (Thomsen *et al.* 2008). During wet oxidation of corn silage, a high glucose yield is achieved in the pretreatment stage due to the hydrolysis of the starch contained in the raw material, which consists of the whole plant, including stem, leaves, and grain, harvested and ensiled anaerobically.

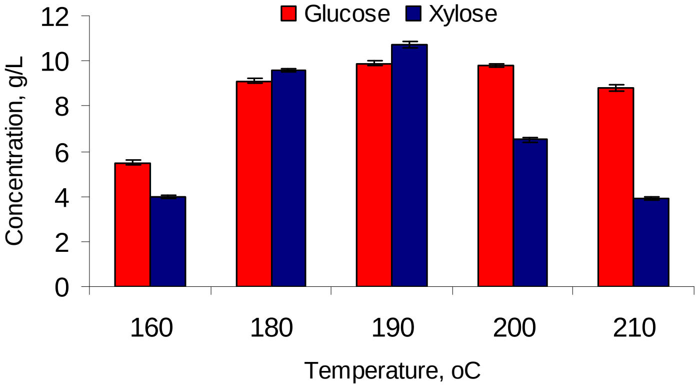

**Fig. 1.** Glucose and xylose formation under different hydrolysis temperatures. Mean from two replicates. The standard deviations are shown as error bars.

Above 160$^o$C, some additional glucose formation was observed (Fig. 1). However, it is more reasonable to attribute it not to hydrolysis of starch, but to hydrolysis of xyloglucans and β-glucans. Xyloglucans are contained in rice hulls hemicelluloses (Watanabe *et al.* 1984), while β-glucans are known components of the hemicelluloses present in grains and bran of cereals (Johansson *et al.* 2004; Burton and Fincher 2009). The hydrolysis of the easy-to-hydrolyse cellulose fraction can also partially explain the increase of glucose concentration that occurred at high temperatures. At the same time, as a result of the increase of the severity, glucose started to degrade, as it is revealed by the decrease of its concentration above 190$^o$C and by the increase in HMF formation. The increase of the temperature led to 5-fold and 8-fold increases, respectively at 180 and 190$^o$C, of HMF concentration in the hydrolysates (Fig. 2).

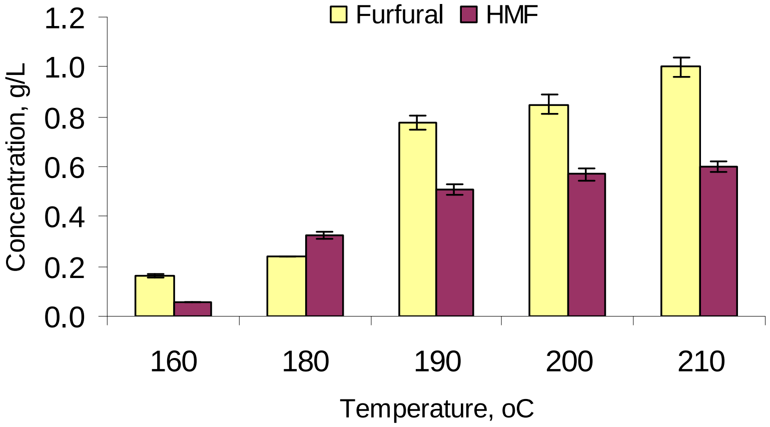

**Fig. 2**. Formation of furan aldehydes under different hydrolysis temperatures. Mean from two replicates. The standard deviations are shown as error bars.

At 160$^o$C, xylose concentration was only 4 g/L (Fig. 1), which represents hardly one fourth of the potentially achievable sugar formation from xylan hydrolysis (Fig. 3). The hydrolytic conversion of hemicelluloses increased in the temperature range between 160 and 190$^o$C. The concentration of xylose was two times higher in the hydrolysate obtained at 180$^o$C as compared with the one obtained at 160$^o$C (Fig. 1). An additional slight increase of xylose concentration was also observed at 190$^o$C, where the xylan-to-xylose conversion reached a maximal value of 67.8% (Fig. 3). However, at that temperature xylan hydrolysis competed with xylose degradation, as is revealed by the formation of furfural (Fig. 2). Furfural formation displayed a dramatic increase from 0.24 g/L at 180$^o$C to 0.78 g/L at 190$^o$C.

Above 190$^o$C, degradation reactions were dominant over hydrolysis reactions. Xylose concentration decreased sharply from 10.7 g/L at 190$^o$C to 3.9 g/L at 210$^o$C (Fig. 1), and xylan conversion decreased to 24.7% (Fig. 3).

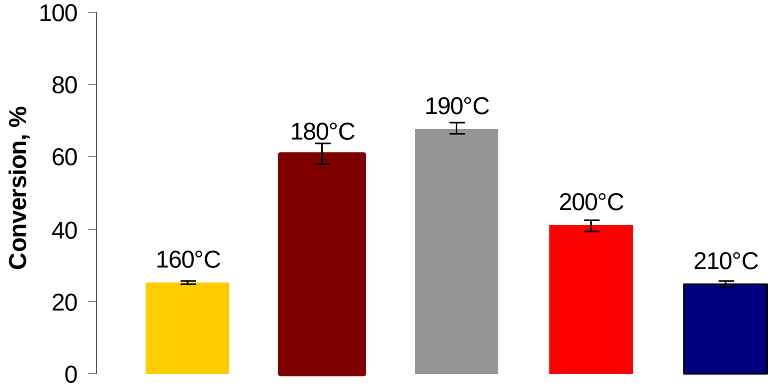

**Fig. 3**. Xylan to xylose conversion under different hydrolysis temperatures. Mean from two replicates. The standard deviations are shown as error bars.

Some decrease of glucose concentration was also observed (Fig. 1). The higher degree of xylose degradation than that of glucose is in agreement with previous knowledge on side dehydration reactions of sugars in acidic media (Qi *et al.* 2008). However, the increase of furfural formation, from 0.78 g/L at 190°C to 1.0 g/L at 210°C, was lower than that it would be expected from the sharp decrease in xylose concentration discussed above. The same applies for HMF, whose concentration above 200°C only slightly increased (Fig. 2). This fact can be explained by the high reactivity of furan aldehydes in high-temperature acidic media. It is well documented that both furfural and HMF are rather instable in the dehydrative medium and follows a typical growth-and-decay curve (Fengel and Wegener 1989).

For future experiments with artisan rice hulls it is advisable to explore milder acid hydrolysis conditions that could maximize the saccharification of starch and xylan, and minimize sugar degradation, as well as to explore the enzymatic convertibility of the resulting cellulignin. Work in that direction is underway by our group.

## CONCLUSIONS

1. The carbohydrate fraction of the artisan rice hulls investigated in this work, in addition to cellulose and xylan, contained appreciable amounts of starch, which makes that material attractive for production of ethanol and other glucose-derived chemicals.
2. Hydrolysates containing considerable amounts of glucose were obtained at relatively low temperatures due to the hydrolysis of starch.
3. The hydrolysis of xylan proceeded slower than that of starch, and the maximal conversion (67.7%) was reached at 190°C.
4. A high degree of sugar degradation was observed at high temperatures.

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