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Subcritical water technology for wheat straw hydrolysis to produce value added products

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ABSTRACT

The cellulosic nature of agriculture wastes makes them suitable raw materials for conversion processing to produce end products with high value added. The present works described the using of subcritical water technology for the utilization of wheat straw through hydrolysis to produce reducing sugar. The experiments were carried out under different conditions and the optimum hydrolysis parameters were investigated. The results revealed that the optimum conditions for hydrolysis were 190 °C temperature, 30 min hydrolysis time, water to straw ratio of 6/1 and feedstock particle size of 180–355 μm. The maximum obtained yield the reducing sugars (RS) under the optimum hydrolysis condition amounted to 51.5% (as weight percent) of the raw wheat straw. HPLC analysis for the produced RS showed the presence of 3.2% of total RS as glucose and 7.6% as xylose, the balance being other reducing sugars, e.g. arabinose, galactose and probably other oligomers. Finally, the ethanol production from the produced glucose was tested through fermentation process. Based on the obtained results, it was possible to propose a design for a process combining both sugars and bioethanol production.

1. Introduction

Agriculture wastes valorization is currently receiving much attention (Abdelmoez et al., 2013; Mostafa et al., 2013). Cellulose wastes represent an attractive source of renewable energy. The cellulosic nature of agriculture wastes makes them suitable raw materials for bioconversion processing to produce end products with high value added. They are renewable, available in large quantities, and cheap. The utilization of agriculture wastes as a feedstock has a double effect consequence, environmentally and economically, by minimizing the waste disposal problems, and producing valuable products from low-cost cellulosic wastes. About 26–28 million tons of agriculture wastes including cotton stalk, rice and wheat straw, maize residual, etc, are produced annually in Egypt. The amount of wheat straw produced was estimated to be 4.65 million tons according to data in the report of the Egyptian ministry of agriculture and land reclamation (Ministry of Arab Republic of Egypt. Ministry of Agriculture and Land Reclamation – Economical Affairs Sector, 2012). In practice these agriculture wastes are burned, which creates environmental pollution problems (Mona, 2007). The Utilizations of these waste for energy production through ethanol fermentation may represents a very interesting and promising route. The use of ethanol as a fuel for internal combustion engines, either alone or in combination with other fuels, has been given much attention mostly because of its possible environmental and long-term economical advantages over fossil fuel.

There are several technologies available for the hydrolysis of wheat straw and other cellulosic wastes, such as acid hydrolyses, enzymatic hydrolyses and others. Many researchers studied acid hydrolysis under different operating conditions (Vázquez et al., 2007; Rahman et al., 2006; Karimi et al., 2006). The results indicated that acid hydrolysis could produce high yields of hydrolysate. However, this technique has many drawbacks like using toxic and corrosive chemicals (Xu et al., 2007). Also, acid pretreatment is considered too expensive because it requires corrosion resistant materials of construction and some mineral acids produce degradation products (Li et al., 2009). To overcome the drawbacks of the acid hydrolysis and to go through a more environmentally friendly process, enzymatic hydrolysis was thoroughly studied (Fubao and Hongzhang, 2008; Yoon et al., 2006). The results showed that high yields of hydrolysate could be obtained by using enzymatic hydrolysis, but the economic feasibility of the process is uncertain

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so far. Still, the potential of these processes encourages further developmental work. Other techniques studied include extraction, hydrothermal pretreatment and multi-step detoxification pretreatment (Curling et al., 2007; Voca et al., 2009; Wei et al., 2009). All have their advantages and disadvantages and share the major leak of being still under primer stage of development.

A new emerging technique using critical fluid has been recently developed. The discovery of the presence of critical point for fluids dates back to 1822 (Kiran et al., 2000a,b). At critical conditions, the fluid does not meet the definition of a liquid because it cannot boil by decreasing the pressure at constant temperature. Also, it is not a vapor because cooling at constant pressure won't cause it to condense. Supercritical fluids have both gas-like and liquid-like properties. The gas-like low viscosity promotes mass transfer while the liquid-like density promotes solvation. Water begins to enter the supercritical region above 374 °C and 22 MPa. Supercritical water is a very promising reaction medium for different applications. Supercritical fluid processes have found applications in many fields (Hutchenson and Foster, 1995) such as supercritical fluid separation, i.e. petroleum chemistry separation and purification, food industry (McHugh and Krukonis, 1998; Cansell et al., 1997) and supercritical fluid chromatography. Supercritical fluids are used as reaction media with continuously adjustable properties from gas to liquid in different fields such as polymers, low density polyethylene, waste destruction and polymer recycling (Kiran et al., 2000a,b; Savage et al., 1995), formation of particles, fibers and substrates, such as pharmaceuticals, explosives and coatings (Ksibi and Subra, 1996) or in drying materials, gel (Laudise and Johnson, 1986; Rangarajan and Lira, 1999). However, water under supercritical condition becomes aggressively corrosive which may limit its applications and it increases the capital cost in the case of commercialization.

On the other hand, on heating within the critical point of water under enough pressure to maintain the liquid state, water becomes near the critical state (which is internationally known as subcritical water). Subcritical water is not as corrosive as in the case of supercritical water, while still maintaining many distinctive properties of that of supercritical water, such as low dielectric constant and high ion product. Such properties facilitate the application of subcritical water in different fields such as the conversion of biomass to value-added products and at the same time avoiding the destructive properties of the supercritical water. The key properties of water that influence the most important interactions are the ion product and dielectric constant (which reflect the polarity and solvent ability of water). Therefore, under high ion product values water possesses the effect of an acid catalyst. On the contrary, a decrease of the dielectric constant decreases the water polarity. Subcritical water is unique in its properties. Both density and dielectric constant are dramatically decreasing while hydrocarbon solubility is increasing. Such properties allow the very wide application of subcritical water in many fields. Through our way to explore the applications of subcritical water technology in the field of biomass hydrolysis, two of the present authors carried out different studies in the field of protein hydrolysis and oil extraction (Abdelmoez and Yoshida, 2006a,b, 2007a,b, 2008; Abdelmoez et al., 2010, 2011, 2012; Abdelmoez and Yoshida, 2013).

Cellulose hydrolysis in subcritical and supercritical water was been studied (Matsunaga et al., 2008; Wiboonsirikul et al., 2007; Williams and Onwudili, 2006; Yan et al., 2009, 2011). The results revealed that subcritical water technology is a promising technique and it is strongly nominated to be an alternative route for not only cellulose hydrolysis but also other biomass conversions. Despite the energy cost associated with the technology of subcritical water, this technique has immediate advantages over traditional hydrolysis techniques, as it represents a flexible process due to the possibility of continuous changing of the solvent power selectivity of the subcritical water. Also, it allows the elimination of polluting acid solvents and the expensive post-processing of the hydrolyzates for solvent elimination. The present work represents an investigation for the using of subcritical water in hydrolyzing wheat straw to recover available sugars for subsequent fermentation to produce ethanol or other sugar-based fermented products.

2. Materials and methods

2.1. Materials

Wheat straw was harvested and collected at Elminia City, Upper Egypt. The wheat straw was chopped into pieces of 2–10 cm by a crop chopper and further crushed into a small size using a mill. Distilled water, was used as a solvent in subcritical water hydrolysis. xylose, glucose, fructose, mannose, sucrose, phenol, sulfuric acid (98%), hydrochloric acid, Fehling A (copper II sulfate) and Fehling B (Sodium hydroxide, sodium potassium tartarate) obtained from ELnaser Company for Chemicals, Cairo, Egypt. *Saccharomyces cerevisiae* baker yeast was granted from the Faculty of Agriculture, Cairo University. A mixture of edible oil (sunflower oil) and paraffin wax was used as a heating medium for subcritical water hydrolysis. This mixture could be used for temperatures up to 290 °C without boiling. Both materials were obtained from the local market (El Minia City, Egypt).

2.2. Experimental procedures

The experiments were divided into two steps. The first step was to carry out the hydrolysis reaction. Then, the second one was to separate the hydrolyzing products. In all hydrolysis experiments, raw straw was brought as it is without pretreatment unless mentioned otherwise. By using water at its near critical condition, wheat straw was subjected to hydrolysis at different conditions. The reactor configuration and setup used in this study are shown in Fig. 1. In each experiment; 0.5 g sample was used for subcritical water hydrolysis. For the optimization experiments, the subcritical water hydrolysis was carried out in stainless steel pipes SUS 316, i.d, 0.8 cm × 15 cm (with a reactor volume of 7.54 cm3), with Swagelok caps made in Japan. The straw is charged into the reactor tube. The reactor was then closed tightly and immersed in a preheated oil-paraffin bath (Thomas Kagaku Co. Ltd., Japan). The hydrolysis was carried out in the range of 130–270 °C, and the pressure inside the reactor was estimated from the steam tables for the subcritical conditions. After the desired reaction time, the reactor was immediately cooled down by immersing it into a cold-water bath. The calculations of the yield were done based on a maximum hydrolysis yield of 75% of the total weight of the used straw, since the Egyptian wheat strew contains 75% by weight cellulose and hemicellulose which represent the source of sugar during the hydrolysis. This means that the maximum amount of sugar that could be hydrolyzed should be 75% of the total weight of the straw. Second step, was the separation of the hydrolysis products. Solid and liquid phases were separated using vacuum filtration followed by centrifugation. Then, resulting liquid mixture was filtered one or two times using filter papers to separate the residual solids. The final mixture was then stored in a deep freezer at −20 °C until further analysis.

2.3. Analytical procedures

2.3.1. Determination of total reducing sugar (TRS)

The total reducing sugar (TRS) was determined using the phenol method as described elsewhere (Dubois et al., 1956). After