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Effects of Severity Levels on Degree of Delignification of Sugarcane Bagasse Using Hydrogen Peroxide and Sodium Hydroxide

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ARTICLE INFORMATION

ABSTRACT

Harnessing energy from lignocellulosic materials such as sugarcane bagasse is increasingly coming to the forefront to replace fossil fuels. This is to reduce carbon dioxide emission into the atmosphere associated with use of fossil fuels in order to curb global warming. Processing sugarcane bagasse into an energy precursor must however be preceded by the removal of its protective and recalcitrant lignin layer. Low temperature delignification of sugarcane bagasse was carried out in this work using a potpourri of severity levels (pH, temperature, concentration, time and delignifying agent type) and the degree of delignification compared. Generally, increase in severity levels resulted in increase in degree of delignification for both hydrogen peroxide and sodium hydroxide. However, 100% increase in concentrations of sodium hydroxide and hydrogen peroxide from 30 to 60 g/l and from 3 to 6% respectively resulted in significantly lower increase in degree of delignification for all temperatures and pH values studied. Hence, severity levels arising from higher pH and temperature values is more significant than severity levels arising from lignifying agent type and its concentration.

1. INTRODUCTION

Every activity by man uses energy in one form or another. Hence, domestic and industrial activities depend largely on the availability, quality, and accessibility of energy resource. Also, economic, political, and social interactions of nations of the world depend largely on energy availability and usage (Fischer-Kowalski and Schaffartzik, 2015). Consequently, man is faced with the task of producing or harnessing energy for use. Today, energy accessibility and cost are a viable index for socio-economic and political development of most nations of the world (Vasic *et al.*, 2021).

The International Energy Outlook is critical about energy production circle. The report suggested a rise in the estimate of impending energy demand all over the world (IEO, 2016). The report also specified that the world energy need will increase to 815 quadrillion Btu in 2040, an increase of 48% over the figures of 2016. The fundamental energy source today, is fossil fuel because of its advantages which includes, high energy intensity, relatively low cost, availability in large amounts and convenience in terms of use and storage (Ballesteros et al., 2006; Uihlein and Schebek, 2009). Arising from the projections of 80% of the entire power generation in 2040 attributable to generation from fossil fuels, it is evident that global greenhouse gas (GHG) emissions will increase even further (IEO, 2016). With this scenario, it becomes imperative that the challenge facing the world today is the global reduction in carbon dioxide (CO_2) emissions by up to 80% because CO_2 is the primary gas that causes global warming (Hadjipaschalis *et al.,* 2009). The consequence of the failure of this is that the earth will become dangerous to all life on earth. The specific and sometimes stringent government and regulatory agencies guidelines, at several levels, in favour of renewable energy source, can be put down to the goal of reduction of 80% CO_2 emission thereby reducing the dangers of life on earth (Akerede et al., 2010).

Ethanol is continuously being given serious attention worldwide not only because of its worth as an energy source substitute to non-renewable fossil fuel gasoline, but also due to the increase price of crude oil as well as climatic changes with its attendant consequences (Baba et al., 2018). It is also a renewable and viable energy source, efficient and benign to the environment. As a hygienic and flammable energy source, ethanol is considered as a good alternative to replace gasoline (Thomas and Kwong, 2001).

As a result of the key value of human foodstuff and animal feed, conventional crops used for bioethanol production for example wheat, corn, molasses and sugarcane juice are not available to meet this worldwide demand of bioethanol manufacture (Baba et al., 2018). Lignocellulosic biomass, which are abundant, which form inexpensive resource, and which do not compete with crops as human food and animal feed are now being investigated as viable substitute for food crops (Baba et al., 2022). Considerable studies on ethanol production from several lignocellulosic resources have been reported (Akpan et al., 2005; Gamez et al., 2006; Dawson and Boopathy, 2008; Hendriks and Zeeman, 2009; Baba et al., 2018).

Production of bioethanol from lignocellulosic biomass entails essentially four steps with the pretreatment step posing the greatest challenge because it has to deal with many factors that limit hydrolysis, such as accessibility to the fibers, cellulose crystallinity, and lignin and hemicellulose barrier (Ko et al., 2012). Pretreatment process involves delignification of the feedstock in order to destroy the lignin layer protecting cellulose and hemicellulose, thereby increasing porosity and decreasing the crystallinity of cellulose to have access sugar substrate.

Sugarcane bagasse is a typical example of renewable lignocelluloses biomass. It is a waste matted cellulose fibre residue derived from sugarcane processing after juice extraction. Previously, it is disposed through burning. However, the increasing cost of fuel oil, natural gas and electricity generation has led renewed interest in bagasse as fuel in a number of sugar mills for electricity generation (Shrestha et al., 2012). The process of sugarcane processing is known to generate large quantity of these wastes which can be used to produce bioethanol and other equally useful products (Baba et al., 2018). Delignification of bagasse is conceived to be an intricate process, involving transfer of masses from de-lignifying agent into the raw materials and non-homogeneous chemical reactions between different material constituents employed (Tu *et al.,* 2008). Studies including the works of Baba *et al.* (2006); Baba *et al.* (2022); Kininge and Gogate, (2022) on kinetics of delignification of lignocellulosic materials have been reported. However, comparison of the effects of the severity levels imposed on delignification of sugarcane bagasse from these studies have not been reported. The aim of this study is therefore to establish the relative importance of the effects of temperature, pH, concentration and lignifying agent type on delignification of sugarcane bagasse.

2. MATERIALS AND METHODS

2.1. Bagasse Generation

Sugarcane stalk, from which the bagasse used in this study was obtained, was provided by the National Cereals Research Institute (NCRI) Badeggi, Niger State, Nigeria. The schematic diagram of the process used to generate different sizes of sugarcane bagasse is shown in Figure 1 beginning with crushing of the sugarcane stalk using JEFCO, a heavy-duty crusher shown in Plate 1. The inner structure of the crusher rotates at several revolutions per minute while making the sugarcane stalk to pass through holes and blades that crushes the stalk into bagasse with cane juice shown in Plate 2.
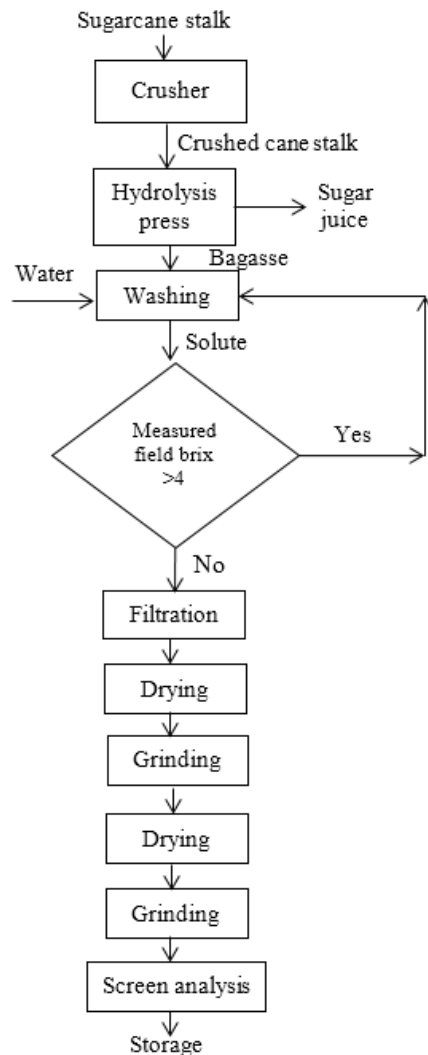

Figure 1: Process flow diagram for bagasse generation

Plate 1: JEFCO heavy duty crusher

Plate 2: Inner structure of JEFCO crusher

Sugarcane juice was then extracted from crushed sugarcane stalk using a hydraulic press resulting in "juice free" bagasse. The bagasse was subsequently washed repeatedly with tap water until free of sugar by measuring the field brix using an Abbey refractometer. This was to ensure that all ethanol subsequently produced was from de-lignified bagasse and not from any juice carried over with the bagasse. The bagasse solution in water was filtered and the cake dried at room temperature. The ground bagasse was subsequently ground using 1.5 kW ASIKO A11 double grinding mill. Screen analysis was then carried out to separate the ground bagasse into various mesh sizes using an automatic sieve shaker D403 by shaking for 30 minutes. Bagasse of each mesh size was stored in mini plastic buckets covered with cotton wool and aluminium foil before placing the lid to avoid absorption of moisture until needed for use.

2.2. Delignification at Various Severity Levels

Sodium hydroxide delignification of 0.3 mm particle diameter sugarcane bagasse was carried out using 3% v/v NaOH solution, with sugarcane bagasse to NaOH ratio of 3% w/v in a 1 litre working volume laboratory fermenter with automatic pH and temperature controls shown in plate 3.

Plate 3: Laboratory reactors with automatic pH and temperature controls

The fermenter temperature was set at 30 °C and controlled at this temperature using automatic temperature controller attached to the fermenter. Water whose temperature was at least 5 °C lower than the set point temperature was made to circulate from a reservoir through a cooling coil attached to the fermenter in order to bring the temperature of the fermenter content to the desired set point. The exit cooling water was channeled into a drain. A heater, also attached to the fermenter, heats up the fermenter content in order to increase the temperature of the fermenter content as may be necessary to maintain set point temperature. The pH was set and controlled at 8. Control of pH values at the desired set point, was achieved via automatically controlled peristaltic pumps attached to the fermenter that ensured the dosage of appropriate amount of

sulphuric acid or sodium hydroxide into the fermenter from separate beaker reservoirs containing these chemicals in order to maintain the pH at the desired set point. Once the pH was above the set point value, a sensor triggers the peristaltic pump to dose in a drop or two of sulphuric acid to lower the pH and bring it to set point. Similarly, if the pH becomes lower than the set point, a sensor triggers the peristaltic pump to dose in a drop or two of NaOH to bring the pH to the set point. Care was taken to ensure that the dosage of acid or base does not compromise the concentration of de-lignifying agent or solid loading being studied. In all the study, temperature was controlled at the set point $\pm$ 1ºC while the pH was controlled at set point $\pm$ 0.2. By successively changing the temperature values to 40 and 50 ºC, pH values successively to 9, 10 and 11 and successively changing bagasse particle size from 0.3 mm to 0.6 and 1.2 mm, other treatment conditions were similarly treated. The process described above for all sodium hydroxide treatments were repeated but using hydrogen peroxide of 3% v/v.

2.3. Preparation of Lignin Concentration Calibration Curve

Standard lignin samples, obtained from the Federal University of Technology, Minna, Nigeria was used to prepare the calibration chart for subsequent lignin measurements. Known concentrations of lignin, obtained by dissolving known masses of sample lignin in hydrogen peroxide were prepared and their absorbance measured at 320 nm using a JENWAY 6705 UV/vis. spectrophotometer. The graph of lignin concentrations versus absorbance values was obtained and subsequently used for lignin concentration measurements.

2.4. Analytical Methods

2.4.1. Measurement of lignin concentration and calculation of degree of delignification

De-lignification was monitored every 6 h by measuring the absorbance of samples taken at 320 nm. The absorbance was measured two times and the average reading recorded. To take sample, a syringe attached to the fermenter sucks about 20 ml of the fermenter content into a sample bottle, by creating a vacuum within the sample bottle. The sample taken was filtered through Whatman filter paper and the absorbance of the filtrate was measured at 320 nm. After 48 h, the fermenter content was emptied into a beaker and then filtered through Whatman filter paper and the residue washed with distilled water. The calibration curve was used to obtain the corresponding lignin concentration. Degree of delignification was subsequently calculated using Equation 1.

$$D = \frac{C_{L0} - C_{i(t)}}{C_{L0}} \times 100 \qquad\qquad (1)$$

Where D =degree of delignification, C_{L0} =initial lignin concentration (g/m³), $C_{i(t)}$ =lignin concentration at any time (g/m³)

2.4.2. Determination of bagasse composition

Composition of bagasse was determined prior to de-lignification as described by Baba *et al.* (2022) to ascertain the amount of lignin, cellulose, hemicellulose and ash content of it, while flame photometric method was used to determine the minerals composition of bagasse. Masses used in this work were taken using AL 204 Mettler Toledo balance while pH measurements were taken using HI 2211 pH/ORP meter. The sugar content in the liquid extract from sugarcane bagasse was determined using an Abbey refractometer. Absorbance of the extract were taken using JENWAY 6705 UV/vis. spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Composition of Sugarcane Bagasse

The composition of sugarcane bagasse is given in Table 1 while Table 2 shows the mineral composition. Table 1 indicates that cellulose and hemicelluloses combined, accounted for over 74% of sugarcane bagasse, which can be treated to obtain ethanol. This percentage is a motivating factor for the removal of lignin to

expose the cellulose and hemicellulose to further treatments using hydrolysis and finally fermentation to ethanol. This composition is similar to most found by other researchers (Zhao, *et al.*, 2010; Omoniyi and Olurunnisola, 2014; Zhou *et al.*, 2016). The implication of the mineral composition is that some minerals such as potassium which may be needed by the microorganisms in subsequent fermentation of de-lignified bagasse to ethanol already existed and only augmentation may be necessary during the fermentation stage.

Table 1: Composition of Sugarcane Bagasse

Composition	% by weight
Lignin	22.0
Cellulose	43.2
Hemicellulose	31.5
Ash	3.3

Table 2: Minerals analysis of sugarcane bagasse

Mineral type	Composition (ppm)
Na	355
K	875
Ca	975
P	544

3.2. Effect of Severity Levels on Delignification of Sugarcane Bagasse

Effects of various severity levels (temperature, concentration, pH and delignifying agent type) on delignification of sugarcane bagasse while particle diameter is constant are presented in Figure 2 for hydrogen peroxide treatment and Figure 3 for treatment using sodium hydroxide. The Figures show that increase in delignification consequent upon increase in concentration of delignifying agent at the same pH and temperature values is not commensurate as delignification only marginally increased for 100% increase in concentration of the delignifying agent for all temperatures and pH values. However, delignification increased significantly with pH from 8 to 11 compared to increase obtained for 100% increase in concentration for all temperatures between 30 ^{o}C and 50 ^{o}C. This result is in agreement with the findings of Zhao et al. (2013). This may be due to lower activation energy in higher pH and higher temperature treatments.
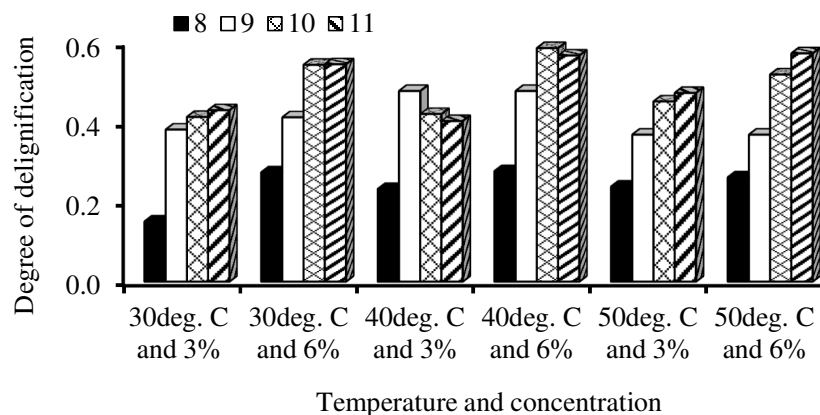
Figure 2: Effect of temperature, pH and H_2O_2 concentration on degree of delignification of sugarcane bagasse
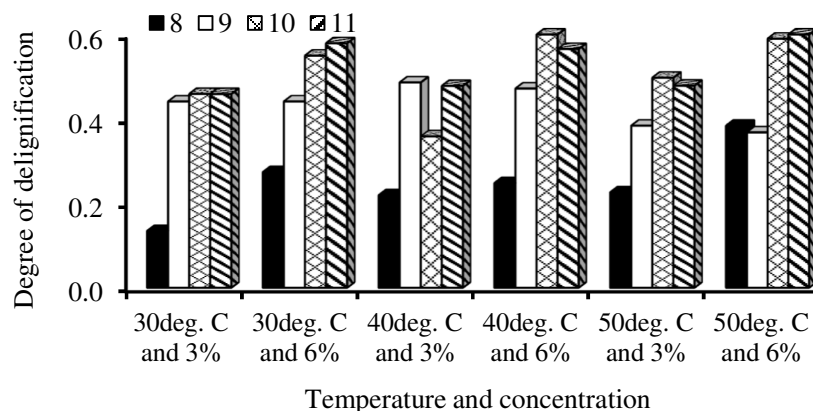
Figure 3: Effect of temperature, pH and NaOH concentration on degree of delignification of sugarcane bagasse

4. CONCLUSION

This works concludes that severity conditions arising from increase in temperature and pH is more important than severity conditions arising from increase in delignifying agent concentration for both hydrogen peroxide and sodium hydroxide.

5. ACKNOWLEDGMENT

6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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