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A Comparative Kinetic Study of Acidic Hydrolysis of Wastes Cellulose from Agricultural Derived Biomass

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ABSTRACT: Bioconversion of agricultural waste products to produce value-added fuels and chemicals offers potential economical, environmental and strategic advantages over traditional fossil-based products. The kinetics of acid hydrolysis of cellulose isolated from banana skin, cowpea shells, maize stalks and rice husk (agricultural waste) were studied at temperature ranging between 70 – 100°C in a stirred conical flask which served as a batch reactor. The effect of acid concentration on cellulose hydrolysis was also investigated. The results showed that the rate of hydrolysis by virtue of glucose yield generally increased with increase in temperature and acid concentration for all the four agricultural wastes used. The experimental data were fitted to integrated first order rate kinetics and the results obtained suggested a first order rate of glucose formation from four agricultural wastes cellulose used. The activation energies estimated from Arrhenius equation are 39.60 KJ/mole, 38.83 KJ/mole, 44.37 KJ/mole and 34.29 KJ/mole for banana skin, cowpea shells, maize stalks and rice husk cellulose, respectively. These values suggests the ease with which hydrolysis can occur between the four agricultural wastes cellulose. @JASEM

Keywords: Agricultural wastes; cellulose; acid hydrolysis; first-order rate kinetics; activation energy, Arrhenius equation

The agricultural activities of man have resulted in the production of large quantities of agricultural waste biomass that tends to dominate and pollute the environment. Many of these agro-wastes are allowed to rot away not utilized (Obot et al., 2008). These wastes biomass consist of cellulose, hemicellulose, lignin and other materials called extractive (Ghose, 1956, Aberuagba, 1997). Among all the constituents of agricultural wastes biomass, cellulose constitutes the highest percentage because it is a strong elastic material that forms the cell wall of nearly all plants (Aberuagba, 1997). The cellulose can be hydrolyzed to produce glucose for human needs, which can further be used as substrates for fermentative production of useful products like alcohols (John et al., 2007; Benkun et al., 2008).

Bioconversion of agricultural wastes biomass to produce value-added fuels and chemicals offers potential economical, environmental and strategic advantages over traditional fossil-based products (Anex et al., 2007). Generally, agricultural wastes from different sources have different physical properties such as surface area, lignifications, crystallinity and other different chemical compositions that could hinder the accessibility susceptibility of cellulose for hydrolysis (Aberuagba, 1997; Caritas and Humphrey, 2006). However, they may be modified to enhance their susceptibility to hydrolysis through pretreatment processes. The pretreatment process (physical, chemical and/or microbial) alters the structure and compositions of the agricultural wastes biomass and this removes extractives, lignin and hemi-cellulose, reduce cellulose crystallinity and increase porosity (Aberuagba, 1997; Ander and Ericson, 1983; Sun and Cheng, 2002). Over the last decades, the hydrolysis of cellulose and lignocellulosic materials has been a subject of intensive research for the development of large scale conversion processes that would be of benefit to mankind (Patel and Bhatt, 1992; Nicolettal et al., 2002; Hahn-Hagerdal et al., 2006; Qu et al., 2006). These processes would among other things help to solve modern disposal problems, reduce pollution of the environment and reduce man's dependence on fossil fuels by providing a convenient and renewable source of energy in the form of bioethanol (Cowling et al., 1976). Conversion of cellulose and lignocellulosic biomass to glucose and other monomeric sugars can be achieved by acid and enzyme hydrolysis (Badger, 2002; Benkun, et al, 2008, Megawati et al., 2010; Wu et al., 2010). The relative advantages of enzyme and acid hydrolysis of cellulose is a subject of continuing research study.

The enzymatic process is believed to be the most promising technology because enzymatic hydrolysis is milder and more specific and does not produce by products (Wen et al., 2004; Benkun et al, 2008). However, enzymatic hydrolysis of cellulose have been observed not to be economically viable because of high cost of enzymes, slow rate of depolymerization and high enzyme loading to realize reasonable rates and yields (Layokun, 1981; Aberuagba, 19997; Grohmann and Baldwin, 1995; Wyman, 1999). The advantages of acid hydrolysis for

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peel liquefaction and releasing carbohydrates prior to enzymatic treatment have been studied (Vaccarino et al; 1989; Grohmann et al., 1995; Talebnia et al., 2008). Acid hydrolysis of cellulosic biomass is relatively fast and of low cost (Palmqvist and Hagerdal, 2000; Megawati et al., 2010). The key variables that might have impacts on the rate and extent of cellulose and lignocellulosic biomass by acid hydrolysis are temperature, acid concentration (or pH), total solid fraction (TS) and time duration (Grohmann, et al., 1995; Talebnia et al., 2008). Several studies have been made on cellulose hydrolysis using purified raw materials especially commercial cellulose, but very few studies using cellulose derived from agricultural wastes (Aberuagba, 1997; Talebnia et al., 2008; Benkun et al., 2008; Megawati et al., 2010).

The objective of this study is to examine the effects of sulfuric acid concentration and temperature on the hydrolysis of cellulose that is naturally occurring in banana skin (peels), cowpea shells, maize stalks and rice husk which abound as agricultural wastes in many part of the world and to evaluate their kinetics.

MATERIALS AND METHODS

Materials: Banana skin (peels), cowpea shells, maize stalks and rice husk were obtained from farmers in Ogbomoso, Nigeria. Sulfuric acid (specific gravity 1.8; 98% purity) and Diethyl ether which are products of E. Merck (Darmstadt Germany) were purchased from a chemical store in Ibadan, Nigeria. These were used for the removal of extractives. Other chemicals used were of analytical or biochemical grade.

Pretreatment of Agricultural Waste: Samples of each agricultural waste (i.e. banana skin, cowpea shells, maize stalks and rice husk) were sun dried and then reduced to very small sized particles by grinding, using a serrated disk grinder. The particles were then sieved to obtain an average particle size of 300 µm for each sample.

Isolation of Cellulose from Agricultural Waste: Cellulose was isolated from each sample of agricultural waste using the modified procedure described by Layokun (1981). Diethyl ether (20 ml) was added to each sample (10 g) of agricultural waste in a 250 ml Erlenmeyer conical flask so as to remove the extractives. The resultant residue (free of extractives) was filtered and washed thoroughly with sterile distilled water. To the washed residue was added 20 ml of 14M sulfuric acid which then dissolved the cellulose and hemi cellulose leaving lignin as a hard precipitate. Lignin was filtered off and 8M sodium hydroxide solution was added to the filterate to obtain a residue that was predominantly cellulose, while hemi cellulose remained in solution. The solution was filtered and the resultant cellulose residue was then washed thoroughly with sterile distilled water until a neutral pH was obtained. The cellulose residue was then dried at 80^{o}C in an oven until a constant weight was obtained for subsequent hydrolysis.

*Experimental Design for Acid Hydrolysis of Cellulose:*To each sample of the cellulose (5 g) obtained from the agricultural wastes (banana skin, cowpea shells, maize stalks and rice husk) was added 50 ml of concentrated sulfuric acid (1.5 moles/dm^3) in a 250 ml conical flask which served as a batch reactor and placed in a gyratory shaker set at a temperature of 70^{o}C with an agitation speed of 150 rpm. This operation was carried out for 2 h, and at intervals of 30 min, samples were withdrawn to determine the glucose concentration. The experiment was conducted at other temperatures of 80, 90,100^{o}C and sulfuric acid concentrations of 2.5, 3.5 and 4.5 moles/ dm^3, respectively.

Determination of Glucose Concentration: The reducing sugar content (glucose) was determined by the DNS method with glucose as standard (Miller, 1959; Marsden et al., 1982). Absorbance was measured at 540 nm. However, the DNS reagent was modified according to Mwesigye (1988). Two hundred grams of potassium sodium tartarate (Rochelle salt) were dissolved in 200 ml of sterile distilled water. Ten grams of sodium hydroxide was also dissolved separately in 200 ml of sterile distilled water in a 500 ml beaker. To the sodium hydroxide solution was added 10 g of DNS (3, 5-dinitrosalicyclic acid) and 2.52 ml (2 g) of 80% (w/v) phenol simultaneously. After stirring to complete dissolution, the mixture was added to the Rochelle salt solution. The resultant solution was then made up to one litre with sterile distilled water. This mixture gave the stock of the modified DNS reagent containing 1% (w/v) DNS acid, 0.2% (w/v) phenol, 1% (w/v) sodium hydroxide and 20% (w/v) Rochelle salt (Mwesigye, 1988). The DNS reagent was then stored under refrigeration in an amber coloured bottle.

Kinetics of Acid Hydrolysis: The change in the concentration of waste cellulose either positively or negatively at a constant temperature over a period of time can be described by a relationship as given in equation (1):

$$C_o - X = C_o \exp(kt) \quad \text{-----------} (1)$$

Where C_o, the total initial waste cellulose concentration, k, specific rate constant (min^{-1}), $C_o - X$, waste cellulose concentration at time t (g/l), X, glucose content (g/l), and t, time (min). On the basis of a first-order reaction for the hydrolysis, equation (1) becomes:

$$\ln(C_o / C_o - X) = -kt \text{ ---------- (2)}$$

Thus, equation (2) allows the natural logarithmic plots of experimental values of $C_o / C_o - X$ versus process time (t) in which straight lines obtained are indications of the validity of first-order reaction kinetics for the waste cellulose acid hydrolysis. The intensity of heat on hydrolysis of waste cellulose can be described by the

Arrhenius model such that temperature dependence of k closely follows the equation:

$$k = k_R \exp[-E_a / R (1/T)t] \text{ ------------ (3)}$$

Where k_R, pre-exponential constant (min^{-1}); E_a, activation energy (KJ/mol); R, ideal gas constant (8.314 J/mol.K); T, actual temperature (K) and t, time (min). The regression of the natural logarithm of the degradation rate constant (k) against ($1/T$) in which a straight line curve is obtained indicates that the Arrhenius model was fulfilled and slope of this curve (Arrhenius plot) is equal to E_a / R and allowed calculation of the activation energy.

RESULTS AND DISCUSSION

The percentage cellulose yield from each of the agricultural waste are 28.4%, 37.2%, 56.7% and 31.5% for banana skin, cowpea shells, maize stalks and rice husk, respectively. Benkun et al. (2009) obtained 60.12% cellulose from the acid hydrolysis of wheat straw. The effect of temperature on glucose yield from acid hydrolysis of wastes cellulose from banana skin, cowpea shells, maize stalks and rice husk is shown in Fig.1.

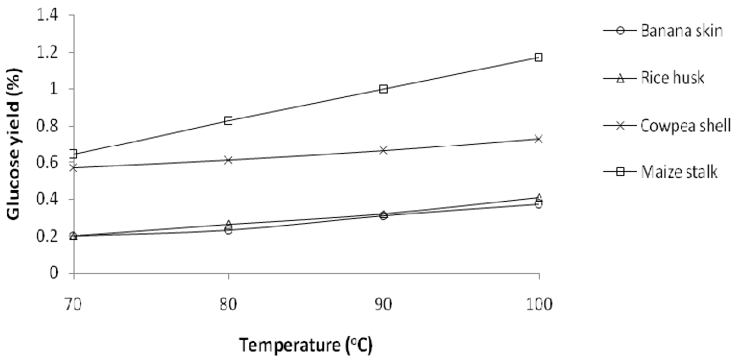

Fig. 1: Effect of temperature on glucose yield from different agricultural waste cellulose acid hydrolysis

From Fig 1, it is seen that the glucose yield from each of the agricultural waste cellulose increased with increase in temperature. A similar observation has been reported (Aberuagba, 1997). Talebnia et al. (2008) reported that in the acid hydrolysis of orange peels at low temperature range, sugar yield increased with increase in temperature and at very high temperature range, sugar yield declines. However, Megawati et al. (2010) reported that in the acid hydrolysis of rice husk, at high temperature range (160 – 220°C), total sugar concentrations increased with increase in temperature. Layokun (1981) has also observed an increase in glucose yield with temperature for acid hydrolysis of saw dust. Furthermore, the yields of glucose from wastes cellulose of banana skin (0.20 - 0.37%) and maize stalks (0.20 - 0.41%) are relatively comparable at the temperature of 70 – 100°C. However, they are both lower than the glucose yield from wastes cellulose of cowpea shells and rice husk, respectively. Also, the glucose yield obtained from wastes cellulose of cowpea shells (0.64%) and rice husk (0.57%) are relatively comparable at lower temperature range of 70°C, however, the yields from wastes cellulose of cowpea shells (0.83 - 1.17%) are higher than the yields from rice husk (0.61 - 0.73%) at higher temperature range of 80-100°C. Aberuagba (1997) reported a glucose yield of 0.74 - 1.27% from wastes cellulose of maize cobs and 0.67 - 1.17% from groundnut shells in an acid hydrolysis at a temperature range of 65 – 80°C and 2.5M sulfuric acid concentration. Megawati et al (2010) reported a sugar yield of 12.70% at a temperature of 220°C.

Fig 2 show the effect of acid concentration on glucose yield from the acid hydrolysis of waste cellulose obtained from banana skin, cowpea shells, maize stalks and rice husk, respectively.

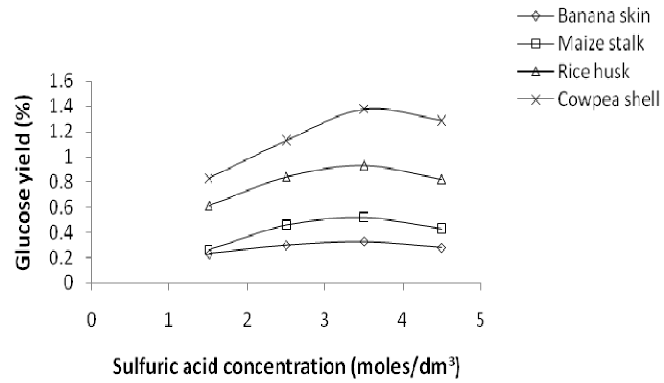

Fig. 2: Effect of sulfuric acid concentration on glucose yield from different agricultural waste cellulose acid hydrolysis

The results revealed that in all the different waste cellulose considered, there was a general increase in glucose yield as the acid concentration increased in the range 1.5 - 4.5 mole/dm$^{3.}$ However, there was a decline in yield from an acid concentration of 3.5 to 4.5 moles/dm^3. A similar observation has been reported for the acid hydrolysis of cellulose from maize cobs and groundnut shells (Aberuagba, 1997). This observation could be attributed to the fact at high acid concentration and relatively high temperature; glucose can be converted to organic acid which led to a decrease in glucose concentration (Aberuagba, 1997). This suggests that maximum glucose yield could be obtained at low to moderate acid concentration. Talebnia et al. (2008) reported that at low acid concentration and low temperature, sugar yield increases with increase in dilute acid concentration. The glucose yield obtained from wastes cellulose of banana skin (0.20%) and maize stalks (0.20%) at acid concentration of 1.5 moles/dm^3 are relatively comparable. However, the yield obtained at 2.5 to 4.5 mole/dm^3 sulfuric acid concentration from wastes cellulose of maize stalks (0.45 - 0.50%) is higher than that from banana skin (0.20 - 0.33%). The yields of both wastes cellulose at an acid concentration range of 1.5 - 4.5 moles/dm^3 are generally lower than that from both cowpea shells and rice husk, respectively.

The glucose yield from wastes cellulose of cowpea shells (0.64%) and rice husk (0.57%) at 1.5 mole/dm^3 sulfuric acid concentration are relatively comparable. However, at an acid concentration range of 2.5 - 4.5 moles/dm^3, the yield from wastes cellulose of cowpea shells (1.13 - 1.38%) is higher than that from rice husk (0.84 - 0.93%). Aberuagba (1997) reported a glucose yield of 1.0 - 1.17% from wastes cellulose of maize cobs and 1.04 - 1.3% from groundnut shells in an acid hydrolysis with a sulfuric acid concentration range of 2.5 - 5.0M, respectively. Rahman et al. (2006) also reported that the acid hydrolysis of oil palm empty fruit bunch with acid concentration of 2 - 6% produced a sugar yield of 31.74%.

An integrated pseudo first- order rate kinetics (equation 1) was applied to the experimental result data obtained for banana skin, cowpea shells, maize stalks and rice husk, respectively, at a temperature range of 70 - 100°C and acid concentration of 1.5 moles/dm^3. The plot of $\ln\left(C_o / (C_o - X) \right)$ versus time (t) gave a straight line for each of the agricultural waste cellulose as shown in Figs 3 – 6, with the specific rate constant 'k' estimated from the slope. The straight line obtained in Figs 3 - 6 for temperature (70 -100°C) investigated suggests a first order rate of glucose formation from banana skin, cowpea shells, maize stalks and rice husk hydrolysis by sulfuric acid. The specific rate constant values obtained from Figs. 3 - 6 were fitted to Arrhenius equation (equation 3) and the activation energies were estimated from the slope of the plot of $\ln k$ versus ($1/T$) as shown in Fig.7. A value of 39.60 KJ/gmole, 37.83 KJ/gmole, 44.37 KJ/gmole and 34.29 KJ/gmole were obtained for banana skin, cowpea shells maize stalks and rice husk, respectively. The difference in the activation energies between these four agricultural wastes cellulose can be attributed to difference in their degree of polymerization and crystallinity (i.e. structural features). Crystallinity values have been reported to vary widely with a value of 73% in cotton linters and 29% in maize cobs (Ghose, 1956, Aberuagba, 1997). Furthermore, it has been reported that even when the ultimate chemical composition of two cellulosic materials is approximately the same, their response to cellulose attack can be surprisingly different (Ghose, 1956, Aberuagba, 1997). The activation energy values for the four agricultural waste cellulose suggests that the ease with which hydrolysis can occur between the four agricultural waste can be arranged in this order: Rice husk > cowpea shells > Banana skin > maize stalks. Activation energies of 26.6 KJ/mole, 45 KJ/mole, 76.71 KJ/mole, 78.35 KJ/mole, 80.34 KJ/mole. 72.6 KJ/mole and 64.35 KJ/mole have correspondingly been obtained for the acid hydrolysis of sawdust, maize cobs, groundnut shells, sunflower seed hull, corn cob, corn fiber (a co-product of corn wet-milling) and rice husk (Layokun, 1981; Aberuagba, 1997; Saracoglu et al., 1998; Mosier et al., 2002; Megawati et al., 2010).

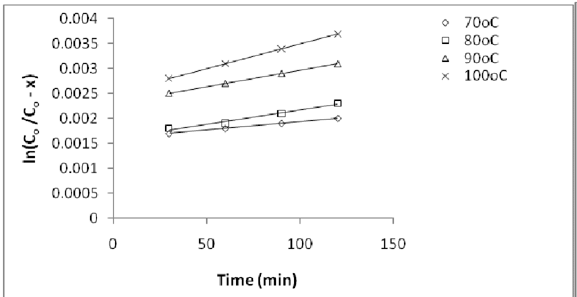

Fig. 3: Test of first order kinetics for banana skin acid hydrolysis

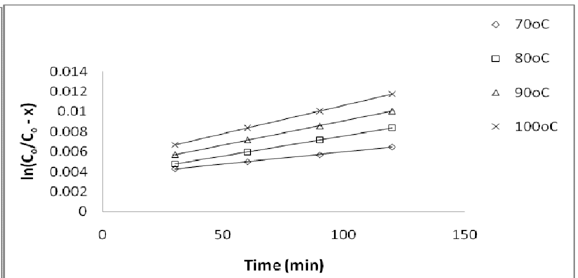

Fig. 4: Test of first order kinetics for cowpea shell acid hydrolysis

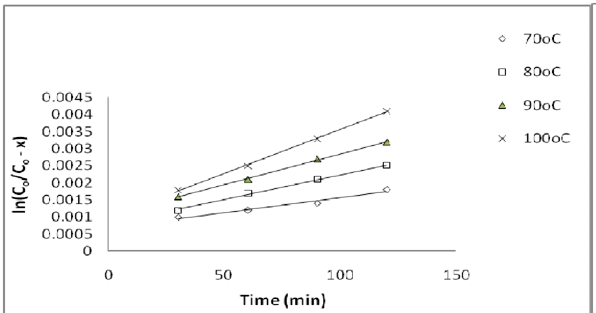

Fig. 5: Test of first order kinetics for maize stalk acid hydrolysis

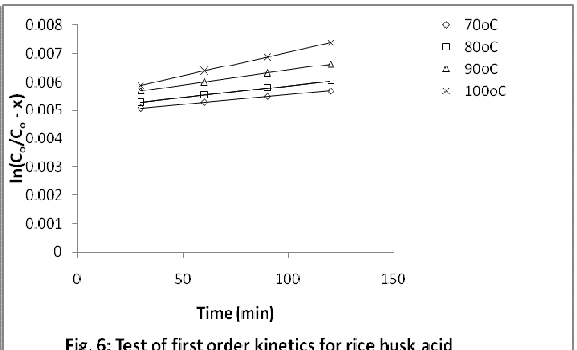

Fig. 6: Test of first order kinetics for rice husk acid hydrolysis

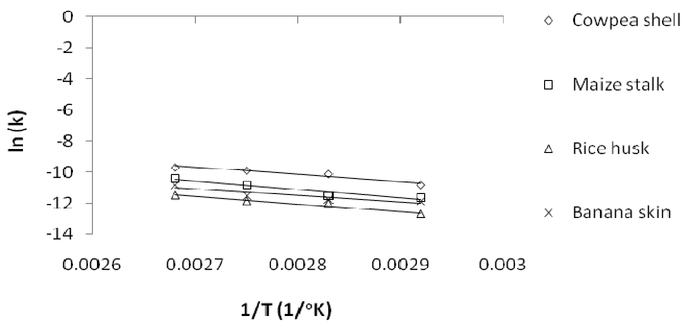

Fig. 7:Arrhenius plot for different agricultural waste cellulose acid hydrolysis

Conclusion: The kinetics of concentrated acid hydrolysis of banana skin, cowpea shells, maize stalks and rice husk can be quantitatively described by a pseudo first-order rate of homogenous reaction. Kinetic constant can be expressed by Arrhenius equation with activation energies of 39.60, 37.83, 44.37 and 34.29 KJ/mole for sulfuric acid hydrolysis of cellulose from banana skin, cowpea shells, maize stalks and rice husk, respectively. Temperature and acid concentration strongly influences the rate of cellulose hydrolysis and thus the glucose yield. Thus, from this work coupled with results of other researchers, it seems possible to totally convert agricultural wastes into useful products for the benefit of mankind.

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