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## Comparative Study of the Efficiency of Mineral Acid Catalysts in the Conversion of Starch to Glucose

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### Abstract

The efficiency of H<sub>3</sub>PO<sub>4</sub>, HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, HCl and HNO<sub>3</sub> in the hydrolysis of corn starch was studied by taking the time dependence of glucose yield during hydrolysis, in the presence of mineral acid catalysts. Hydrolysis in H<sub>3</sub>PO<sub>4</sub> occurred at 12 % v/v of the acid with less than 2 % glucose yield. Hydrolysis could not occur at concentrations between 1 – 11 % v/v and higher than 20 % v/v. Steady increases in glucose yield were obtained using other mineral acids with H<sub>2</sub>SO<sub>4</sub> showing a decrease in yield above 4 % v/v due to possible degradation of glucose in the acidic medium. A direct relationship between glucose yield and increase in weight of starch was observed using HCl and HNO<sub>3</sub> catalysts, with HNO<sub>3</sub> giving two times more glucose than HCl in 30 minutes. The hydrolyzing ability of HClO<sub>4</sub> was independent of the weight of starch used in the process. HClO<sub>4</sub> gave a maximum yield of 16.5 % glucose in 32 minutes before glucose degradation commenced. Glucose yield in HNO<sub>3</sub> and HCl increased with 68.6 % and 38.2 % of glucose formed in 60 minutes respectively, making HNO<sub>3</sub> the most efficient catalyst for starch to glucose conversion.

**Keywords:** Catalyst, Glucose, Glucose degradation, Hydrolysis, Mineral acids, Starch

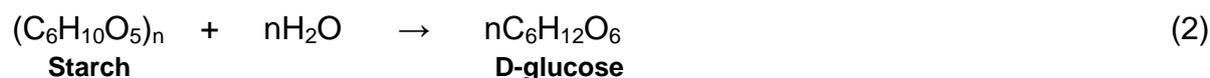
### 1. Introduction

The drop in the world's fossil fuel reserves has necessitated the search for alternative and more ecofriendly replacements for this natural product. In many countries, Nigeria inclusive, energy consumption is based on imported refined fossil

fuel. There is however need for alternative sources of energy which can compete with fossil fuel, in terms of cost and quality. The starch in feedstocks like cassava, maize, sorghum etc, has been harnessed for the production of bioethanol an alternative for petrol, derived from fossil fuel petroleum (Ado, Olukotun, Ameh & Yabaya, 2009; Ademiluyi & Mepba, 2012; Mojovic, Pejin, Grujic, Markov, Pejin, ...& Savic, 2009):

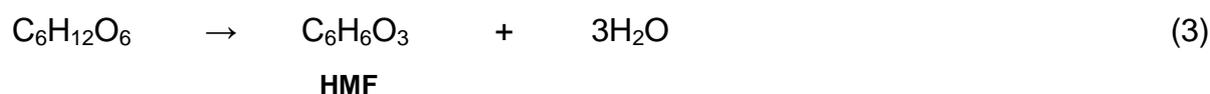


Starch is a well-known polymer of glucose, linked by glycosidic bonds (Maarel, Mjec, Uitdehaa, Leemuhuis & Dijkhuizen, 2002). The first stage in exploiting the energy in starch is to hydrolyze it to glucose. Starch hydrolysis is expressed as (Kearsley and Dziedzic, 1995):



The two commonly used technologies in the conversion of starch to glucose are acid and enzymatic hydrolyses. Acid concentration, operating temperature and duration of hydrolysis play significant roles in determining both the quantity and quality of glucose, during acid hydrolysis (Teerapatr, Cholada, Bongotrat, Wichien & Sirintip, 2004).

The use of mineral acids as catalysts in the hydrolysis of starch to glucose is associated with many side reactions (Thompson & Grethlein, 1979; Pilath, Nimlos, Mittal, Himmel & Johnson, 2010; Summerskii, Krutov & Zarumin, 2010; Usuki, Kimura & Adachi, 2007). One of these is that the produced glucose is converted to 5-hydroxymethylfurfural (HMF) (Patil & Lund, 2011; Duru *et al*, 2012):



This reaction is enabled by the acidic medium and leads to a drop in the yield of glucose formed.

The aim of this study is to determine the efficiency of common mineral acids in the conversion of corn starch to glucose and their susceptibility to glucose degrading side reactions.

## **1.0 Materials and Methods**

### **2.1 Reagents and sample preparation**

All the mineral acids and corn starch used for this study were of analytical grade, purchased from FINLAB Nigeria Ltd and used without further purification.

### **2.2 Instrumentation**

Glucose concentrations were determined using HI96803 Digital Glucose Refractometer by HANNA Instruments.

### **2.3 Procedure**

#### **2.3.1 Effect of Acid Concentration**

Starch of weight 1.0 g was transferred into a 500 mL beaker. 300 mL of 1 % v/v  $\text{H}_3\text{PO}_4$  was added and the mixture was stirred for few seconds. 100 mL each of this solution was transferred into three glass reactors of volume 200 mL and corked. The reactors and their content were quickly immersed in a water-bath set at 100 °C and allowed for 5 minutes to equilibrate with the temperature of the bath and then left for 30 minutes. At the end of the 35 minutes reaction time, the mixtures were quickly neutralized with excess anhydrous sodium hydrogen carbonate ( $\text{NaHCO}_3$ ) and the glucose concentrations in the solutions were measured. The process was repeated using 2 % v/v, 4 % v/v, 8 % v/v, 16 % v/v and 20 % v/v of the acid. The experiment was repeated using the same concentrations of  $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{HNO}_3$ .

#### **2.3.2 Effect of Biomass Weight**

Starch of weight 0.5 g was weighed and transferred into a 500 mL beaker. 300 mL of 8 % v/v  $\text{HCl}$  were added and the mixture was stirred for few seconds. 100

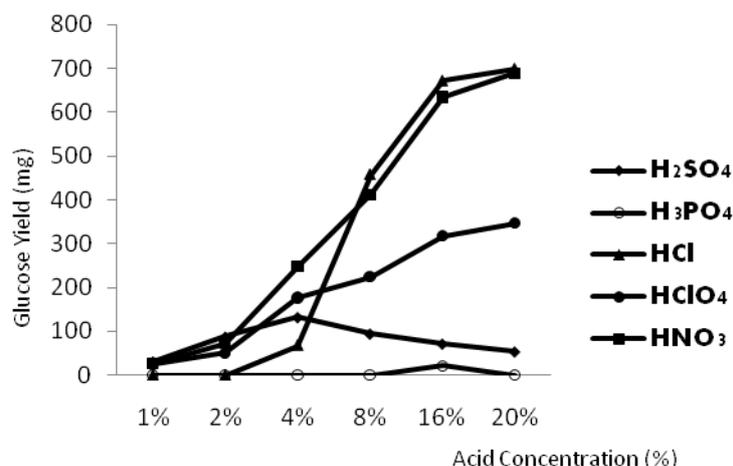
mL each of this solution were transferred into three glass reactors of volume 200 mL and corked. The reactors and their contents were quickly immersed in a water-bath set at 100 °C and allowed 5 minutes to equilibrate with the temperature of the bath and then left for 30 minutes. At the end of this time, the mixtures were quickly neutralized with excess anhydrous sodium hydrogen carbonate ( $\text{NaHCO}_3$ ) and the glucose concentrations in the solutions were measured. The process was repeated using 1.0 g, 1.5 g and 2.0 g of starch respectively. The procedure was repeated using 8 % v/v  $\text{HNO}_3$  and  $\text{HClO}_4$  respectively.

### 2.3.3 Effect of Contact Time

Starch of weight 2.0 g were transferred into a 500 mL beaker. 300 mL of 8 % v/v HCl were added and the mixture was stirred for few seconds. 30 mL of this solution were transferred in 10 separate reactors which were all simultaneously placed in a water-bath set at 100 °C and allowed 5 minutes to equilibrate with the temperature of the bath. After 10 minutes a reactor was removed from the water-bath, quickly neutralized with excess anhydrous sodium hydrogen carbonate ( $\text{NaHCO}_3$ ) and the glucose concentrations in the solutions were measured. Other reactors were removed at 10 minutes intervals and their glucose contents measured. The experiment was repeated using 8 % v/v  $\text{HNO}_3$  and  $\text{HClO}_4$  respectively.

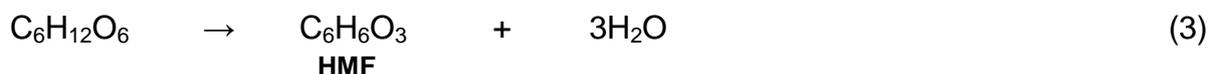
### 3.0 Results and Discussion

The effect of the concentrations of the different acids on the yield of glucose is shown in figure 1.



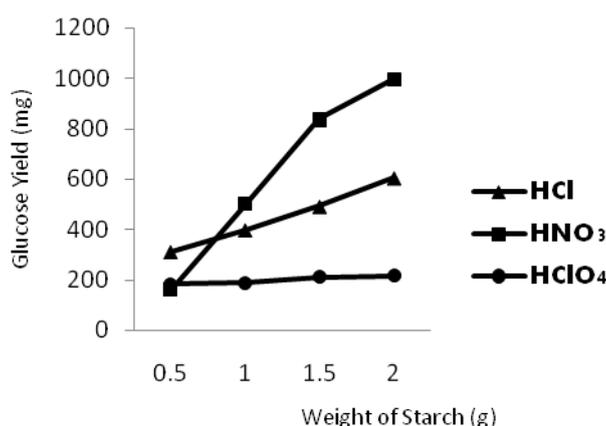
**Fig. 1: Effect of Acid Concentration on Glucose Yield**

Between 1 – 11 % v/v phosphoric acid, starch hydrolysis could not occur. At 16 % v/v, 2 % starch to glucose conversion occurred after 30 minutes. At concentrations higher than 16 %, starch conversion to glucose reduced and became zero at about 19 % v/v. The triprotic dissociation of this acid which is energetically less favourable at the second and third dissociations, as well as its buffering properties might be factors affecting the availability of protons for the hydrolysis process. When sulphuric acid was used as the catalyst, starch conversion increased steadily between concentrations between 1 and 4 % v/v, but experienced a sharp reduction above this concentration. Though sulphuric acid is a strong acid, the hydrolyzed glucose in this medium could have been converted to HMF (Duru *et al*, 2012), reducing the glucose concentration in the solution.



This is buttressed by the fact that glucose concentration drastically reduced as the acid concentration increased. The conversion of starch to glucose increased steadily when the process was catalysed by HNO<sub>3</sub>, HCl and HClO<sub>4</sub> respectively. Starch to

glucose conversion in 8 % v/v of these acids were found to be 64 %, 67 % and 32 % respectively in 30 minutes, making hydrochloric acid and nitric acid the most efficient catalysts at the studied acid concentrations. Glucose to HMF conversion which occurs in acidic medium resulting in glucose yield reduction was not observed in these media between 6-16 % v/v. This could be because the acid concentration points for glucose to HMF conversion in these media were not reached in this study. The effect of weight of starch on the rate of starch hydrolyses in  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{HClO}_4$  is shown in figure 2.

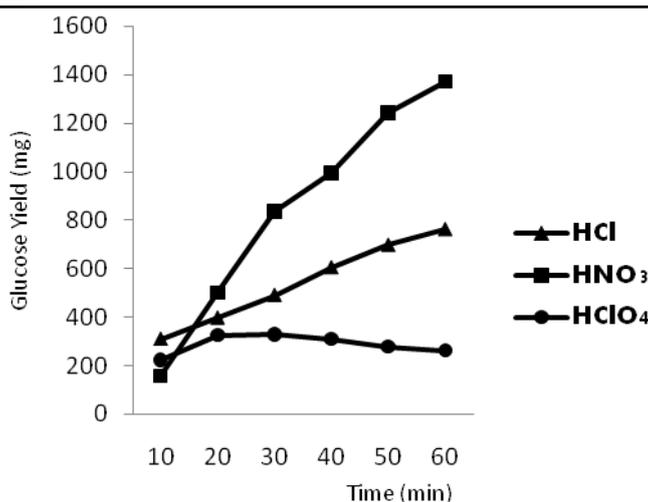


**Fig. 2: Effect of Biomass Weight on Glucose Yield**

Glucose yield in the perchloric acid catalyst gave a pseudo-first order like relationship where glucose yield was not independent on the weight of starch used. This observation is an indication that perchloric acid might be degrading the glucose formed and therefore not favourable in the industrial scale production of glucose from starch.

Hydrochloric acid gave a higher yield of glucose than nitric acid at lower starch weights. With an increase in the weight of starch an exponential increase in the rate of starch hydrolysis was observed in the nitric acid catalyst. This medium gave a 1.3 to 1.7 times increase in yield with increase in starch weight from 1.0 g to 2.0 g. This observation favours the use of nitric acid catalyst in the large scale conversion of starch to glucose.

The time dependence of starch hydrolyses to glucose in  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{HClO}_4$  is shown in figure 3.



**Fig. 3: Effect of Contact Time on Glucose Yield**

Glucose yield of about 0.33 g was observed in 20 minutes when perchloric acid was used as catalyst, which gradually dropped as time increased. The drop in the yield of glucose using this acid could indicate that the conversion of glucose to HMF in the reaction solution sets in after this time period. This observation further gives credence to the fact that this acid cannot be applied in the large scale production of glucose from starch.

Nitric acid and hydrochloric acid gave glucose yields of 68.6 % and 38.2 % respectively in 60 minutes, making nitric acid almost twice more efficient than hydrochloric acid in starch hydrolysis to glucose in this acid medium.

#### 4.0 Conclusion

Starch to glucose conversion is possible in different acid environments but the efficiency of this process differs greatly. Phosphoric acid is not efficient for this process under the studied conditions. Even though sulphuric acid, hydrochloric acid and perchloric acid can convert starch to glucose, their processes are not industrially feasible. Nitric acid however gave a good yield of glucose from starch with no observed degradation of the product under the study conditions, making it the most efficient acid catalyst for the hydrolysis of starch to glucose.

## References

- Ademiluyi, F.T. & Mepba, H.D. (2012). Yield and properties of ethanol biofuel produced from different whole cassava flours. *Biotechno., 1*, 1-6.
- Ado, S.A., Olukotun, G.B., Ameh, J.B. & Yabaya, A. (2009). Bioconversion of cassava starch to ethanol in a simultaneous saccharification and fermentation process by cocultures of *Aspergillus niger* and *Saccharomyces cerevisiae*. *Sci. World J., 4*, 19-22.
- Duru, C.E., Duru, I.A & Nwagbara, N.K. (2012). Glucose conversion to 5-hydroxymethylfurfural – pH enhanced product formation using CrCl<sub>2</sub> in liquid water. *Macromolecules An Indian Journal, 8*(1), 24-27.
- Kearsley, M.W. & Dziedzic, S.Z. (1995). *Handbook of starch hydrolysis products and their derivatives*. Cambridge: The University Press, 9.
- Maarel, V.D., Mjec Veen, B.V.D., Uitdehaa, J.C.M., Leemhuis, H. & Dijkhuizen, L. (2002). Properties and applications of starch-converting enzymes of the alpha-amylase family. *J. Biotechnol., 94*, 137-155.
- Mojovic, L., Pejin, D., Grujic, O., Markov, S., Pejin, J., Rakin, M., Vukasinovic, M., Nikolic, S. & Savic, D. (2009). Progress in the production of bioethanol on starch-based feedstocks. *Chem. Ind. Chem. Eng. Quarterly, 15*, 211-226.
- Patil, S.K. & Lund, C. (2011). Formation and growth of humins via aldol addition and condensation during acid-catalyzed conversion of 5-hydroxymethylfurfural. *Energy Fuel, 25*, 4745-4755.
- Pilath, H., Nimlos, M., Mittal, A., Himmel, M. & Johnson, D. (2010). Glucose reversion reaction kinetics. *J. Agric. Food Chem., 58*, 6131-6140.
- Sumerskii, V.I., Krutov, S.M.K. & Zarumin. M.Y. (2010). Humin-like substances formed under the conditions of industrial hydrolysis of wood. *Russ. J. Appl. Chem., 83*, 320-327.
- Teerapatr, S., Cholada, S., Bongotrat, P., Wichien, K. & Sirintip, C. (2004). Utilization of waste from cassava starch plant for ethanol production. The Joint International Conference on "Sustainable Energy and the Environment (SEE)", Hua Hin Thailand.
- Thompson, D.R. & Grethlein, H.E. (1979). Design and evaluation of a plug flow reactor for acid hydrolysis of cellulose. *Ind. Eng. Chem. Prod., 18*, 166-169.
- Usuki, C., Kimura, Y. & Adachi, S. (2007). Isomerization of hexoses in subcritical water, *Food Sci. Technol. Res., 13*, 205-209.