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Glucose conversion to 5-hydroxymethylfurfural- pH enhanced product formation using $CrCl_2$ in liquid water

Chidi Edbert Duru[1*], Ijeoma Akunna Duru[1], Nkechi Kelechi Nwagbara[2]
[1]Department of Chemistry, Federal University of Technology, Owerri, P.M.B.1526, Owerri Imo State, (NIGERIA)
[2]Projects Development Institute, P.M.B. 01609, Enugu, (NIGERIA)
E-mail : chydik2002@yahoo.co.uk

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ABSTRACT

The effect of liquid water pH on the conversion of glucose to 5-hydroxymethylfurfural (HMF) catalysed by $CrCl_2$, $CoCl_2$, $CuCl_2$, $SnCl_2$ and $FeCl_3$ respectively has been studied at 373 K using UV/Vis Spectrophotometry. Absorbance values of HMF in the different study solutions were used for its quantification. Best yields of HMF were obtained with $CrCl_2$ and $CuCl_2$ with absorbance values of 0.687 and 0.284 respectively. The effect of liquid water pH using $CrCl_2$ as catalyst for glucose conversion to HMF gave a geometric increase in HMF yield above pH of 9. This result suggests that optimum conversion of glucose to HMF in liquid water is effective in alkaline media using $CrCl_2$. Studies on the kinetics of the reaction at pH 12 using $CrCl_2$ as catalyst, gave maximum product yield in 40 minutes at the study conditions. The rate data obtained indicated that the reaction is a unimolecular first order process with rate constant $6.5\ 10^{-6}\ s^{-1}$.

KEYWORDS

Glucose;
5-hydroxymethylfurfural;
Chromium (II) chloride;
Rate constant;
Liquid water.

INTRODUCTION

The potentials of 2,5-dimethylfuran (DMF) as a biofuel have been the focus of research in recent times[1,2]. This compound is produced by the hydrogenation of 5-hydroxymethylfurfural (HMF). Cheap and commercial methods of HMF production have therefore necessitated current attention on it than the biofuel DMF. HMF was initially produced by inorganic acid catalysed dehydration of fructose in water[3-7]. The inorganic acid catalysts however degrade the produced HMF to levulinic and formic acids as well as other by-products[8-11]. Due to this reason, other effective and environmentally friendly methods of HMF production have been sought. Solvents like dimethylsulphoxide, metal halides in 1-alkyl-3-methylimidazolium chloride, 1-H-3-methylimidazolium chloride, sub- and supercritical acetone and metal salts in protonic acids have been used to optimize fructose conversion to HMF[12-15].

Cellulosic biomass is the cheapest source of raw material for HMF production. Its hydrolysis produces D-glucose which can be converted to HMF under favourable conditions.

An initial attempt to convert D-glucose directly to

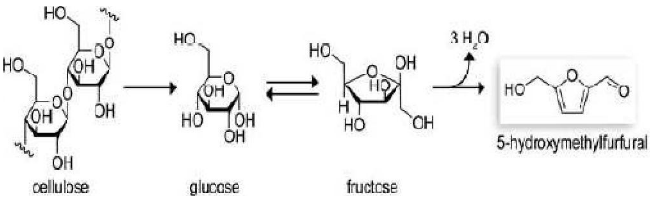

Figure 1 : Biomass conversion stages for HMF production

HMF in water was a great challenge to researchers. This is because of the difficulty in D-glucose isomerisation to D-fructose before HMF can be formed. Only recently was this conversion achieved by some workers using different modifications of the reaction media. Zhao et al.[13] achieved 70 % conversion of D-glucose to HMF using 1-alky-3-methylimidazolium chloride as solvent and chromium (II) chloride as catalyst. Binder and Raines[17] reported the use of *N*,*N*-dimethylacetamide (DMA) containing lithium chloride (LiCl) to give high yields of HMF from D-glucose. Metal chlorides have been claimed to catalyze the isomerisation of D-glucose to D-fructose[13].

Despite these advances, the use of cheaper and more environmentally friendly media for D-glucose conversion to HMF have not yet been extensively studied. The present research therefore considers the use of the environmentally friendly medium, liquid water, for the conversion of D-glucose to HMF in the presence of metal chlorides as catalysts. HMF yield optimisation by the modification of the pH of this medium would also be studied.

EXPERIMENTAL

Reagents and sample preparation

D-glucose, metal chlorides and buffer solutions used for this work were of analytical grade, purchased from FINLAB Nigeria PLC Lagos, and were used without further purification. The sample and reagents were further prepared with distilled water.

Instrumentation

Quantification of HMF in the different study solutions were carried out using JENWAY 6405 UV/Vis Spectrophotometer[18, 19]. The instrument was set at a wavelength range of 200 – 500 nm, and HMF was detected at a wavelength (λ_{max}) of 285 nm[20].

Procedure

The effect of metal chlorides on D-glucose conversion to HMF was studied using: $CrCl_2$, $CoCl_2$, $CuCl_2$, $SnCl_2$ and $FeCl_3$. 100 cm^3 of 0.01 M D-glucose solutions were prepared in distilled water at pH 7 and 0.001 M weight of each metal chloride was dissolved separately in each of the D-glucose solutions. 50 cm^3 of each of these solutions was transferred in triplicates into a series of ampoules. The ampoules were sealed and arranged on a rack, and were placed in a constant-temperature oven set at 373 K and left for 2 hours. The ampoules were taken from the oven and directly quenched in an ice-bath at 278 K to stop the reaction. The ampoules were opened and the solutions were transferred into a 50 cm^3 volumetric flask and made up to volume with distilled water. The solutions were analysed in triplicates for HMF using a UV/Vis Spectrophotometer. 0.01 M solution of D-glucose prepared with distilled water at the same pH was used as blank.

Rate studies

Buffer solutions at pH 2,4,5,6,8,9 and 12 were used separately to prepare 0.01 M D-glucose solutions and 0.001 M $CrCl_2$ was dissolved in each solution. 50 cm^3 of each of these solutions was transferred in triplicates into a series of ampoules. The ampoules were sealed and arranged on a rack, and were placed in a constant-temperature oven set at 373 K and left for 1 hour. The ampoules were taken from the oven and directly quenched in an ice-bath at 278 K to stop the reaction. The ampoules were opened and the solutions were transferred into a 50 cm^3 volumetric flask and made up to volume with distilled water. The absorbances of HMF were taken in triplicates in the resultant solutions.

The kinetics of HMF formation in the solution at pH 12 containing 0.01 M D-glucose and 0.001 M $CrCl_2$ was studied. 50 cm^3 samples of this solution were taken and transferred in a series of eighteen ampoules. The ampoules were sealed and arranged on a rack, and were placed in a constant-temperature oven set at 373 K and left for 10 minutes to attain thermal equilibrium with the oven temperature. They were removed in threes from the oven, at 20 minutes intervals, and directly quenched in an ice-bath at 278 K to stop the reaction. Triplicate absorbances of HMF in each of the solutions were taken.

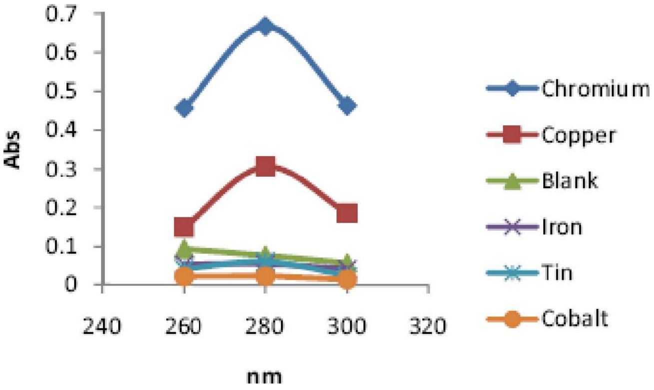

Figure 2 : UV absorbance of HMF in distilled water at pH 7 catalysed by metal chlorides

RESULTS AND DISCUSSION

The HMF absorbance curve for the different metal chloride catalysts in liquid water at 373 K are shown in Figure 2.

Best yields were obtained with $CrCl_2$ and $CuCl_2$ which gave absorbance values of 0.687 and 0.284 respectively. Appreciable yields of HMF were not obtained by the other metal chlorides used in this study using the blank solution as reference. These results show the effectiveness of $CrCl_2$ and $CuCl_2$ in the isomerisation of glucose to fructose and the subsequent conversion of this product to HMF.

The effect of liquid water pH using $CrCl_2$ as catalyst for glucose conversion to HMF at the same study temperature is shown in Figure 3.

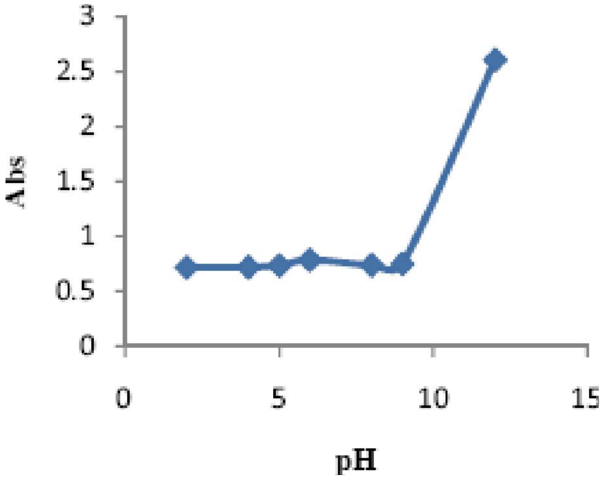

Figure 3 : Effect of pH variation on the conversion of glucose to HMF at 373 K

A constant yield of HMF was observed between the pH of 2 - 9. Above this pH, a sharp and geometric increase in the yield of HMF was obtained. This is an indication that glucose to HMF conversion in liquid water is enhanced above the pH of 9. This implies that alkaline environments are very effective in glucose conversion to HMF in liquid water. Whether there would be degradation products like in the case where acids are used for fructose dehydration to HMF[7, 16] in the liquid water medium is yet to be answered.

Kinetic studies

Liquid water at pH 12 was used to study the rate of glucose conversion to HMF at 373 K, and the result obtained is shown in Figure 4.

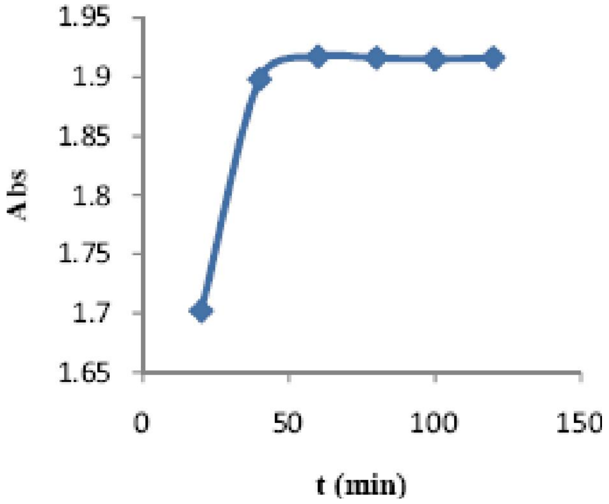

Figure 4 : Rate of glucose conversion to HMF in distilled water at pH 12

The chart shows that the best yield of HMF was obtained in 40 minutes from the sharp increase in yield obtained at this time from the start of the reaction.

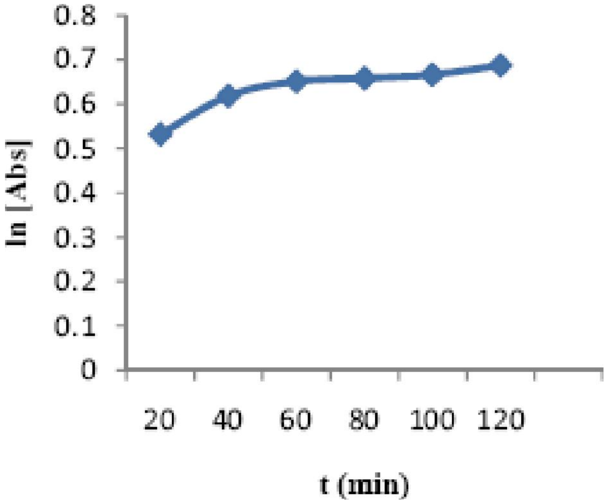

Figure 5 : First order rate plot for glucose conversion to HMF at pH 12

The data obtained in Figure 4 fitted into a first order rate plot with reference to the product (HMF) as shown in Figure 5.

This is an indication that the conversion of glucose to HMF in this medium is a unimolecular first order reaction with the alkaline $CrCl_2$ environment as catalyst for the process. The rate constant for this reaction was calculated to be 6.5×10^{-6} s^{-1}.

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