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Microwave-assisted acid and base pre-treatment of cellulose hydrolysis

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Abstract:

The objective of this study is to hydrolysis the cellulose to glucose. The dilute acid and base hydrolysis of cellulose with hydrochloric, sulfuric acids sodium hydroxide and potassium hydroxide were undertaken alone, The conditions for the dilute acid and base hydrolysis were found to be 5% for both acids and bases at a temperature of 170°C and time 2 hours.

It was found that the glucose yield by acid hydrolysis was 7.8% and by base hydrolysis was 8% .Then the dilute acid hydrolysis of cellulose with hydrochloric & sulfuric acids and the dilute base hydrolysis of cellulose with sodium and potassium hydroxide were undertaken in microwave oven for ten minutes only.

The experimental data indicate that the use of microwave technology can successfully facilitate dilute acid hydrolysis and the dilute base hydrolysis of cellulose allowing high yields of glucose in short reaction times.

These conditions gave a yield of 57% and 58% glucose by acids and base hydrolysis respectively. The microwave is the promising way to increase the glucose yield from cellulose.

Keywords: *dilute acid hydrolysis; cellulose hydrolysis; microwave oven.*

الخلاصة:

الهدف من هذه الدراسة هو تحويل السيليلوز الى كلكوز وذلك باستخدام حامض الهيدروكلوريك والكبريتيك وكذلك قواعد هيدروكسيد الصوديوم وهيدروكسيد البوتاسيوم وبتركيز 5% ولكلاهما وبدرجة حرارة 170 درجة مئوية ولفترة ساعتين وكان الناتج 7.8% كلكوز لكلا الحامضين و8% لكلا القاعدتين وسبب قلة الناتج يعود الى قوة الالفة بين هذه الحوامض المعدنية والاصرة بيتا - 1,4 والتي بدورها تؤدي الى صعوبة كسر الاصرة وانتاج الكلوكوز .

وعند تعريض المحاليل اعلاه الى اشعة مايكرو ويفية ولمدة 10 دقائق فقط زاد ناتج الكلوكوزالى نسبة 57% بالنسبة للحوامض و 58% بالنسبة للقواعد .

والسبب يعود الى اشعة المايكرو ويف تلعب دور كبير في زيادة فعالية جزيئات السيليلوز وزيادة قوة التصادم بينها مما يؤدي الى سهولة كسر الرابط بيتا - 4,1

تعتبر طريقة استخدام المايكرو ويف في انتاج الكلوكوز من السيليلوز وبنسب جيدة طريقة واعدة بتكاليف قليلة جدا وحامية للبيئة من التلوث .

Introduction:

Currently, there are two major ways of converting cellulose to glucose: chemical versus enzymatic.

The research on both methods has for decades occupied the attention of many investigators worldwide. Because each cellulose molecule is an unbranched polymer of 1000 to 1 million D-glucose units, linked together with beta-1, 4 glycosidic bonds, cellulose from various sources are all the same at the molecular level. However, they differ in the crystalline structures and bindings by other biochemicals.

This difference that makes possible a persistent research on cellulose. The model chemical compounds most commonly used in today's research are carboxymethyl cellulose (CMC), which has a generally amorphous structure. [1,2,3].

There are two types of hydrogen bonds in cellulose molecules: those that form between the C_3 OH group and the oxygen in the pyranose ring within the same molecule and those that form between the C_6 OH group of one molecule and the oxygen of the glucosidic bond of another molecule, as shown in figure-1.

X-ray analysis and electron microscopy indicate that the long chains of cellulose lie side by side in bundles, undoubtedly held together by hydrogen bonds between the numerous neighboring -OH groups [4].

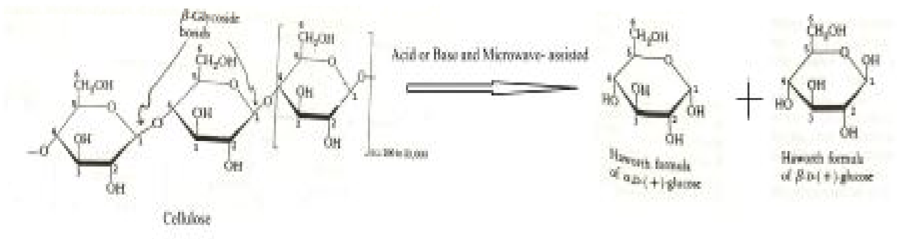


Figure -1: Hydrolysis of cellulose

Ordinarily, the beta-1, 4 glycosidic bonds themselves are not too difficult to break. However, because of these hydrogen bonds, cellulose can form very tightly packed crystallites as shown in figure-2. These crystals are sometimes so tight that neither water nor enzyme can penetrate them; only *exogluconase*, a subgroup of cellulase that attacks the terminal glucosidic bond, is effective in degrading it. The inability of water to penetrate cellulose also explains why crystalline cellulose is insoluble.

On the other hand, amorphous cellulose allows the penetration of *endogluconase*, another subgroup of cellulase that catalyzes the hydrolysis of internal bonds.

The natural consequence of this difference in the crystalline structure is that the hydrolysis rate is much faster for amorphous cellulose than crystalline cellulose [5].

The process of breaking the glucosidic bonds that hold the glucose basic units together to form a large cellulose molecule is called *hydrolysis* because a water molecule must be supplied torender each broken bond inactive. In addition to crystallinity, the chemical compounds surrounding the cellulose in plants, e.g. lignin, also limits the diffusion of the enzyme into the reaction sites and plays an important role in determining the rate of hydrolysis.

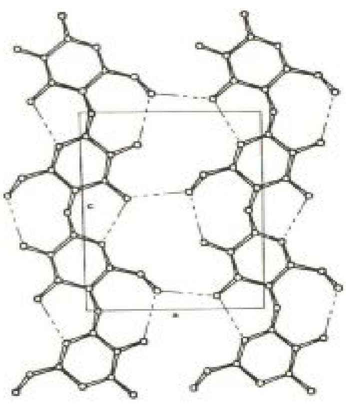


Figure-2: Hydrogen bonding network in cellulose (by American chemical society, Washington DC [5].

Sometimes, wood chips are pretreated with acid at approximately 160°C to strip hemicellulose and lignin) before they are treated with an enzyme or a mixture of enzymes. In general, 20 to 70% yield of glucose can be expected after 24 hours.[6,7].(unlikecellulose, hemicelluloses consists of shorter chains 500-3000 sugar units as opposed to 7000-15000 glucose molecules per polymer seen in cellulose .In addition, hemicelluloses is a branched polymer, while cellulose is unbranched. lignin is an organic substance binding the cell, fibers and vessels which constitute wood and the lignified elements of plant, formed by removal of water from sugar to create aromatic structure). [8].

There has been a large amount of research works done on the digestion of cellulose into glucose, Zhenyu D U and Sun X B [9] stated in their work that the corn stalks pretreated with dilute acid & microwave irradiation had the best glucose yield as 58.09%**.** The experimental data indicate that the use of microwave technology can successfully facilitate dilute acid hydrolysis of cellulose allowing high yields of glucose in short reaction times.

The optimum conditions gave a yield of 90% glucose**.** Microwave was also used in the treatment of a cellulosic waste product to produce the cellulose acetate at the reaction time for 30 ^{o} C with the microwave power 400 W using the 15% iodine. Youyn [10] found in his work that the hydrolysis of cellulose into reducing sugars can be one of the key technologies for making full use of cellulosic biomass in the future. Here, a biomass char sulfonic acid (BC-SO_3H)-catalyzed hydrolysis of cellulose in water was achieved under microwave irradiation giving a high yield of reducing sugar.

Recent published work in this area combined microwave radiation with alkali reagent in the pretreatment of rice straw and wheat straw (Zhu . 2006) [11] ,Gomes [12] found in their work that the rice straw and bagasse with water content 84 or 94% were irradiated with microwave (2450MHz) in sealed glass vessels.

This treatment enhanced markedly the accessibility of the cellulosic materials for the enzymatic hydrolysis: for example, 1.6 times in the rice straw by the microwave treatment at 170°C for 5 min and 3.2 times in the bagasse by the treatment at 200 °C for 5 min, compared with the untreated.

Materials and Methods:

0.2g shred pieces of cellulose filter paper was added to 10ml of 5% acids (HCL and H_2SO_4) solutions and 5% Bases (NaOH and KOH) solutions in a tightly capped test tubes for each solutions separately, and carry out the reaction at 170°C.

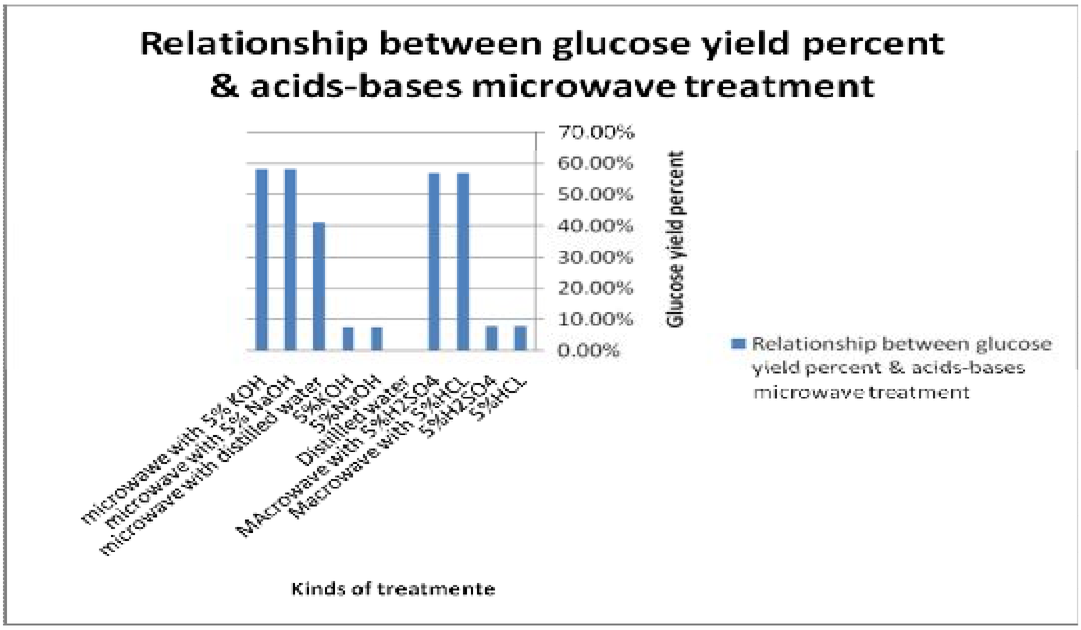
1- This reaction should last for 2 hours. Take 1 ml samples at some predetermined appropriate intervals.
2- The hydrolysis reaction in the sample was stopped by neutralizing the solutions of the cellulose samples with the addition of a small volume of a concentrated base or acid solution. The glucose concentrations of the samples were measurred with the dinitrosali-cylate colorimetric method[13].
3 - The apparatus provided microwave radiation at variable power levels ranging from 125 to 1000 watts.The microwave based pretreatments were carried out in a microwave oven made by KENWOOD (Model M W 940\947). Cellulose samples of filter papers were immersed in dilute solutions of (H2So4), (HCl), (NaOH and (KOH) at concentrations of 5 % (w/v) .in addition to distilled. The samples were placed in an open 250 ml glass beaker and exposed to microwave radiation at 250 watts.

The method tests for the presence of free carbonyl group (C=O), the so-called reducing sugars. This involves the oxi-dation of the aldehyde functional group present in, for example, glucose and the ketone functional group in fructose. (DNS) is reduced to 3-amino 5-nitrosalicylic acid under alkaline conditions.3 ml of 1% DNS reagent is added to 3 ml of glucose sample in a tightly capped test tube. (To avoid the loss of liquid due to evaporation, cover the test tube with a piece of paraffin film if a plain test tube is used).

The mixture was heated at 90º C for 5-15 minutes to develop the red-brown color (3-amino 5-nitrosalicylic acid). 1 ml of a 40% potassium sodium tartrate (Rochelle salt) solution was added to stabilize the color. After cooling to room temperature in a cold water bath, record the absorbance with a spectrophotometer (OPTIMA sp-300 spectrophotometer) at 575 nm.

Table -1: shows the Percent of glucose yield with acids -bases and microwave

Treated the cellulose with	Percent of glucose yield
5% HCl	7.8%
5% H2SO4	8%
Microwave with 5% HCl	57%
Microwave with 5% H2SO4	57%
Distilled water	0.0%
5% NaOH	7.6%
5% KOH	7.7%
Microwave with distilled water	41%
Microwave with 5% NaOH	58%
Microwave with 5% KOH	58%



Graph-1: The relationship between glucose yield percent and acids microwaves treatment.

Result and Discussion:

The dilute acid and base hydrolysis of cellulose with 5% (Hydrochloric acid).

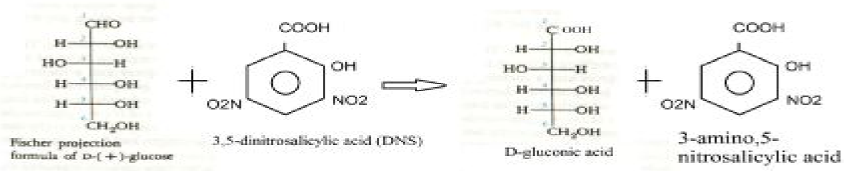
Sulfuric acid, sodium hydroxide and potassium hydroxide) was investigated at a temperature of 170°C & for two hours it gave yield of 7.8%, 8%, 7.6% and 7.7 glucose respectively (Table-1 and Graph-1), The low yield of glucose in this work when use The dilute acids and bases hydrolysis of cellulose which was likely due to their strong affinity to β-1,4-glycosidic bonds of celluloseogen bonds (forming hydrogen bonds) .

The experimental data indicate that the use of microwave technology can successfully facilitate dilute acids and base hydrolysis of cellulose allowing high yields of glucose in short reaction times (10 minutes). it gave a yield of 57% glucose for each acids and 58% for each bases, while gave a yield of 41% with just distilled water, in the conditions of this work, this due to that the microwave irradiation played key roles in activating cellulose molecules and strengthening particle collision, which can lead to a remarkable acceleration effect on this heterogeneously catalytic process and gave a high yield of glucose 57%, 58% for each acids and bases respectively.

In general, acids or bases must be added in order to achieve hydrolysis where water has no effect, the acids or bases are considered as catalysts.

The reaction between glucose and DNS shows that one mole of sugar will react with one mole of 3, 5-dinitrosalicylic acid. However, it is suspected that there are many side reactions, and the actual reaction stoichiometry is more complicated. The type of side reaction depends on the exact nature of the reducing sugars. Different reducing sugars generally yield different color intensities; thus, it is necessary to calibrate for each[14,15]. The microwave is the promising way to increase the glucose yield from cellulose. The experimental data indicate that the use of microwave technology can successfully facilitate dilute acids and bases hydrolysis of cellulose allowing high yields of glucose in short reaction times.

These conditions gave a yield of 57% and 58% glucose by acids and base hydrolysis respectively.



Conclusion:

The results obtained from this study suggested that microwave-assisted cellulose with 5% acids or bases is a promising method to produce glucose, the production of glucose by this method is more economical and environmentally friendly via minimization of energy consumption, solvent, and amount of catalyst quantities, and especially, by minimizing toxicity, may be possible. The microwave assisted time and temperature had a prominent influence on the increase the high yield of glucose.

The recommendation is to use another sources of cellulose like cotton, wood and rice straw with different reagents and condions to increase the yield of glucose.

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