



F⁻/Cl⁻ mediated microwave assisted breakdown of cellulose to glucose



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ABSTRACT

Microwave irradiation of aqueous solution of cellulose in the presence of NaF/NaCl resulted into disintegration of cellulose to its monomeric unit, glucose (55%) in 20 min.

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Millions of tons of cellulose are being generated through the process of photosynthesis, either in the form of natural vegetation or during cultivation of various crops. While Nature has its own means of management, a major chunk of the anthropogenic biomass (crop wastes, etc.) is left unused or burnt into flames producing huge quantity of toxic substances.¹ For rice crop alone, only a fraction of global production of 140 million tons of rice straw or husk is utilized as animal food and for the production of biofuels annually.² Similarly, in case of other primary crops like wheat and maize; the cellulose rich large stem part of these crops mainly goes waste, hence creating a big issue of environmental and economic concern. Chemically, 35–60% of the total mass of stem of rice, wheat, and maize (Table 1) is constituted by cellulose^{3,4} which could be a pleasant source of energy, fuel, food, and chemicals. But to achieve this goal, a highly economical and viable technique is needed to meet the challenge of breaking down of polymeric cellulose structure (Chart 1) to its monomeric units for further utilization.

Because of the presence of free alcoholic groups, the cellulosic chains are bound by strong intra- and intermolecular hydrogen bonding (Chart 1). As a result, there occurs even a solubility problem with cellulose in aqueous media, what to talk about its hydrolysis to glucose. A number of conventional methodologies for the hydrolysis of cellulose include the use of supercritical temperature, acid catalysts, solid acid catalysts, enzymes etc.^{5–9} However, requirement of much effective reactors for attaining supercritical

temperature and high pressure, costly solid acid catalysts, much sensitive and highly expensive enzymes, and difficulty in quenching and disposing of high acid concentrations are some of the factors which hamper the industrial utilization of the reported methods. Since microwaves (MWs) are taking over conventional sources of heating in terms of effectiveness, economical, and short

Table 1
Chemical composition (% w/w) of rice, wheat, and maize straw

S. No.	Source	Cellulose	Hemicellulose	Lignin	Other
1	Rice straw	39.2	23.5	36.1	1.2
2	Wheat straw	34.2	23.6	13.8	28.4
3	Maize straw	61.2	19.3	16.9	2.6

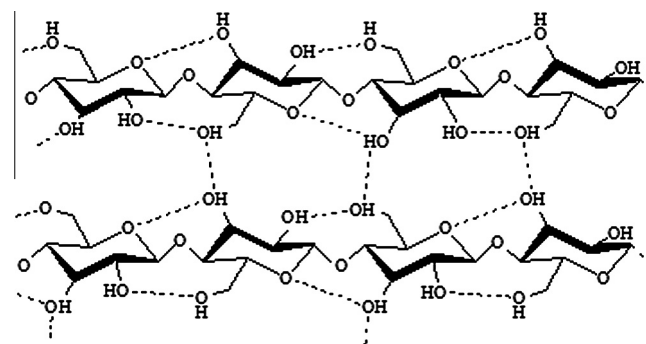


Chart 1. H-Bond network of cellulose.

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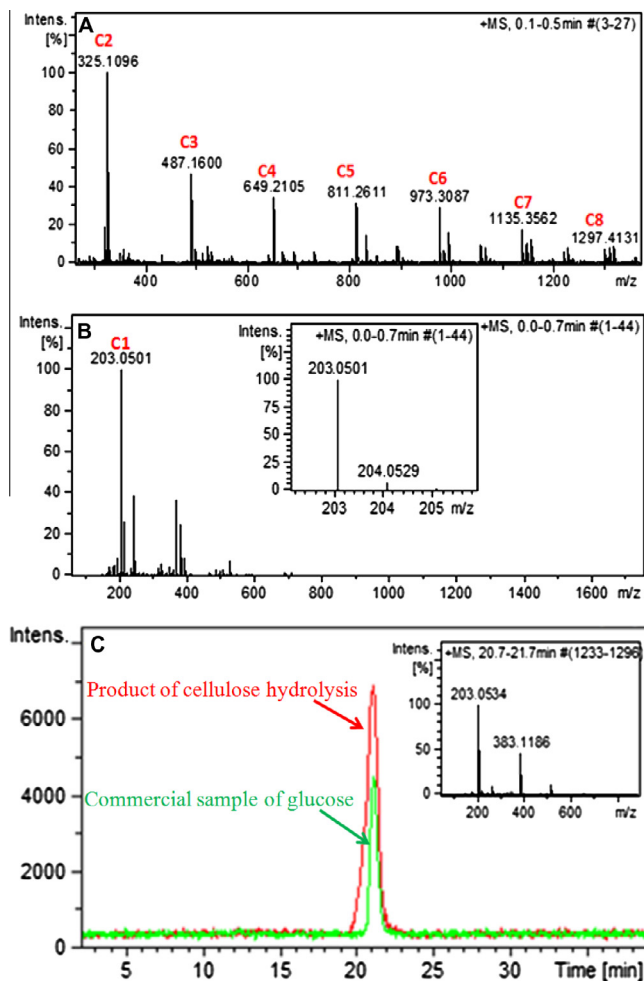


Figure 1. Mass spectra of cellulose reaction mixture after treatment with microwave irradiations at 150 °C for (A) 20 min, (B) 60 min. (C) LC-MS (MeOH-H₂O, 2:3) of product obtained after microwave irradiation of cellulose at 150 °C for 60 min and its comparison with commercial sample of D-glucose.

reaction time,^{10–12} experimental methods for the hydrolysis of cellulose, making use of microwaves at high temperatures and under significant acidic conditions are also reported.^{13,14} Further, making the methodology more environmental friendly, here, we demonstrate microwave assisted conversion of cellulose to monosaccharide under very mild conditions, at relatively low temperatures in the presence of catalytic amount of F⁻/Cl⁻. Mass spectrometry (MS), HPLC, LC-MS, and scanning electron microscopy (SEM) were some of the analytical techniques used for the analysis of the product.

The warmed water suspension of cellulose at pH 6 was irradiated under microwaves at 100 °C.¹⁵ Cellulose remains suspended in water even on irradiation for 60 min. The temperature was increased stepwise and the progress of cellulose hydrolysis was monitored by recording the mass spectrum of the reaction mixture (Table S1). The reaction mixture becomes homogeneous at 150 °C. Mass spectrum of the reaction mixture after 20 min of irradiation at 150 °C showed the presence of various oligosaccharides (Fig. 1A; C2–C8, Chart 2). However, after 60 min of irradiation, the mass spectrum of the reaction mixture exhibited a major peak at *m/z* 203.0501 corresponding to mass of glucose (calcd *m/z* 203.0526 [M+Na]⁺) (Fig. 1B). After removing the solvent, a thick oil was obtained (55%, [α]_D²⁰ = +60°). Comparison of LC-MS of this product with a commercial sample of D-glucose (Fig. 1C) confirmed the formation of glucose when cellulose was irradiated under microwaves.

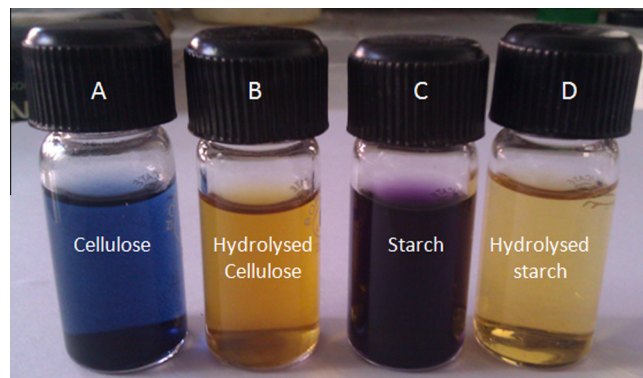


Figure 2. Iodine test performed with (A) cellulose, (B) cellulose treated with microwaves at 150 °C for 60 min, (C) starch, (D) starch treated with microwaves at 150 °C for 60 min.

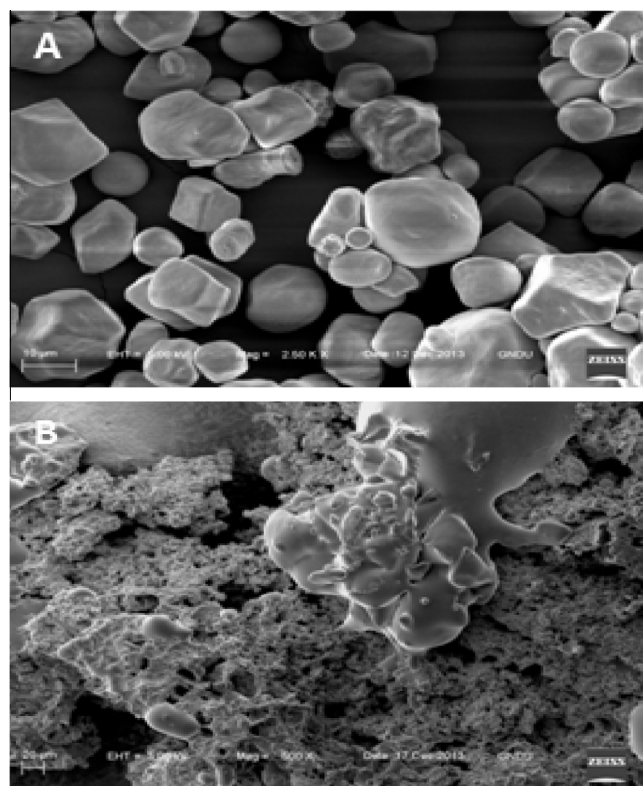


Figure 3. SEM micrographs of (A) cellulose; (B) cellulose treated for 1 h at 150 °C under microwave irradiations.

Therefore, in consistent with the literature reports, it seems that microwaves disturb the H-bond network of the cellulose and promote its breaking to its monomeric units. For comparison, starch solution was also treated with microwaves at 150 °C for 60 min. The mass spectrum of the reaction mixture also showed a major peak at *m/z* 222.1262 [M+CH₃CN]⁺ supporting the formation of glucose (calcd *m/z* 222.1172) (Fig. S1). The classical iodine test of cellulose and its reaction mixture also supported the observations of breakdown of cellulose to its monomeric units under the effect of microwaves (Fig. 2). Furthermore, silver mirror test was also performed to check the presence of glucose and the obvious results were obtained (Fig. S2).

As it is evident from the SEM images, the cellulose particles (Fig. 3A) on treatment with microwaves were disintegrated (Fig. 3B) into smaller particles. Similar results were obtained on recording the SEM images of hydrolysate of starch treated under same conditions (Fig. S3).

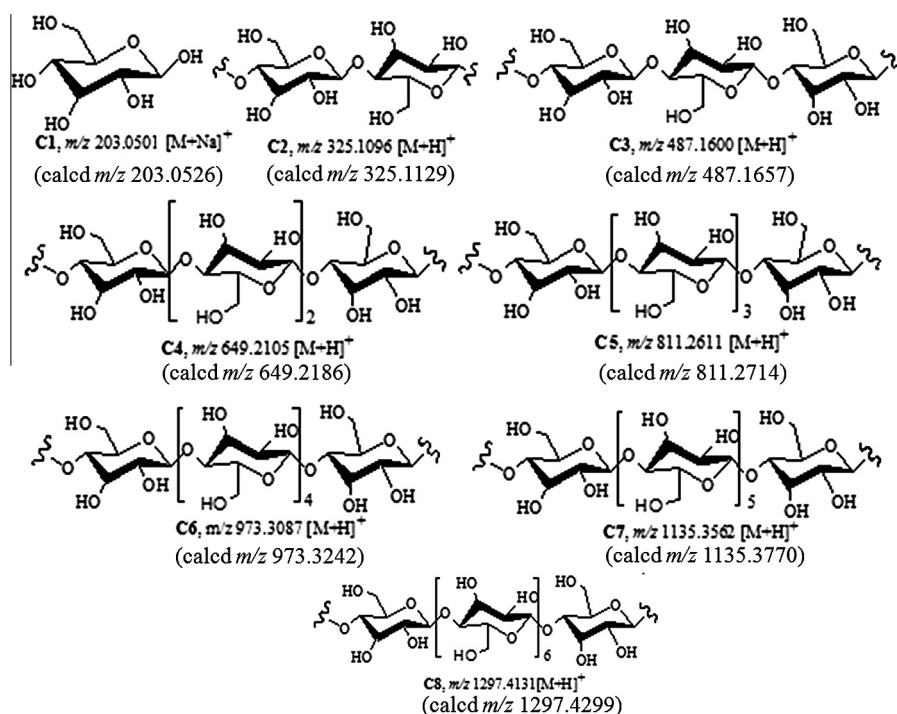


Chart 2. Species detected in the mass spectra of reaction mixture of cellulose during microwave irradiation.

Apparently, the H-bond networking of cellulose undergoes breakdown when irradiated with microwaves. On the basis of these results, it was envisaged that the presence of strong H-acceptors like F⁻/Cl⁻ in the cellulose solution may penetrate into its H-bond network, break the inter- and intra-strand H-bonds, and speed up the conversion of cellulose to monomers. Accordingly, a solution of cellulose in water in the presence of NaF/NaCl was irradiated under microwaves at 150 °C.¹⁶ To our surprise, the mass spectrum of the reaction mixture after heating for 20 min showed an intense peak at m/z 242.2855 (Fig. S4) corresponding to the mass of sodiated glucose. Removal of solvent under vacuum provided sufficiently pure (LC–MS) glucose (55%). Hence the same results were achieved in 20 min which otherwise were attained after 60 min in the absence of NaF/NaCl. In order to confirm the role of F⁻/Cl⁻, same reactions were performed in the presence of NaBr/NaI where the reaction took 60 min for conversion of cellulose to glucose indicating no significant role of Br⁻/I⁻ in the breakage of cellulose. Moreover, it also ruled out the possibility of participation of Na⁺ in the breakage of H-bond networking of cellulose. While I₂ does enter the cellulose network (well known iodine test), but due to its low H-acceptability, it may not be showing the same effect as given by F⁻/Cl⁻. Therefore, under almost neutral reaction conditions, treatment of cellulose solution with microwaves in the presence of NaF/NaCl provided a highly convenient and practicable method for breakage of cellulose to glucose.

In summary, a very simple technique is demonstrated for the conversion of cellulose to glucose. Instead of the formation of a number of products as demonstrated in various literature reports, only glucose was obtained under the present mild reaction conditions. The experimental protocol may help in the industrial transformation of cellulose to glucose for making a judicious use of the biomass.

Acknowledgments

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Supplementary data

Supplementary data (Mass spectra, SEM images, Tables. This material is available on the internet via www.sciencedirect.com) associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2014.03.006>.

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- Reaction procedure*: Cellulose and starch (powder) were purchased from CDH (central drug house, New Delhi). 100 mg of the cellulose/starch sample was suspended in 5 ml distilled water. The reaction mixture was acidified to pH 6 using dil. H₂SO₄. The reaction mixture was slightly heated on a water bath to make it somewhat transparent and then introduced to microwave irradiation on Biotage initiator microwave. The reactions were processed at 100–150 °C at an average power of 85 W. Aliquots of the samples were withdrawn from the reaction vials after regular intervals for 60 min for recording mass spectra. The reaction mixture was then distilled off on rotary evaporator and dried in vacuo to get the hydrolyzed material.

Recording of mass spectra and LC-MS: Mass spectra were recorded in ACN-H₂O solution on Bruker microTOF QII mass spectrometer in +ve ESI mode and the species formed were identified from their respective *m/z*. For LC-MS, Dionex Ultimate 3000 system was linked to mass spectrometer. C-18 column (Acclaim® 120 C18 5 µm 120 Å (4.6 × 250 mm) was used for HPLC. Methanol-water (2:3) was used as eluent. 2 µL of sample (injection volume) was loaded to the column, flow rate was kept 0.2 ml and absorbance was set at 254 nm. Sodium formate was used as internal calibrant.

SEM imaging: All the samples were vacuum dried and were precoated with silver using Quorum Q150R ES coating machine. SEM images were recorded on ZEISS EVO LS10 scanning electron microscope.

Iodine test: Iodine solution was prepared according to the conventional method. 1 g of KI was taken in 10 ml of distilled water and then 0.5 g of I₂

was added and the mixture was shaken to get a brownish colored solution and was stored in the dark. In order to test the compound solutions for the presence of polysaccharides, a drop of the prepared iodine solution was added and the change in color was observed for each solution.

16. 100 mg of the cellulose and 10 mg NaF or NaCl were taken in 5 ml distilled water (amount of the salt was optimized, starting with 2 mg/100 mg of cellulose). The reaction mixture was slightly heated on a water bath to make it somewhat transparent and then introduced to microwave irradiation on Biotage initiator microwave operating at 150 °C and 85 W. Aliquots of the samples were withdrawn from the reaction vials after regular intervals for 60 min for recording mass spectra. The reaction mixture was then distilled off on rotary evaporator and the residue was washed with acetone to get pure product.