

# Isosaccharinic Acid Mediated Fine Chemicals Production from Cellulose

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## Abstract

Cellulose (Avicel®) is converted to potentially useful products (formic acid, ethylene glycol, and lactic acid). Isosaccharinic acid is identified as the reaction intermediate. Homogeneous aqueous dispersions of cellulose were obtained with the aid of sonication (1 h.). The degradation of the cellulose dispersion was carried out in an alkaline (NaOH) medium under microwave (domestic) irradiation conditions. With 1, 4 and 10 wt. % cellulose dispersions, conversion values of 44, 58 and 54 wt. %, respectively, were observed upon 5 min. of microwave irradiation. The reaction products in each case have been analyzed by <sup>1</sup>H and <sup>13</sup>C NMR.

**Keywords:** Cellulose; Avicel®; Sonication; Microwave irradiation; Fine chemicals; Fuel cells

## Introduction

The chemical industry is currently undergoing a paradigm shift from the use of fossil fuels to plants (cellulose) for the production of fine and bulk chemicals [1-3]. Important chemicals derived from cellulose include glucose, sorbitol, mannitol, sorbitan, isosorbide, xylitol, erythritol, glycerol, propylene glycol, methanol, ethylene glycol, formic acid, glycol aldehyde and levulinic acid [4]. Transition from nonrenewable carbon resources (petroleum) to renewable bioresources is inevitable to meet the growing societal needs. In addition to meeting the future societal demands (for fuels and chemicals) such a transition also prevents the adverse climate change due to global warming [5].

Cellulose is a polysaccharide, with abundant glucose monomer units, where hydroxyl groups are involved in extensive inter and intra molecular hydrogen bonding resulting in a highly crystalline structure. This makes the transformation of cellulose to either glucose monomers or other chemicals difficult [6]. The insolubility of cellulose in either water or common organic solvents also constitutes a hurdle in the transformation of cellulose [7]. Even though ionic liquids were suggested as being able to dissolve cellulose, such studies are only in the exploratory stage [8]. The structural complexity of cellulose necessitates pretreatment (physical, chemical or biological) prior to the hydrolysis to sugars and their subsequent conversion to fuels [9,10]. Possible fuels from cellulose include ethanol, methane and ethoxy methyl furfural [11-16]. Photocatalytic and electrocatalytic methods are also being explored to potentially degrade cellulose to useful chemicals like 5-hydroxy methyl furfural (HMF) [17]. Producing formic acid from cellulose is as important as converting CO<sub>2</sub> to formic acid owing to the renewable nature of cellulose [18]. The current work reports on Transforming cellulose (Avicel® PH 101) to Formic acid (FA), Ethylene glycol (EG), and Lactic acid (LA) through the formation of isosaccharinic acid as the reaction intermediate in the presence of NaOH under microwave reaction conditions. Such small organic molecules (FA and EG) were found to be better fuels than methanol for fuel cell applications, owing to the best tolerance to the surface poisoning of the electrode [19]. Lactic acid (LA) is an industrially important chemical (e.g., in polymers, pharmaceuticals, food, textiles, cosmetics and leather). Polylactic acid (PLA) produced through the polymerization of lactic acid is an environmentally-benign substitute for petroleum-based materials [20].

An energy and atom-efficient process for the production of formic acid, ethylene glycol and lactic acid from cellulose (sugars) has still not

been discovered. The strategy currently adopted to transform cellulose to chemicals through  $\mu$ -D-isosaccharinic acid has the advantage of the carbon atom economy compared to the strategy employed in the production of cellulosic ethanol (schematically represented in Scheme 1). This has a poor atom economy due to the fact that for every gram of ethanol produced 0.96 g of CO<sub>2</sub> is generated (loss of carbon atoms) during the fermentation stage in the conversion of glucose to ethanol.

## Materials and Methods

### Materials

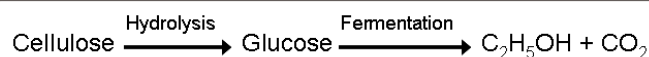
The chemicals used in this work, namely, cellulose powder (Avicel® PH-101) isosaccharinic acid and NaOH, were purchased from Sigma Aldrich. The chemicals were used as received without further purification. Deionized water was used in all the experiments.

### Preparation of aqueous dispersion of Avicel®

Aqueous dispersions of cellulose (1, 4, 10 wt. %) were prepared by taking requisite amounts of cellulose powder and water in a sonic reactor cell and subjecting them to sonication for 1 h. The sonication process was carried out by employing a direct immersion titanium horn (Sonics and Materials, VC-600, 20 kHz, 100 W/cm<sup>2</sup>) for 1 h.

### Cellulose decomposition reaction under microwave irradiation

The cellulose decomposition reaction was carried out in a domestic microwave oven (DMWO) operating at 2.45 GHz in a batch mode



Scheme 1: Schematic representation of the formation of cellulosic ethanol.

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under atmospheric pressure in the presence of air. The output of the domestic microwave reactor was 900 W. The microwave oven was modified so as to have provision for a distillation column passing through the MW oven (for enhanced safety of operation) as well as a stirring facility during the reaction [21]. The cellulose decomposition reaction was carried out in a batch mode in a round bottom flask with provision for a reflux condenser. Typically, each batch comprise of 10 mL of the aqueous dispersion of cellulose powder (1, 4 and 10 wt. %) and the requisite amount of NaOH. The ratio of amount of cellulose in the dispersion to the NaOH (wt./wt. %) is 1. For instant, in the case when 10 mL, 1 wt. % dispersion of cellulose was used as substrate, the amount of cellulose present in the reaction vessel was 0.1 g. To this amount of substrate, 0.1 g NaOH is added and thus the wt./wt.% ratio of cellulose to NaOH is 1. The aqueous suspensions of cellulose powder in an alkaline (NaOH) medium were the subjected to microwave irradiation for a maximum of 5 min. under stirring conditions. The unreacted residual cellulose was separated from the reaction products by filtration through a Whatman® (150 MM Φ) filter paper.

### Characterization

The morphology of the cellulose before and after sonication process was evaluated by HRSEM (JEOL-JSN 7000 F). The reaction products in the filtrate were analyzed by <sup>1</sup>H and <sup>13</sup>C and DEPT (Distortionless Enhancement by Polarization Transfer) NMR spectroscopy. The residue (unreacted cellulose) was washed with water, dried in an air oven overnight at 353 K and weighed. The difference in the initial (before exposure to microwave) and final (after exposure to microwave) weight is a measure of the amount of cellulose converted to the reaction products [22]. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker Avance DPX 300. The measurements were conducted in D<sub>2</sub>O (solvent) at 27 °C. <sup>13</sup>C-NMR spectra were recorded on the spectrometer at a frequency of 300 MHz using a complete decoupling or DEPT mode. For DEPT NMR a 135° pulse width of <sup>1</sup>H 16.2 μs was adopted.

### Results and discussion

Sonication was found to have a useful effect in obtaining homogeneous suspensions of cellulose in water even at a cellulose concentration as high as 10 wt. %. As depicted in Figure 1A. prior to sonication, the cellulose is insoluble in water and settles down at the bottom of the container Figure 1A (a). Upon sonication, the stable and homogeneous dispersion of cellulose in water was generated Figure 1A (b). Xiang et al. have reported such a change in the physical structure of α-cellulose from a fibrous form to a gelatinous form when treated with 65% H<sub>2</sub>SO<sub>4</sub>. The change in the physical form of the α-cellulose was attributed to the disruption of the hydrogen bonding network [23]. Lan et al. succeeded in transforming crystalline cellulose isolated from sugar cane bagasse to an amorphous form with the aid of ultrasonic irradiation of 2 wt. % cellulose in ionic liquid solvents [24].

The HRSEM images of cellulose (10 wt. %) before and after sonication are shown in Figure 1B. Before sonication the cellulose particles resembled like blocks and logs of wood. After sonication the original identity of the cellulose particles is lost. Thin layers and fibers of cellulose are generated upon sonication. Such a transformation in the shape and size of the cellulose particles upon sonication will facilitate a better exposure of the surface of the cellulose to an alkaline medium and easy decomposition upon microwave irradiation.

The microwave reaction followed the sonication process. The aqueous dispersion obtained after the 1 h. of sonication was subjected to the alkaline MW irradiation as described before. The reaction

products in the filtrate were analyzed using NMR (<sup>1</sup>H, <sup>13</sup>C, DEPT) without further separation. In a large scale production process, based on the wide variation in the boiling point of ethylene glycol relative to formic acid and lactic acid, ethylene glycol could be separated using ordinary distillation whereas fractional distillation to be employed for the separation of formic acid and lactic acid from the product mixture as their boiling points are close.

<sup>1</sup>H and <sup>13</sup>C NMR spectra of reaction products obtained from 1 wt. % cellulose (aqueous dispersion in alkaline medium) are shown in Figure 2. Two peaks at 61.1 and 168 ppm in the <sup>13</sup>C NMR spectrum were assigned to ethylene glycol and formic acid, respectively. The presence of formic acid, ethylene glycol and lactic acid, were confirmed by the observation of <sup>1</sup>H (s) at 8.3 ppm, <sup>4</sup>H (s) at 3.86 and <sup>1</sup>H (d) at 1.18 and 1.20 ppm, respectively in the <sup>1</sup>H NMR spectrum Figure 2 (b). A 44 wt. % conversion of cellulose is obtained upon the microwave irradiation of 1 wt. % cellulose (aqueous dispersion in alkaline medium).

When the initial concentration of the cellulose (in the aqueous dispersion) is increased from 1 to 4 wt. %, a conversion of 58 wt. % is observed. <sup>1</sup>H and <sup>13</sup>C NMR spectra of reaction products obtained from 4 wt. % cellulose (aqueous dispersion in alkaline medium) are shown in Figure 3. The peaks at 20.2, 61.3 and 168.3 ppm in the <sup>13</sup>C NMR spectrum were assigned to lactic acid, ethylene glycol and formic acid. The formation of the afore mentioned chemicals upon cellulose degradation is also confirmed by the presence of <sup>1</sup>H, doublet at 1.18 and 1.20 ppm (lactic acid), <sup>4</sup>H, singlet at 3.81 ppm (ethylene glycol) and <sup>1</sup>H, singlet at 8.3 ppm (formic acid). Peaks typical of formic acid, ethylene glycol and lactic acid were observed in the <sup>1</sup>H and <sup>13</sup>C NMR spectra (Figure 3) and the respective chemical shift values are summarized in Table 1. For comparison, the <sup>1</sup>H and <sup>13</sup>C NMR spectra of authentic samples of formic acid, ethylene glycol and lactic acid are shown in Figure S1 and S2 respectively. Slight up field shift in the δ values of the reaction product formic acid (8.5 ppm, Figure 2 (a)) relative to the authentic sample (7.5 ppm, Figure S1) is attributed to the alkali

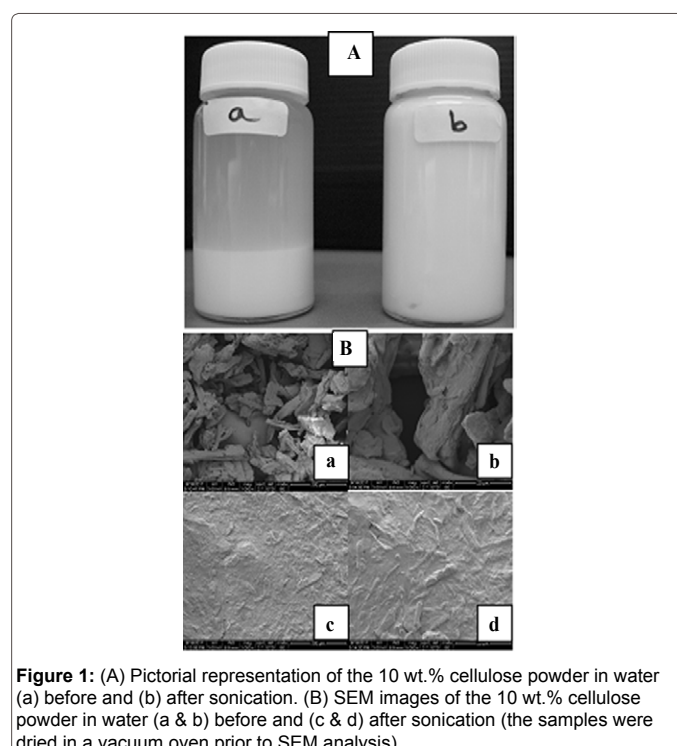


Figure 1: (A) Pictorial representation of the 10 wt.% cellulose powder in water (a) before and (b) after sonication. (B) SEM images of the 10 wt.% cellulose powder in water (a & b) before and (c & d) after sonication (the samples were dried in a vacuum oven prior to SEM analysis).

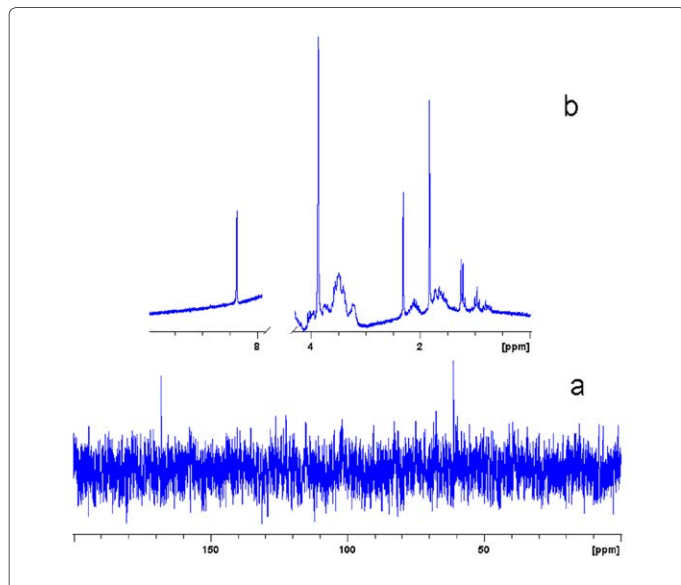


Figure 2: <sup>13</sup>C (a) and <sup>1</sup>H (b) NMR spectra of the reaction product from 1 wt.% cellulose upon microwave irradiation for 5 min.

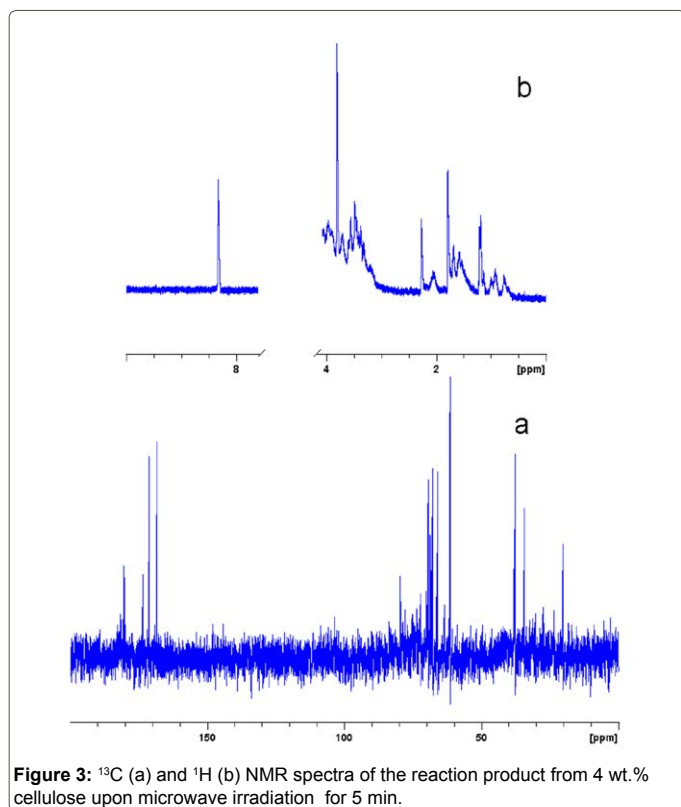


Figure 3: <sup>13</sup>C (a) and <sup>1</sup>H (b) NMR spectra of the reaction product from 4 wt.% cellulose upon microwave irradiation for 5 min.

Compound	<sup>1</sup> H Chemical shift (δ, ppm)	<sup>13</sup> C Chemical shift (δ, ppm)
Formic acid	one H (singlet) at 8.3	168.3
Ethylene glycol	four H (singlet) at 3.86	61.3
Lactic acid	one H (doublet) at 1.18 and 1.2	20.2

Table 1: <sup>1</sup>H chemical shift (δ, ppm) values of the decomposition products of cellulose (4 wt.%).

medium of the reaction. In addition to the typical peaks corresponding to lactic acid, ethylene glycol and formic acid, the <sup>13</sup>C NMR spectrum of the reaction product also comprises of six characteristic peaks typical of isosaccharinic acid [25]. The <sup>13</sup>C NMR chemical shift values and the respective assignment to a particular carbon nucleus of isosaccharinic acid were summarized in Table 2.

With the initial cellulose concentration of 10 wt. % (aqueous dispersion in an alkaline medium) a cellulose conversion of 54 wt. % is observed. <sup>1</sup>H and <sup>13</sup>C NMR spectra of reaction products obtained from 10 wt. % cellulose are shown in Figure S3. The peaks at 20.2, 61.3 and 168.3 ppm appeared consistently in the <sup>13</sup>C NMR spectrum of the reaction product obtained from 10 wt. % cellulose indicating the formation of lactic acid, ethylene glycol and formic acid. Peaks typical of isosaccharinic acid are also seen in the <sup>13</sup>C NMR depicted in Figure S3. Unlike the 1 and 4 wt. % initial concentration of cellulose, in the case of reaction with 10 wt. % cellulose yielded some minor unidentified products (additional peaks in the NMR spectrum) in addition to formic acid, ethylene glycol, lactic acid and isosaccharinic acid. In order to confirm whether isosaccharinic acid is indeed the reaction intermediate formed during the alkaline decomposition of cellulose under microwave irradiation, a decomposition reaction with 10 wt. % cellulose (aqueous dispersion in an alkaline medium) was carried out for only 30 sec. under microwave irradiation. The reaction product was analyzed by <sup>13</sup>C and DEPT 135 NMR and the spectra of the product obtained by irradiating 10 wt. % cellulose dispersion under microwave for 30 sec. are depicted in Figure 4. In the DEPT spectrum the positive signals indicate methine carbons, negative signals indicate methylene carbons and no signals appear for quaternary carbons (C) [26].

The peaks marked 1, 2, 3, 4, 5, located at 37.5, 65.7, 67.5, 69.2 and 79.2 represent the five carbon atoms, methylene, primary alcohol, primary alcohol, secondary alcohol and tertiary alcohol of the isosaccharinic acid respectively. Furthermore, the negative signal at 37.5, 65.7 and 67.5 ppm in the DEPT 135 spectrum could be attributed to the methylene carbons, C3, C1 and C5, respectively. In addition, the

<sup>13</sup> C Chemical shift (δ, ppm)	Assignment to the carbon nuclei
37.5	methylene
65.7 and 67.5	primary alcohols
69.2	secondary alcohols
79.2	tertiary alcohols
180.0	carboxylic acid

Table 2: <sup>13</sup>C chemical shift (δ, ppm) values of isosaccharinic acid, the reaction intermediate formed in the decomposition of cellulose (4 wt.%).

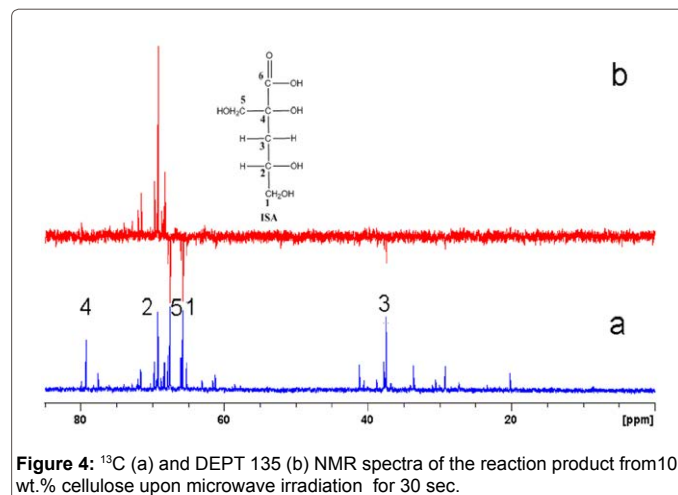
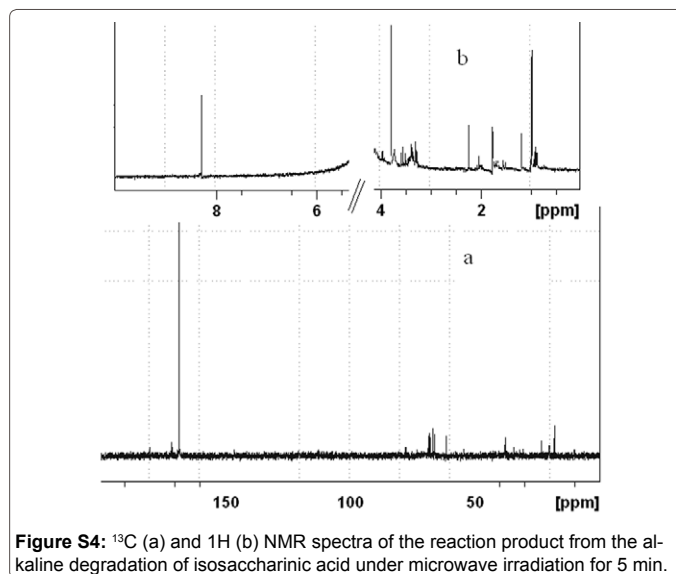
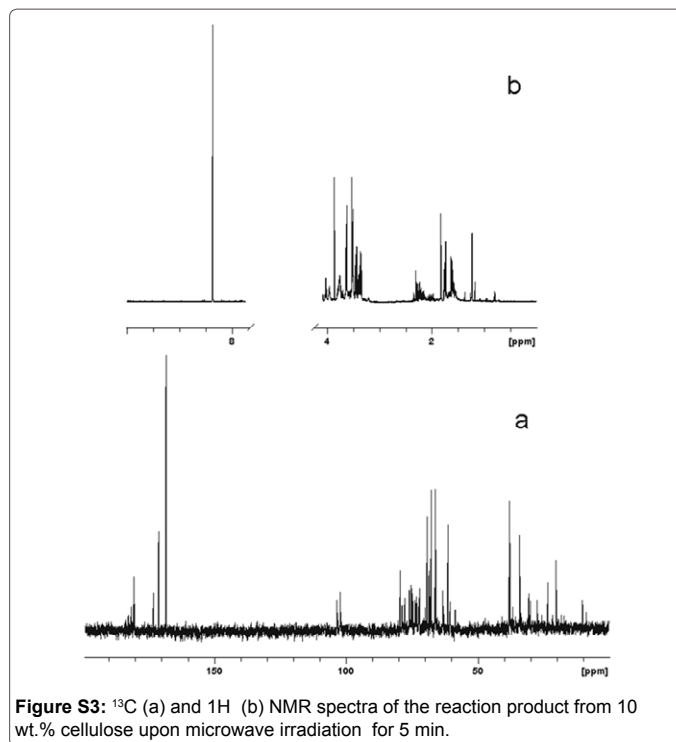
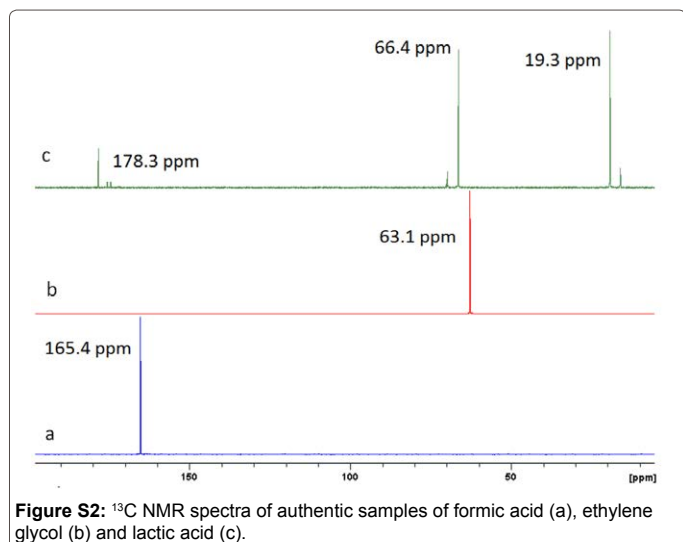
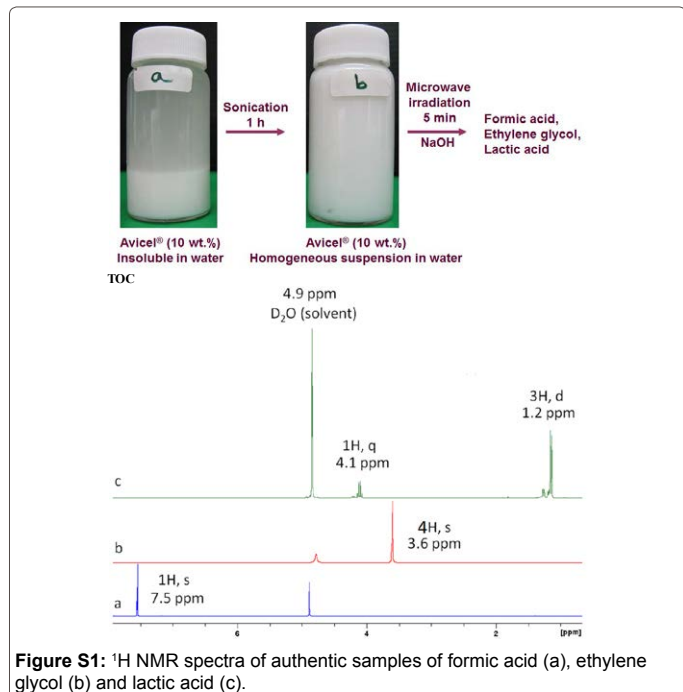
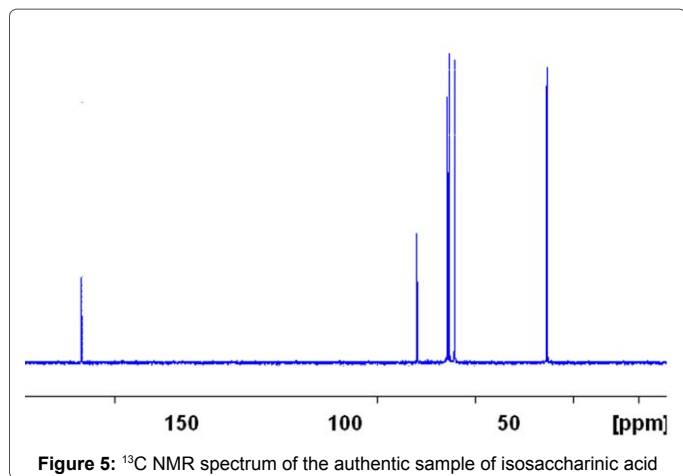


Figure 4: <sup>13</sup>C (a) and DEPT 135 (b) NMR spectra of the reaction product from 10 wt.% cellulose upon microwave irradiation for 30 sec.



presence of a peak at 79.2 ppm in the  $^{13}\text{C}$  NMR and the absence of the peak in the DEPT 135 indicate that this peak is a result of the presence of quaternary carbon (C4). The  $^{13}\text{C}$  NMR peak observed at 180.0 ppm corresponds to the carboxylic acid group (C1). Thus the  $^{13}\text{C}$  NMR and DEPT 135 NMR spectra of the reaction product obtained from 10 wt. % cellulose upon the 30 sec. irradiation with microwave, unequivocally indicate that isosaccharinic acid is formed as the reaction intermediate in the degradation of cellulose to chemical compounds like formic acid, ethylene glycol and lactic acid. Bovaird et al. have also suggested isosaccharinic acid (ISA) to be the primary degradation product of cellulosic materials under alkaline conditions [27]. In addition, to further substantiate the claim that ISA was formed as intermediate during the alkaline degradation of cellulose, authentic sample of ISA is prepared from lactose monohydrate and calcium hydroxide and the



$^{13}\text{C}$  NMR spectrum was recorded (Figure 5) [28]. Six peaks typical of isosaccharinic acid as summarized in Table 1 were observed. The  $^{13}\text{C}$  NMR spectrum of the reaction intermediate formed during the alkaline degradation of cellulose (Figure 4) is similar to that of the authentic sample of isosaccharinic acid (Figure 5) implying that the reaction intermediate is indeed isosaccharinic acid.

To further examine if the alkaline degradation products of cellulose, namely, ethylene glycol, lactic acid and formic acid could also be obtained directly by the alkaline degradation of isosaccharinic acid (authentic sample), the afore-mentioned sample of ISA (0.4 g) was subjected to microwave irradiation in the presence of NaOH (0.4 g in 10 mL) for 5 min. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the degradation product of ISA showed peaks at 20.2, 61.3 and 168.3 ppm attributable to lactic acid, ethylene glycol and formic acid. Presence of one H, doublet at 1.18 and 1.20 ppm,  $^4\text{H}$ , singlet at 3.81 ppm and  $^1\text{H}$ , singlet at 8.3 ppm confirm the formation of lactic acid, ethylene glycol and formic acid (Figure S4). Thus, a simple two-stage process (sonication followed by microwave irradiation) has been developed to decompose the complex macromolecular structure of cellulose (Avicel®) to simple chemicals like formic acid, ethylene glycol and lactic acid, through the formation of isosaccharinic acid as the reaction intermediate.

## Conclusion

A fast and simple method has been developed to transform the highly crystalline commercial cellulose (Avicel®) into valuable chemicals like formic acid, ethylene glycol and lactic acid. The strategy for decomposing cellulose comprises of two stages: (i) to reduce the crystallinity of cellulose by sonication and (ii) expose the aqueous dispersions of cellulose in an alkaline (NaOH) medium to microwave irradiation for a maximum of 5 min. The wt. % conversion values of 44, 58 and 54 were observed with 1, 4 and 10 wt. % cellulose dispersions. Thus the feasibility of employing cellulose as a feedstock for fine chemicals production is demonstrated.

## Acknowledgements

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## Highlights

Conversion of Cellulose (Avicel®) into industrially useful chemicals via sonication followed by microwave irradiation.

Short duration of 1 h sonication followed by 5 min. microwave irradiation for cellulose conversion.

Isosaccharinic acid was found to be the reaction intermediate in the conversion of cellulose to formic acid, ethylene glycol and lactic acid.

Formic acid and ethylene glycol could be a substitute to methanol in DMFC's.

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