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Efficient hydrolysis of cellulose into glucose over sulfonated polynaphthalene (SPN) and rapid determination of glucose using positive corona discharge ion mobility spectrometry†

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Sulfonated polynaphthalene (SPN) was successfully developed as solid acid catalysts for the hydrolysis of cellulose into high yields of glucose. The catalytic results indicate that the solid acid exhibits excellent activity, selectivity and recyclability. In addition two simple, rapid, selective, precise and accurate methods for the determination of glucose and cellulose were developed. The first method was based on the direct ion mobility spectrometry (IMS) measurements of glucose in reaction solution. The second method was based on UV-visible spectrophotometry, measurement of absorbance at 286 nm for cellulose.

Introduction

Cellulose, the most abundant polysaccharide with β-glycosidic linkage, is a major component of nonfood biomass. The hydrolysis of polysaccharide, especially cellulose, to obtain reducing sugars such as glucose (a major platform for the synthesis of a variety of chemicals, fuel and food) is an important process for chemical and biochemical industries.[1–5]

However, cellulose shows high chemical stability and insolubility in most solvents because of its high crystallinity. Therefore hydrolysis of cellulose to glucose with high selectivity is one of the most attractive subjects in sustainable chemistry.[6,7] Until now, many efforts have been devoted to the hydrolysis of cellulose by using mineral acids,[8–10] enzyme[11,12] and supercritical water.[13,14] However acid corrosion, high costs of enzyme, severe controls of reaction conditions, production of chemical waste, difficult separation of products and catalysts make this method unattractive.

Solid acids are conventional materials that have wide applications in chemical production, separation/purification, and the chemical industry is currently searching for a highly active and stable solid acid to improve the environmental safety of the production of chemicals and energy.[15–18]

In recent years, several kind of solid acid have been developed to facilitate the hydrolysis of cellulose with moderate to good glucose yields. Among them sulfonated carbon-based solid acid showed superior catalytic activity.[19–21]

Moreover introduced chlorine group in to solid acids can be improved catalytic activities. In these catalysts, chlorine groups act as cellulose binders by forming hydrogen bonds with hydroxyl groups of cellulose and strongly acidic sulfonic groups function as active sites for breaking β-1,4-glycosidic linkages of cellulose.[22–25] Recently, Tanemura and coworkers reported the synthesis of a sulfonated polynaphthalene (SPN) with high acid activities. This solid acid has some advantages. First, it contains chlorine and sulfonic groups. Second, the catalyst is recoverable without decreasing its activity and insoluble to boiling water and many hot organic solvents. Third, it can be successfully used instead of sulfuric acid as a catalyst.[26]

Detection and identification of carbohydrate in aqueous solutions is very important in the several areas of environmental research.[27,28] Many methods have been developed to measure the total concentration and type of carbohydrates including colorimetric,[29] chromatography,[30] infrared spectroscopy,[31] light scattering detection[32] and nuclear magnetic resonance spectroscopy.[33] However these techniques often are time consuming, quite laborious, expensive and requires advanced analytical skills.

Ion mobility spectrometry (IMS) is an analytical technique that characterises chemical substances using gas-phase mobilities of ions in homogenous electric field. In this technique different types of ions are separated based on their mass, size, shape, and charge within a milliseconds time scale. IMS has found widespread application as an analytical technique for different organic and inorganic compounds such as drugs, metal, biological compounds, pesticides and volatile and explosives compounds. High sensitivity, simplicity, and short response time are the major IMS advantages.[34–39]

In the present study we report the chemical conversion of cellulose to glucose by hydrolysis of the SPN catalysts under

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relatively mild conditions and develop a new, simple, rapid, and accurate IMS-based method for the direct determination of glucose in reaction solution. In addition a UV-visible spectrophotometric method was proposed for cellulose determination.

Experimental

All chemicals were commercial products. Absorption measurements were made on a Perkin Elmer UV/vis Lambda 2 Spectrophotometer. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet IMPACT 400D instrument. Scanning electron microscopy images (SEM) were taken on SEM SERON TECHNOLOGY AIS-2100. X-ray diffraction patterns (XRD) were obtained on a Bruker D8 ADVANCE instrument. The elementary analysis was obtained from Vario EL III of Elementar Company. HPLC measurements were carried out on an Agilent 1200 series (with a refractive index detector). The IMS used in this study was constructed in Malek-Ashtar University of Technology, Iran, Shahin-Shahr. The continuous corona discharge ionization source with positive mode was used in this study. The optimized experimental conditions for obtaining ion mobility spectra of glucose are given in Table S1 (see ESI†). The ultrasonic pretreatment was carried out in Ultrasonic Generator (TOPSONIC 10416) all sonication runs were at 20 kHz.

Catalyst preparation

The SPN catalysts was prepared according to the reported procedure by Tanemura *et al.*[26] In a typical synthesis, to a magnetically stirred mixture of naphthalene (10.2 g, 80 mmol) in nitrobenzene (140 mL), $FeCl_3$ (28.6 g, 176 mmol) was added at room temperature under nitrogen. After addition was complete, the mixture was stirred at 80 °C for 1 h and then maintained at 150 °C to form black solid. The mixture was poured into 700 mL methanol containing a small amount of concentrated HCl (3 mL). The mixture was filtered and washed with methanol (3 × 20 mL), chloroform (3 × 20 mL) and then the resultant polynaphthalene was finally dried at 120 °C for 3 h under reduced pressure.

In the sulfonation step, 4 mL of chlorosulfonic acid was slowly added to the mixture of 2.5 g polynaphthalene in 60 mL dichloromethane at room temperature under N_2. After addition was complete, the mixture was stirred for 24 h. Precipitated sulfonated polymer was recovered, washed with distilled water until pH reach values 6–7. The product was then dried in an oven at 150 °C for 4 h. The solid acid was characterized by XRD, FT-IR and elementary analysis (see Fig. S1 and S2 in the ESI†). The acid density (2.2 mmol g^{-1}) was measured using NaOH (0.01 mol L^{-1}) as titrant by acid–base potentiometric titration. The composition of the catalyst obtained was $CH_{0.46}Cl_{0.03}O_{0.16}S_{0.04}$ from elemental analysis.

Cellulose pretreatment

Prior to hydrolysis, microcrystalline cellulose (AVICEL®PH-101) was pretreated by ultrasonic.[40,41] Micro crystalline cellulose (5 g) was added in distilled water (200 mL) and sonicated at a power of 350 W, frequency of 20 kHz for 45 min at room temperatures.

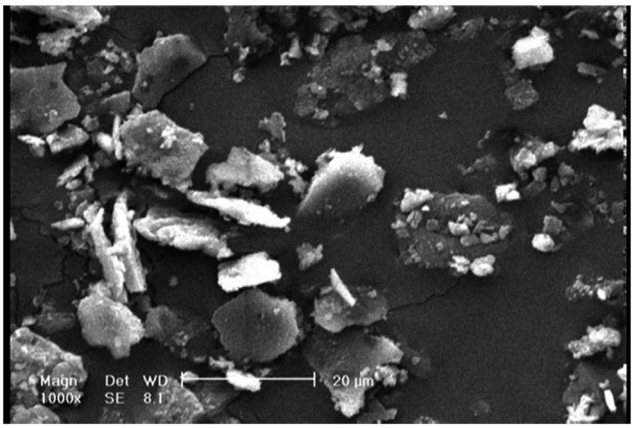

Fig. 1 The SEM image for the prepared pretreatment cellulose particles.

The SEM analysis (Fig. 1) showed that the pretreated cellulose particles exhibited an irregular morphology with the particle size ranging from 0.5 to 20 μm.

Hydrolysis of cellobiose and cellulose

In a typical reaction, cellobiose (0.1 g) or pretreated cellulose (0.05 g), catalyst (0.1 g), water (4 mL) or sulfuric acid 0.025 mol L^{-1} (4 mL) and were added into Teflon-lined stainless steel autoclave and reacted at 120 °C for prescribed time under magnetic stirring. Then, the autoclave was cooled by cold water immediately to avoid further reaction. The mixture was separated by filtration or centrifugation. The yield of glucose was calculated as follows:[42]

$$\text{Yield of glucose (\%)} = (\text{weight of glucose} \times 0.9/\text{weight of cellulose}) \times 100$$

$$\text{Glucose selectivity (\%)} = (\text{yield of glucose/conversation of cellulose}) \times 100$$

Adsorption of cellobiose and glucose on catalyst

0.1 g of each catalyst was added to 2 mL of aqueous cellobiose (0.14 mol L^{-1}) or glucose (0.28 mol L^{-1}) solution and then stirred at room temperature and the amount of adsorbed cellobiose and glucose in supernatant was estimated by UV spectrophotometry and IMS method respectively.

Hydrolysate analysis

Glucose analysis was conducted using an ion mobility spectrometry system. Samples were solved in water to make standard solutions. 1 μL of the working solution was loaded on the needle, the solvent was allowed to evaporate and then immediately inserted into the injection port of the IMS. UV spectrophotometry based method for determining cellulose was developed. In a typical reaction, about 0.05 g of cellulose was taken in a test tube, added 3 mL of conc. sulfuric acid and was

mixed for 45 minutes. Then the solution was further diluted to 250 mL with water and mixed well. Finally, UV light absorption at 286 nm is read using UV spectrophotometer.

Cellobiose was determined using an UV spectrophotometry system according to a method similar to that reported previously by Albalasmeh *et al.*[43] A volume of 1 mL of 0.1 g L^{-1} cellobiose solution is rapidly mixed with 3 mL of concentrated sulfuric acid in a test tube. After 1 min, test tube was cooled by cold water to bring it to room temperature and absorbance was measured at 315 nm.

Results and discussion

Hydrolysis of cellobiose

Hydrolysis of cellobiose as model compound for cellulose was carried out at 120 °C over 0.1 g of catalyst in cellobiose solution (cellobiose 0.1 g, water 4 mL) and catalytic performance of SPN was compared with Amberlyst-15. The specific surface area and amount of sulfonic groups per gram of SPN catalyst was 20 m^2 g^{-1} and 2.1 mmol g^{-1} *vs.* 50 m^2 g^{-1} and 4.8 mmol g^{-1} for Amberlyst-15. As shown in Fig. 2 approximately 95% cellobiose was hydrolyzed to glucose in two hours while 39% was hydrolyzed by Amberlyst-15 at same conditions. Although the SPN has a small surface area and acid density, this catalyst has much greater catalytic activity than Amberlyst-15 in hydrolyzing cellobiose. The high catalytic activity of the SPN can be attributed to increases in adsorption capacity.[22–25] To confirm this conjecture, adsorption of glucose and cellobiose on the SPN surface was studied in aqueous solution at room temperature. As shown in Fig. 2, 16.7% of the added cellobiose was absorbed by the SPN within 2 h, whereas the Amberlyst-15 did not adsorb cellobiose in water. Similarly, the SPN catalyst absorbed 7.0% of the added glucose (less than the cellobiose absorbed by this catalyst), and Amberlyst-15 did not adsorb glucose in water. The adsorptive capacity of the SPN, suggests that –Cl, phenolic –OH or –COOH groups are favorable for cellobiose (the shortest β-1-4-linked polysaccharide) because more hydrogen bond formed between the catalyst and cellobiose than glucose.[20,22]

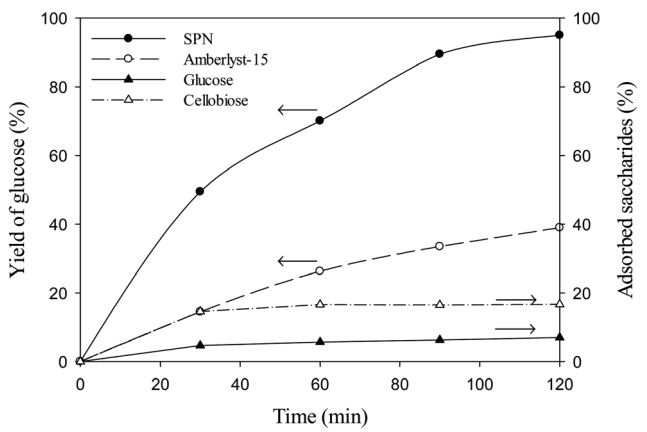

Fig. 2 Time courses for glucose formation from cellobiose and adsorption curve of glucose and cellobiose.

Hydrolysis of cellulose

The catalytic performances of SPN were investigated in the hydrolysis of cellulose to glucose and the optimizing reaction conditions determined. In order to rationally evaluate the activity of SPN catalyst in this reaction, a comparative study was made with Amberlyst-15. In Table 1, we compared our result on the hydrolysis of cellulose to glucose with data from some other workers. The previously reported procedures suffer from one or more drawbacks such as elevated reaction temperatures, low selectivity and yields of glucose, low yield of cellulose conversion, long pretreatment time, and the need for ionic liquids. Additionally, a comparison of hydrolysis using pretreated cellulose with that using cellulose (AVICEL®PH-101) was also conducted. The conversion and selectivity for the pretreated cellulose was higher than that obtained using un-pretreated cellulose (Table 1, entry 2).

Effects of the amount of catalyst

Fig. 3 shows the effects of catalyst amount on the cellulose conversion. In the absence of acid catalyst, the conversion of cellulose was only 5% after 24 h of reaction. The results show that the initial reaction rate and final conversion were dependent on the amount of catalyst and when the amount of catalyst increased, the final conversion increased as well.

Table 2 and 3 show glucose selectivity at 120 °C for experiments using different amount of catalyst. Increases in amount of catalyst (0.1 g to 0.12 g) resulted in a decrease in glucose selectivity from 90.8 (Table 2 entry 5) to 86.7% (Table 3 entry 5).

Effects of the temperature and time

The effects of temperature on cellulose conversion and glucose yield under otherwise similar conditions were studied at 100, 120 and respectively 140 °C and the results are illustrated in Fig. 4 and Table 4. The results in Fig. 4 indicate that the yield of cellulose conversion slightly increased (from 62.6% to 70.4%) when the system temperature increased from 100 °C to 120 °C. At 140 °C, the yield rose noticeably to 79.6%. It is noted that increases in temperature resulted in a decrease in the glucose selectivity (see Table 2 and 4) additionally, a gradual increase in the cellulose conversion was seen with increase in the duration of the reaction time. The higher temperature helps to disrupt partially the structure of cellulose and increase the accessibility of glycosidic bond to the acid sites. Furthermore, the glucose is not stable enough at higher temperature and degraded into other products.

The effect of reaction period on the cellulose conversion and glucose yield were studied at 120 and 140 °C with 0.1 g catalyst (SPN). The results are illustrated in Table 2 and 4. As seen from the Table 2, 18 h of reaction completes 67.6% conversion with 90.8% selectivity whereas at the end of 24 h 86.6% of selectivity was observed. It is clearly evident from the above observation that 18 h may be the optimum period of this reaction.

Effects of the amount of water

In this study, the effect of the presence of water between 2 and 10 mL was determined on the hydrolysis of cellulose at the

Table 1 Comparison of the activity of various catalysts in the hydrolysis of cellulose to glucose

Entry	Catalyst	Substrate	Catalyst/substrate ratios (g per g)	t (h)	T (°C)	Cellulose conversion (%)	Glucose yield (%)	Glucose selectivity (%)	Ref.
1	SPN	Sonicated cellulose	2	18	120	67.6	61.4 (64.7)[a]	90.8 (95.7)	This work
2	SPN	Microcrystalline	2	18	120	51.3	20.4	39.7	This work
3	Amberlyst-15	Sonicated cellulose	2	18	120	10.3	—	—	This work
4	AC–SO_3H	Ball-milled	1.1	24	150	43	41	95.3	19
5	C–SO_3H	Microcrystalline	12	3	100	64	4	6.2	20
6	CMK-3–SO_3H	Ball-milled	1.1	24	150	94.4	74.5	78.9	21
7	HA–CC–SO_3H	Microcrystalline	0.25	4	155	11.3	10.8	95.8	23
8	SUCRA–SO_3H	Ionic liquids pretreated cellulose	2	24	120	—	55	—	24
9	$Si_{33}C_{66-823}$–SO_3H	Ball-milled	1	24	150	61	51	83.6	44

[a] Yield was determined by HPLC.

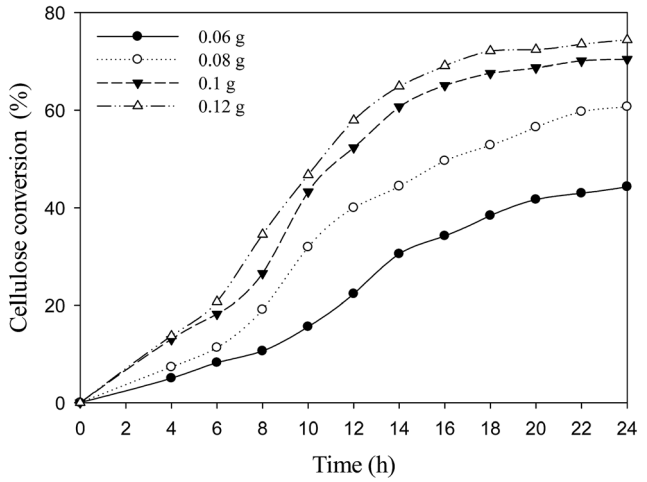

Fig. 3 Effects of catalyst amount on the cellulose conversion (pretreated cellulose, 0.05 g; water, 4 mL; reaction temperature, 120 °C).

Table 2 Hydrolysis of cellulose at 120 °C and 0.1 g catalyst[a]

Entry	Time (h)	Cellulose conversion (%)	Glucose yield (%)	Glucose selectivity (%)
1	10	43.3	29.4	67.8
2	12	52.3	39.0	74.6
3	14	60.7	49.3	81.2
4	16	65.1	55.5	85.2
5	18	67.6	61.4	90.8
6	20	68.7	62.0	90.0
7	22	70.1	62.3	88.9
8	24	70.4	61.0	86.6

[a] Pretreated cellulose, 0.05 g; water, 4 mL.

Table 3 Hydrolysis of cellulose at 120 °C and 0.12 g catalyst[a]

Entry	Time (h)	Cellulose conversion (%)	Glucose yield (%)	Glucose selectivity (%)
1	10	46.7	31.3	67
2	12	57.9	42.2	72.9
3	14	64.9	50.4	77.6
4	16	69.1	57.2	82.8
5	18	72.1	62.5	86.7
6	20	72.4	62.2	85.9
7	22	73.5	62.8	85.4
8	24	74.4	60.9	81.8

[a] Pretreated cellulose, 0.05 g; water, 4 mL.

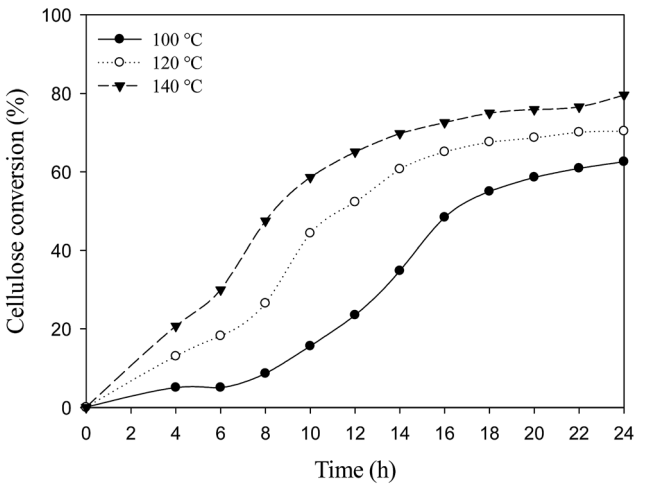

Fig. 4 Effects of hydrolysis temperature on the cellulose conversion (pretreated cellulose, 0.05 g; catalyst, 0.1 g; water, 4 mL).

temperature of 120 °C, reaction time of 18 h, and 0.05 g cellulose over 0.1 g of catalyst (the best operational conditions studied on this work which will give the best final conversion and glucose selectivity). Table 5 shows the relation between the amounts of cellulose conversion, glucose yield and water content. The conversion of cellulose and glucose yield increased with increasing in amount of water up to 4 mL and after that decreased substantially. The glucose selectivity increased with increase in amount of water from 81.4% to 90.8%. Introduction of an optimum content of water is valuable for hydrolysis reaction and maintains the Brønsted acidity of the catalyst.

Table 4 Hydrolysis of cellulose at 140 °C and catalyst, 0.1 g[a]

Entry	Time (h)	Cellulose conversion (%)	Glucose yield (%)	Glucose selectivity (%)
1	10	58.6	43.0	73.4
2	12	65.1	50.6	77.8
3	14	69.8	56.3	80.6
4	16	72.6	62.7	86.4
5	18	75.0	60.0	80.0
6	20	75.9	60.4	79.6
7	22	76.6	59.5	77.7
8	24	79.6	58.7	73.7

[a] Pretreated cellulose, 0.05 g; water, 4 mL.

Table 5 Effects of water amount on the cellulose conversion and glucose selectivity

Entry	Water (mL)	Cellulose conversion (%)	Glucose yield (%)	Glucose selectivity (%)
1	2	54.8	44.6	81.4
2	3	62.8	55.0	87.6
3	4	67.6	61.4	90.8
4	6	67.5	61.0	90.4
5	8	63.4	57.5	90.7
6	10	57.6	52	90.3

Reusability of the catalyst

The stability of SPN was investigated by performing the conversion of cellulose with the same catalyst. After the first run, the reusability of the SPN was tested. The recycled solid acid was used for three times. The obtained results demonstrating that SPN can be reused in these hydrolysis reactions (see Table S2 in the ESI†).

Measurement of glucose concentrations

The ion mobility spectra of blank sample and glucose at the optimum IMS conditions are shown in Fig. 5. Adding ammonia to the carrier gas as the dopant improved sensitivity and selectivity, furthermore reduced mobilities are calculated for positive ion mode using $(H_2O)\cdot n NH_4^+$ as an internal calibrant. The blank spectrum show one peak with reduced mobility values of 3.04 V^{-1} cm^2 s^{-1}. The glucose spectrum shows two peaks, G1 and G2, with reduced mobility values (K_o) of 1.58 and 1.48 cm^2 V^{-1} s^{-1}, respectively. There is no reported reduced mobility for product ions originated from glucose in the literature. Therefore the chemical formula of the product ions cannot be fully without a mass spectrometer coupled to the IMS. Table 6 presents the reduced mobility constant values and drift time.

The calibration curves for the glucose obtained by plotting their respective response (the area under corresponding peaks for the glucose was considered as the response) against the amount of glucose. Linear dynamic range is shown in Fig. 6.

Under optimum conditions, a linear calibration curve was obtained for glucose from 50 to 400 ng. The equation for the analytical curve was $y = -6.2292 + 1.8113x$. The correlation coefficient (R^2) and relative standard deviation percentage (RSD (%) for 200 ng and $n = 6$) are found to be 0.995 and 7.01% respectively. Detection limit (DL) of this method for determination of glucose was 25 ng at a signal-to-noise ratio (S/N) of 3. This result represent an improvement in sensitivity of more than 100 times over that of refractive index detection (3–5 μg).[45,46]

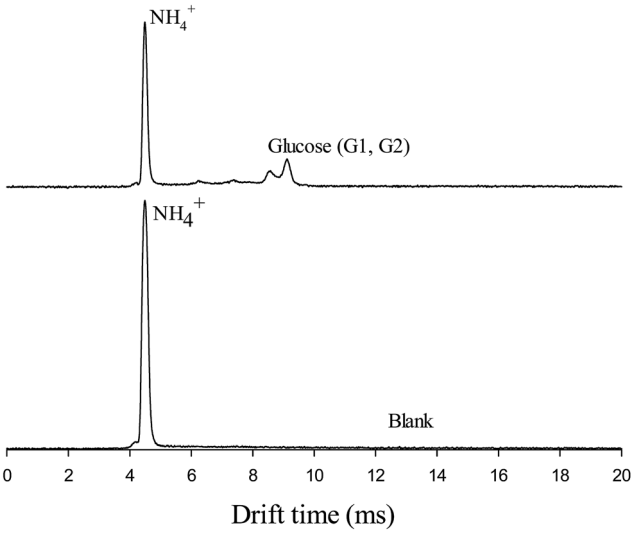

Fig. 5 The ion mobility spectra of the glucose and blank.

Table 6 Characteristic ions for glucose and blank ion mobility spectra

Peak	Reduced mobility, K_o (cm^2 V^{-1} s^{-1})	Drift time t (ms)
NH_4^+	3.04 ± 0.09	4.30
Glucose (G1)	1.58 ± 0.04	8.83
Glucose (G2)	1.48 ± 0.04	8.26

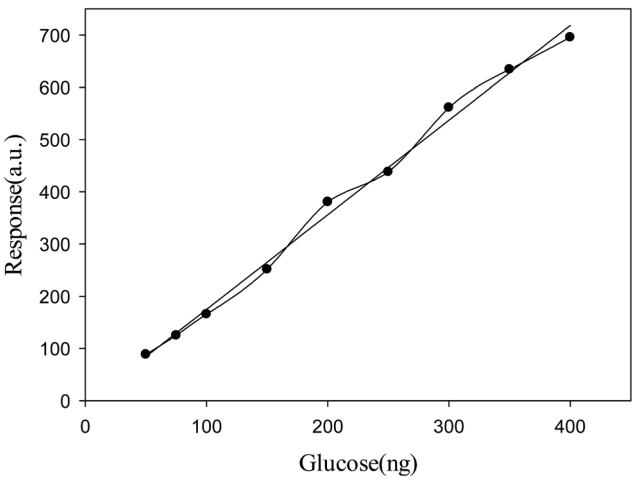

Fig. 6 Plots of IMS response against the amount of glucose.

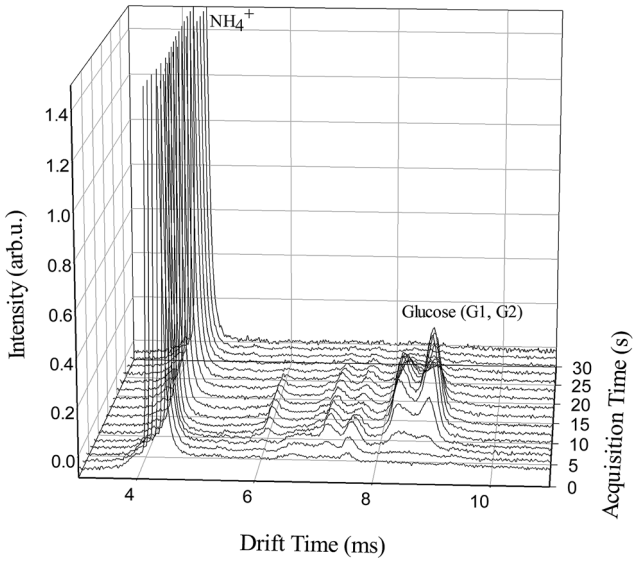

Fig. 7 The section of the watershed 3D plots of the ion mobility spectra of glucose.

A typical watershed 3D plot of the ion mobility spectra of the glucose in filtrate sample (real sample) is shown in Fig. 7. The figure shows that the peak intensities are changed from the injection time until the sample peaks disappear. The spectra show a gradual increasing signal intensity after a short period of time, reach to maximum and then decay. This figure shows that the ionic peaks of glucose do not overlap with each other's. The standard additions method is used to determine amount of produced glucose in the hydrolysis of cellulose. The recovery percentages for two samples are listed in Table S3 (see ESI†). Therefore, the experimental results demonstrated the potential IMS method for the determination of glucose in samples and no needs any separation technique in quantitative analysis of glucose before the sample is introduced into the IMS.

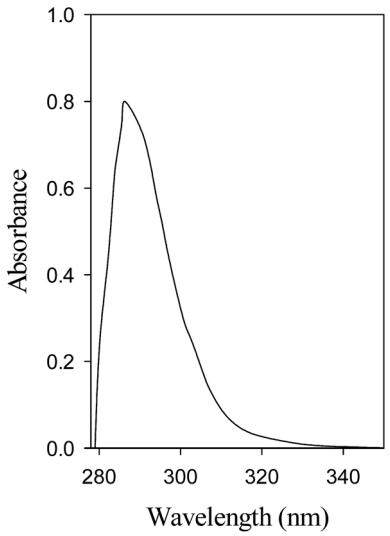

Fig. 8 UV spectrum of the hydrolysis products of cellulose.

Measurement amounts of cellulose and cellobiose

Cellulose conversions were determined by UV spectrophotometry based method. This new method was based on the direct absorbance measurements of hydrolysis products of cellulose formed by reaction with concentrated sulfuric acid. The treatments with concentrated H_2SO_4 at room temperature, solubilize the cellulose by breaking the hydrogen bonds between molecules and the formation of glucose as the product. Then 5-hydroxymethyl-2-furfural is produced by the dehydration of glucose with sulfuric acid. We measured the UV absorption spectrum of 5-hydroxymethyl-2-furfural in aqueous solution.[43,47,48]

The optimal conditions for the determination were: wavelength 286 nm, temperature 25 °C and reaction time 45 min. Fig. 8 shows the spectra of hydrolysis products of cellulose (with concentrations of 0.12 g L^{-1}) in aqueous solution at the optimum conditions.

The concentrations that were prepared for this study are: 0, 0.02, 0.04, 0.08, 0.12, 0.16, and 0.24 g L^{-1}. A linear calibration curve was obtained for cellulose from 0.02 to 0.24 g L^{-1}. The equation for the analytical curve was $y = -0.0244 + 5.9019x$ and the correlation coefficient (R^2) was 0.994. The detection limit (DL) of cellulose in serum blank when using the optimized conditions was determined 8×10^{-3} g L^{-1}, demonstrating that the method is sensitive enough to detect cellulose.

For real samples (hydrolysis of cellulose), the cellulose and catalyst was recovered by filtration, washed thoroughly with distilled water and finally acetone, and dried. Then, residue was take in a test tube, added 3 mL of conc. sulfuric acid and was mixed for 45 minutes. The solution was further diluted to 250 mL with water, mixed well and catalyst was removed by filtration. Finally, the absorbance of the resulting solution was measured at 286 nm.

In this work, standard addition method was used to determine amount of cellulose. The experimental results demonstrated the potential UV spectrophotometry based method for the determination of cellulose in samples (see Table S4 in the ESI†).

Absorbance of the cellobiose solutions were measured at 315 nm and the calibration graph was constructed. The concentrations that were prepared for this study are: 0, 0.01, 0.02, 0.04, 0.08 and 0.1 g L^{-1}. A linear calibration curve was obtained for cellulose from 0.01 to 0.1 g L^{-1}. The equation for the analytical curve was $y = 0.0232 + 10.1422x$ and the correlation coefficient (R^2) and detection limit (DL) were 0.998 and 2.5×10^{-3} g L^{-1}, respectively.

Conclusions

(1) The SPN exhibits high catalytic activity and stability for the direct hydrolysis of cellulose under mild conditions, despite the small surface area. The better catalytic activity can be attributed to the ability to adsorb β-1,4-glucan.

(2) Ion mobility spectrometry was successfully applied to the determination of glucose in aqueous samples. This methodology is simple and fast without using any separation technique.

(3) In this study, UV spectrophotometry based method was successfully applied for determination of cellulose conversions. The simplicity, ease of operation, good sensitivity and low cost are advantages of the proposed method for the determination of cellulose without using any separation technique.

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