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Evaluation of potential of sweet sorghum bagasse for production of value-added chemicals: 5-Hydroxymethyl furfural and its derivatives

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The potential of sweet sorghum bagasse has been evaluated for production of value-added chemicals like 5-hydroxymethyl furfural, 2,5-dimethyl furan, 2,5-furandicarboxylic acid and its ester derivatives. 5-Hydroxymethyl furfural (HMF) has been synthesized from D-glucose and D-fructose separately and D-fructose is found to give higher yields. A catalytic strategy has been developed for the production of 2,5-dimethylfuran from HMF by choosing two different pathways for its production. The pathway involving oxidation with PCC/CH_2Cl_2 followed by Wolf-Kishner reduction is found to be better than the other pathway which involve reduction of HMF with subsequent chlorination with $SOCl_2$ and reduction with $LiAlH_4$. To estimate the production potential of HMF from sweet sorghum bagasse, it is pretreated with different concentrations of alkali *i.e.* 2% H_2O_2, 1% NaOH, 2% H_2O_2+1% NaOH each with *p*H 11.5 and 13 for 24, 48 and 72 h followed by acid saccharification with 0.8M H_2SO_4 for 50 min at 1.05 kg cm^{-2} steam pressure. The maximum production potential of HMF from glucose is found 0.119g HMF/g bagasse. These chemical transformations provide a new paradigm for utilization of sweet sorghum bagasse as a raw material for biofuels and chemicals.

Keywords: 2,5-Dimethylfuran, 5-Furandicarboxylic acid, 5-Hydroxymethylfurfural, Diethyl 2,5-furandicarboxylate, Dimethyl 2,5-furandicarboxylate, Furan 2,5-dialdehyde

Rising prices of fuels and environmental pollution have revived a renewed interest in the exploration for alternative sources of fuels, especially liquid transportation fuels and chemicals to support the pace of growth. Due to concern for the protection of our environment and issues related to sustainability, a gradual shift from a fossil fuel based economy to a biomass based economy, a characteristic feature of the twenty first century, may be globally looked upon as a highly desirable and timely step taken to wean us away from complete dependence on fast-depleting fossil fuels[1].

Biofuels, liquid fuels derived from photosynthetically generated biomass/lignocellulosic plant materials, are driven by factors such as oil price spikes and the need for increased energy security. One of the major lignocellulosic materials to be considered is sweet sorghum bagasse, the fibrous residue obtained after extraction of juice. Overall, out of the many 'new crops' that are currently investigated as potential raw material for energy and industry, sweet sorghum seems to be the most promising one. So there is great interest in developing methods for production of fuel and chemicals that offer economic, environmental and strategic advantages.

Ethanol fuel is the most common biofuel worldwide and widely used in Brazil and in USA. Ethanol is an alcohol made by fermenting the sugar components derived from wheat, corn, sugar beets, sugar cane, and molasses etc. Ethanol can be used as a fuel for vehicles in its pure form, but is usually used as a gasoline additive to increase octane and improve vehicle emissions. Ethanol, the only renewable liquid fuel currently produced in large quantities, suffers from several limitations which include high volatility and contamination by the absorption of water from the atmosphere. A catalytic strategy has already been established for the production of a heterocyclic compound, 2,5-dimethylfuran from D-fructose for using it as a liquid transportation fuel[2]. D-fructose or fruit sugar, a 6-carbon polyhydroxyketone having molecular formula $C_6H_{12}O_6$, is found in many foods. It is one of the three important dietary monosaccharides along with glucose and galactose. D-fructose readily dehydrates to give hydroxymethylfurfural (HMF). This process

may in the future be part of a low-cost, carbon-neutral system to produce replacements for petrol and diesel from plantations. 5-hydroxymethylfurfural (HMF) obtained by acid catalyzed dehydration of fructose is a six carbon commodity with high industrial potential. It has been termed as a key substance between carbohydrate chemistry and mineral based industrial organic chemistry. This six-carbon analogue of commodity chemicals can be converted by straightforward methods into a variety of useful acids, aldehydes, alcohols and amines[3]. Because of its large scale applications, HMF manufacturing is a potential outlet for carbohydrate containing agricultural products towards chemical industry. D-fructose can be converted into 2,5-dimethylfuran in a catalytic biomass-to-liquid process *via* hydroxymethylfurfural. Compared to ethanol, 2,5-dimethylfuran has approximately 40% higher energy density and insoluble in water[4]. The boiling point of 2,5-dimethylfuran (92-94°C) is also higher than ethanol (78.37°C). These attributes of 2,5-dimethylfuran bode well for its use as an alternative liquid transportation fuel. This compound has also been proposed as an internal standard for NMR spectroscopy.

HMF is very useful not only as intermediate for the production of the biofuel 2,5-dimethylfuran (DMF) but for important molecules such as 2,5-furandicarboxylic acid (FDCA), levulinic acid, diformylfuran (DFF), 2,5-bis(hydroxymethyl)furan and 5-hydroxy-4-keto-2-pentenoic acid. 2,5-Furandicarboxylic acid (FDCA), also known as dehydromucic acid, is an oxidized furan derivative. It was identified by the US Department of Energy as one of twelve top priority chemicals for establishing the "green" chemistry industry of the future. 2,5-furandicarboxylic acid, obtained by selective oxidation of 5-hydroxymethyl furfural (HMF) is an important renewable building block because it can substitute for terephthalic acid (PTA) in the production of polyesters and other current polymers containing an aromatic moiety. 2,5 Furandicarboxylic acid can be converted to its ester derivatives by various esterification reactions. FDCA esters have great applications in pharmacology. These are useful as fuel additives and also used as monomers for manufacturing thermoplastic resins by transesterification reactions.

Therefore, the present study was carried out to study the potential of sweet sorghum bagasse for production of 5-hydroxymethylfurfural (HMF), an intermediate for the production of various value-added chemicals.

Experimental Section

All the melting points are uncorrected and were determined in open capillaries, on a Büchi B-545 melting point apparatus. The purity of the compounds was checked by thin layer chromatography (TLC). Evaporation of solvents was carried out by flash distillation on rotary vacuum evaporator (Roteva Equitron). The Infrared and ^{1}H NMR spectra of these compounds were recorded on Perkin-Elmer spectrum RX-1 FTIR spectrophotometer and AC400F, 400MHz Bruker spectrometer, respectively, at Sophisticated Analytical Instrumentation Facility (SAIF), Panjab University, Chandigarh. The mass spectra were recorded on mass spectrometer (WATERS 2489), Department of Chemistry, Punjab Agricultural University, Ludhiana.

Synthesis of 5-hydroxymethylfurfural (HMF) from D-fructose/ D-glucose

To a solution containing fructose (9 g, 0.05 mol) in DMSO (35 mL) was added boron trifluoride etherate $BF_3.Et_2O$ (1.77 g, 0.0125 mol). The reaction mixture was stirred for 45 min at a temperature of 100°C on oil bath under nitrogen atmosphere. The reaction mixture was then quenched by addition of saturated $NaHCO_3$ solution (20 mL) followed by addition of distilled water and dichloromethane (DCM). The layers were separated, the aqueous layer extracted with dichloromethane (3 × 40 mL), the combined organic extract was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The dichloromethane was evaporated by flash distillation and purification of 5-hydroxymethylfurfural using silica gel column chromatography (R_f = 0.40, EtOAc/ Hexane 3:7) gave crude product 1 as a brown liquid. Similar reaction conditions were applied for the synthesis of 5-HMF from D- glucose.

Synthesis of 2, 5-dimethylfuran (DMF) 4 from 5-hydroxymethyl-furfural 1 via pathway I

Synthesis of 2,5-bis-(hydroxymethyl)furan 2 from 5-hydroxymethyl-furfural 1

To a solution of 5-hydroxymethylfurfural 1 (1.26 g, 10 mmol) in methanol (5 mL) was added $NaBH_4$ (456 mg, 12 mmol). The reaction mixture was then quenched by addition of saturated NH_4Cl solution (20 mL) followed by stirring at room temperature

for 2 h. The unreacted methanol in solution was evaporated on flash evaporator. The resulting mixture was extracted with ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4 and concentrated. Silica gel column chromatography using (R_f = 0.25, EtOAc/Hexane 4:6) as eluent afforded the diol 2 as a brown liquid.

Synthesis of 2,5-bis-(chloromethyl)furan 3 from 2,5-bis-(hydroxymethyl)furan 2

A solution of 2,5-bis-(hydroxymethyl)furan (1.92 g, 15 mmol) in 20 mL pyridine was cooled in an ice bath and thionyl chloride (7.14 g, 60 mmol) was added drop wise to the vigorously stirred mixture at a temperature of 5-10°C. After complete addition, removed the ice bath and kept the mixture at room temperature for 12h. Then the reaction mixture was quenched by adding 100 mL ice cold water and extracted with diethyl ether. The ethereal extract was washed with water followed by saturated $CuSO_4$ solution. The ethereal extract was washed with brine, dried over anhydrous Na_2SO_4 and concentrated on flash evaporator. Silica gel column chromatography purification (R_f = 0.55, EtOAc/Hexane, 1:5) of the crude product gave 3 as a brown liquid.

Synthesis of 2, 5-dimethylfuran 4 from 2,5-bis-(chloromethyl) furan 3

A suspension of $LiAlH_4$ (836 mg, 22 mmol) in anhydrous THF (5 mL) was stirred for 5min at 0°C, and a solution of 2,5-bis(chloromethyl)furan (1.65 g, 10 mmol) in anhydrous THF (10 mL) was then added dropwise. The mixture was stirred for 2 h at 0°C further stirred and for 2 h at room temperature. Excess $LiAlH_4$ was destroyed by slow addition of 10% aq NaOH (1.5 mL) and EtOAc (40 mL). The layers were separated; the aqueous layer extracted with ethyl acetate (2 × 40 mL), the combined organic extract was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The ethyl acetate was evaporated by flash distillation and purified 4 using silica gel column chromatography (R_f = 0.50, EtOAc/Hexane 1:19) of the crude product.

Synthesis of 2, 5-dimethylfuran (DMF) 4 from 5-hydroxymethylfurfural 1 via pathway II

Synthesis of furan 2,5-dialdehyde 5 from 5-hydroxymethyl furfural 1

CrO_3 (10.0 g) was added to hydrochloric acid (20 ml of 6.0M HCl) rapidly with stirring. After five minutes, the homogenous mixture was cooled to 0°C and pyridine (10 mL) was carefully added over 10 min. The yellow-orange solid was collected over sintered funnel and dried.

5-Hydroxymethylfurfural (2.15 g, 17 mmol) in dichloromethane (20 mL) was added to pyridinium chlorochromate (4.4 g, 22.4 mmol) in dichloromethane (50 mL). The reaction mixture was stirred for 6 h at room temperature and then CH_2Cl_2 was evaporated and, to the residue was added Et_2O. The slurry was stirred and filtered through a pad of celite. The residue was washed 3 times with Et_2O and filtered. The filtrate was concentrated and purified using silica gel column chromatography (R_f = 0.35, EtOAc/hexane 1:9) of the crude product to gave dialdehyde 5.

Synthesis of 2,5-dimethylfuran 4 from furan 2,5-dialdehyde 5

To a solution of furan 2,5-dialdehyde (6.0 g, 0.25 mol), diethylene glycol (50 mL) were added hydrazine hydrate (5 mL) and potassium hydroxide pellets (7.0 g, 0.125 mol). The mixture was warmed in boiling water bath until KOH had dissolved and then reflux for 1 hour. The reaction mixture was cooled to room temperature and extracted with ether. The layers were separated, the aqueous layer extracted with ether (2×40 mL), the combined organic extract was washed with brine, dried over anhydrous Na_2SO_4 and evaporated by flash distillation and purified 2,5-dimethylfuran using silica gel column chromatography (R_f = 0.50, EtOAc/hexane 1:19) of the crude product gave 4.

Synthesis of 2,5-furandicarboxylic acid (FDCA) 6 from 5-hydroxymethyl furfural 1

To a solution of 5-hydroxymethylfurfural (2 g, 15.9 mmol) in 50 mL H_2O was added a solution of $KMnO_4$ (2 g) in 25 mL of 10% aq. NaOH dropwise with stirring over a period of 30 minutes at room temperature and the resulting precipitate was removed by filtration. The filtrate was treated with 37% HCl solution until *p*H ≤ 1was attained. Resulting solution was then cooled to 0°C, extracted with ethyl acetate, dried over anhydrous Na_2SO_4 and concentrated. Silica gel column chromatography purification (R_f = 0.20, $CH_3OH/CHCl_3$, 1:9) of the crude product gave 6 as a pale yellow solid.

Synthesis of esters of FDCA

Synthesis of dimethyl 2,5-furandicarboxylate 7

To a solution of 2,5-furandicarboxylic acid (0.5 g, 3.20 mmol) in methanol (20 mL) was added concentrated HCl (2.5 mL). The reaction mixture was heated to 80°C under reflux, for 6 h with continuous

stirring. Then, the reaction mixture was cooled to room temperature, quenched with 10% NaOH leading to the crystallization of the main bulk of the ester. The reaction mixture was diluted with ethyl acetate (3×20 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated. Silica gel column chromatography purification (R_f= 0.45, EtOAc/ hexane, 2:8) of the crude product gave 7 as an orange solid.

Synthesis of diethyl 2,5-furandicarboxylate 8

To a solution of 2,5-furandicarboxylic acid (0.5 g, 3.20 mmol) in ethanol (15 mL) was added concentrated HCl (2.5 mL). The reaction mixture was heated to 80°C under reflux, for 6 h with continuous stirring. Then, the reaction mixture was cooled to room temperature, quenched with 10% NaOH leading to the crystallization of the main bulk of the ester. The reaction mixture was diluted with ethyl acetate (3×20 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated. Silica gel column chromatography purification (R_f = 0.47, EtOAc/hexane, 2:8) of the crude product gave 8 as an orange solid.

Production potential of sweet sorghum bagasse for 5-hydroxymethyl furfural

For evaluating the potential of sweet sorghum bagasse for the production of glucose and 5-HMF, the chemical composition of sweet sorghum bagasse was determined. Neutral detergent fiber (NDF), acid detergent fiber (ADF) and acid detergent lignin (ADL) were determined by detergent system method[5]. Hemicellulose, cellulose and lignin% were calculated as below-

Hemicellulose % = NDF % – ADF %
Cellulose % = ADF % - ADL %
Lignin % = ADL %

Alkali pre-treatment process was carried out as reported by Dawson and Boopathy[6]. Fine and dried bagasse was weighed to 3 g. Then 75 mL of 2% H_2O_2, 1% NaOH and (2% H_2O_2+1% NaOH) solutions each with *p*H 11.5 and 13 was added in the individual flasks to submerge the bagasse and allowed to soak for 24, 48 and 72 h. Each flask was placed in shaker at 100 rpm to ensure that all of the bagasse came into contact with the treatment solution. The residue was removed from the solutions by filtration and then rinsed with distilled water three times. The residue was then dried in an oven at 100°C for approximately 12 h. Finally, the residue was re-weighed. The percentage weight loss was equated to the amount of lignin and hemicellulose removed. The bagasse residue obtained from each of pre-treatment combination was treated with 0.8 and 1.0 M H_2SO_4 with solid: liquid ratio of 1: 12 and the mixture was autoclaved for 50 min at 110°C temperature and 1.05 kg cm^{-2} steam pressure. The mixture was filtered and analyzed for estimation of reducing sugars by Nelson method[7]. Then the production potential of sweet sorghum bagasse for 5-hydroxymethyl furfural was estimated.

Results and Discussion

Synthesis of 5-hydroxymethylfurfural (HMF) from D-fructose/ D-glucose

D-glucose was converted to 5-hydroxymethyl-furfural (HMF). As the yield of HMF obtained (40%) was less, the conversion of D-fructose to 5-HMF was explored. Starting with D-fructose, the yield of HMF obtained was 95% in the presence of nitrogen atmosphere (Scheme 1). The ^{1}H NMR spectrum showed a singlet signal at δ 9.58 due to –CHO (aldehydic proton), singlet signal at δ 4.67 due to two methylene protons attached to furan ring, singlet signal at δ 4.45 due to –OH (hydroxyl proton), doublet signal at δ 7.23 and 7.22 due to =C-H proton present adjacent to hydroxyl group with coupling constant of 4.0 Hz with doublet signal at δ 6.52 and 6.51 due to =C-H proton present adjacent to –CHO (aldehydic proton). IR spectrum showed band at 3402 cm^{-1} due to O-H bond, at 2923 cm^{-1} due to C-H bond of methylene group attached to the ring, 2852 cm^{-1} due to C-H bond of aldehydic group, at 1719 cm^{-1} due to C=O stretch, 1668 cm^{-1} due to C=C of the ring, at 1192 cm^{-1}due to C-OH bond, at 1021 cm^{-1} due to C-O-C bond and 964 cm^{-1} due to =C-H of the ring. The presence of the band at 2852 cm^{-1} in IR spectrum showed the presence of aldehydic group, thus confirming the formation of the 5-hydroxymethyl furfural.

Synthesis of 2, 5-dimethylfuran (DMF) from 5-hydroxymethyl-furfural via pathway I

The conversion of 5-hydroxymethylfurfural to 2,5-bis-(hydroxymethyl)furan gave yield of 85% (Scheme 1). The ^{1}H NMR spectrum showed a singlet signal at δ 4.56 due to four protons of two methylene groups attached to hydroxyl groups, singlet signal at δ 6.22 due to two protons of two =C-H groups of the furan ring. IR spectrum showed a band at 3424 cm^{-1}

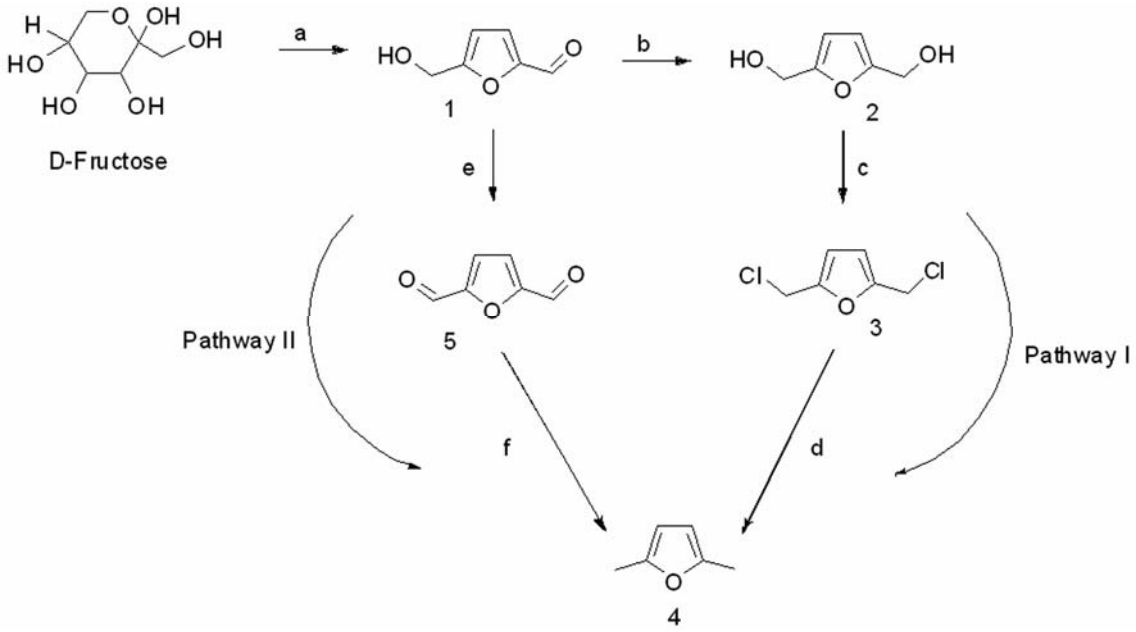
due to O-H stretching, at 2920 cm^{-1} due to C-H bond of methylene group attached to the ring, at 1643 cm^{-1} due to C=C bond of the furan ring, at 1187 cm^{-1} due to C-O-C bond and 1016 cm^{-1} due to C-OH bond. The absence of band at 2852 and 1719 cm^{-1} showed the reduction of -CHO (aldehydic group) into $–CH_2OH$. 2,5-bis-(chloromethyl)furan (72% yield) obtained by chlorination of 2,5-bis-(hydroxymethyl)furan was identified by R_f studies in TLC and mass spectrum. The mass specrum showed a peak at with a mass to charge ratio of 88 due to the removal of $ClCH_2CO^+$, another at 93 due to the removal of both ^{35}Cl and ^{37}Cl atoms and molecular ion peak at m/e of 165. 2,5-Dimethylfuran obtained (68% yield) was identified by R_F studies in TLC, IR, NMR and mass spectrum. ^1H NMR spectrum showed two singlets at δ 2.2 due to two protons attached to carbon 3 and 4 of ring and at δ 5.8 due to six protons of two methyl groups. IR spectrum showed bands at 2960 and 3100 cm^{-1} due to C-H stretching, at 1660 and 1550 cm^{-1} due to C=C of the ring, at 960 cm^{-1} due to =C-H of the ring, at 1230 and 1000 cm^{-1}due to C-O-C ether linkage. The mass spectrum showed a peak at *m/e*=81 due to loss of CH_3^+ and a peak at *m/e*=96 as its molecular ion peak.

Synthesis of 2, 5-dimethylfuran (DMF) from 5-hydroxymethyl furfural via pathway II

In second pathway, 5-HMF was reacted with PCC/CH_2Cl_2 to produce furan 2,5-dialdehyde (60% yield) (Scheme 1). The ^1H NMR spectrum of furan 2,5-dialdehyde showed singlet at δ 9.75, 2H due to –CHO (aldehydic proton) and a singlet at δ 7.30 due to =C-H protons present in furan ring, which are adjacent to aldehydes. The IR spectrum showed strong band at 1680 cm^{-1} which signifies C=O stretching of aldehydic group, a band at 2840 cm^{-1} due to C-H stretching of aldehyde and a band at 1170 cm^{-1} due to C-O-C group. The IR band at 1020 cm^{-1} corresponds to –C-H stretching band. All these data confirmed the structure of the compound as furan 2,5-dialdehyde which was further subjected to Wolf-Kishner reduction to produce 2,5-dimethylfuran. 2,5-Dimethylfuran obtained (74% yield) was identified by R_f studies in TLC, IR, NMR and mass spectrum which were found to be same as given in section 3.2. Second pathway was found to be better pathway for the production of 2,5-dimethylfuran as it gave higher yield of the product and involved cleaner reaction which was carried out in lesser number of steps.

Synthesis of 2, 5-furandicarboxylic acid (FDCA) from 5-hydroxymethylfurfural

The progress of the reaction was monitored by TLC that indicated the conversion of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid with yield of 58% and further by taking IR and NMR data (Scheme 2). The ^1H NMR spectrum



Reagents and conditions: (a) $BF_3.Et_2O$/DMSO, 100°C, 45 min, 95%; (b) $NaBH_4/CH_3OH$, RT, 2h, 85%; (c) $SOCl_2$/Pyridine, 5°C, 12h, 72%; (d) $LiAlH_4$, dry THF, RT, 4 h, 68%; (e) PCC/CH_2Cl_2, RT, 6h, 60%; (f) Ethylene glycol, Hydrazine hydrate/KOH, Reflux, 1h, 74%.

Scheme 1

showed a singlet signal at δ 7.77 due to two protons of two =C-H groups of the furan ring. IR spectrum showed a band at 3128 cm^{-1} due to C-H bond of the furan ring, at 1566 cm^{-1} due to C=C bond of the furan ring, at 1288 cm^{-1} due to furan C-O-C bond and at 1731 cm^{-1} due to C=O bond. The absence of band at 2852 cm^{-1} showed the oxidation of -CHO (aldehydic group) into –COOH. The data confirmed the structure of the compound as 2,5-furandicarboxylic acid.

Synthesis of esters of 2, 5-furandicarboxylic acid (FDCA)

Synthesis of dimethyl 2,5-furandicarboxylate from 2, 5-furandicarboxylic acid

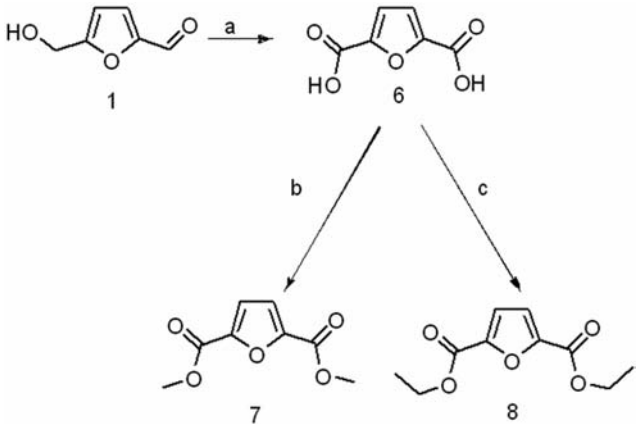
The progress of the reaction was monitored by TLC that indicated the conversion of 2,5-furandicarboxylic acid to dimethyl 2,5-furandicarboxylate with yield of 78% (Scheme 2). The ^1H NMR spectrum showed a singlet signal at δ 3.9 due to six protons of two methyl groups, singlet signal at δ 7.23 due to two protons of two=C-H groups of the furan ring. IR spectrum showed a band at 3142 cm^{-1} due to C-H bond of the furan ring, at 2969 cm^{-1} due to C-H bond of methyl group attached to the ring, at 1719 cm^{-1} due to C=O bond, at 1529 cm^{-1} due to C=C bond of the furan ring and at 1302 cm^{-1} due to C-O ester linkage.

Synthesis of diethyl 2,5-furandicarboxylate from 2, 5-furandicarboxylic acid

The progress of the reaction was monitored by TLC that indicated the conversion of 2,5-Furandicarboxylic acid to diethyl 2,5-furandicarboxylate with yield of 80% (Scheme 2). The ^1H NMR spectrum showed a triplet at δ 1.29 due to six protons of two methyl groups, quartet at 4.27 due to four protons of two methylene groups and singlet signal at δ 7.18 due to two protons of two =C-H groups of the furan ring. IR spectrum showed a band at 3149 cm^{-1} due to C-H bond of the furan ring, at 2943 due to C-H stretch due to ethyl group, at 1731 cm^{-1} due to C=O bond, at 1574 cm^{-1} due to C=C bond of the furan ring and at 1278 cm^{-1} due to C-O ester linkage.

Potential of bagasse of sugar crops for the production of glucose and 5-hydroxymethyl furfural

Cellulosic biomass is an especially promising source for the production of a variety of value-added chemicals because of its inexpensive availability from non-food sources. Therefore we evaluated the potential of sweet sorghum bagasse for production of HMF. The chemical composition of sweet sorghum bagasse is given in Table 1. The



Reagents and conditions: (a) $KMnO_4$/NaOH, 0°C, 30min, 58%; (b) CH_3OH/HCl, Reflux, 6h, 78%; (c) C_2H_5OH/HCl, Reflux, 6h, 80%.
Scheme 2

Table 1 — Chemical composition of sweet sorghum bagasse (%DM basis)

Neutral Detergent Fiber (NDF)	87.9
Acid Detergent Fiber (ADF)	59.8
Acid Detergent Lignin (ADL)	14.0
Cellulose	45.8
Hemicellulose	28.1
Lignin	14.0

cellulose, hemicellulose and lignin contents of bagasse were found to be 45.8, 28.1 and 14.0% respectively. The hydrolysis of cellulose is restricted by crystalline structure of cellulose microfibrils that are aggregated and embedded within the lignified cell wall matrix. Therefore to increase the susceptibility of cellulosic materials to acids, it is essential to expose and separate elementary cellulose microfibrils by various pre-treatment methods. In the present study, alkaline pre-treatment was selected as it was expected to cause less sugar degradation than acid process. The alkaline pre-treatments were performed by soaking bagasse in 2% H_2O_2, 1% NaOH and 2% H_2O_2+1%NaOH solutions at *p*H 11.5 and 13 each and shaking for various time intervals (24, 48 and 72 h) (Table 2). The percent weight loss was used to compare pre-treatment effects on delignification and hemicellulose solublization. Greater weight loss indicated more lignin and hemicellulose removal. Treatment with 2% H_2O_2+1%NaOH solution was found to result in maximum weight loss *i.e.* 43.1% (at 13 *p*H, 72 h) from bagasse. The solid residue left after pre-treatment mainly contained cellulose which was subjected to acid hydrolysis for its breakdown into its monomer glucose units. So the reducing sugars

Table 2 — Pretreatment of sweet sorghum bagasse with H_2O_2 and NaOH solutions of different concentrations and *p*H values for different time intervals

Treatment		% Weight loss Time interval (h)		
Solution (w/v)	*p*H	24	48	72
2% H_2O_2	11.5	18.6	21.8	26.1
	13.0	28.5	24.3	32.1
1% NaOH	11.5	22.6	23.4	29.3
	13.0	30.3	32.3	36.3
2% H_2O_2 +1%NaOH	11.5	26.6	37.1	40.1
	13.0	35.6	41.3	43.1

Table 3 — Production of reducing sugars by acid saccharification with 0.8M H_2SO_4 of pretreated sweet sorghum bagasse.

Reducing sugars (mg/g pretreated bagasse)				
Treatment		Time interval (h)		
Solution (w/v)	*p*H	24	48	72
2% H_2O_2	11.5	217.45	308.62	375.32
	13.0	300.25	350.16	420.21
1% NaOH	11.5	315.21	369.56	451.79
	13.0	371.25	398.70	464.31
2% H_2O_2 +	11.5	418.70	460.56	498.12
1%NaOH	13.0	468.19	488.64	504.85

Table 4 — Production potential of 5-hydroxymethylfurfural (HMF) from sweet sorghum bagasse.

Treatments	%Weight loss	Pretreated bagasse	Glucose (g/g pretreated bagasse)	Glucose (g/g bagasse)	HMF production (g/g bagasse)
2%H_2O_2+1%NaOH; *p*H 13,72 h	43.1	56.9	0.504	0.287	0.115
2%H_2O_2+1%NaOH; *p*H 13,48 h	41.3	58.7	0.488	0.286	0.114
2%H_2O_2+1%NaOH; *p*H 11.5,72 h	40.1	59.9	0.498	0.298	0.119

produced by treating alkali pre-treated bagasse with 0.8M H_2SO_4 for 50 min at pressure of 15 psi mainly contained glucose (Table 3). Maximum amounts of reducing sugars produced were found to be 488.64, 498.12 and 504.85 mg/g bagasse pre-treated with 2% H_2O_2 + 1% NaOH at *p*H 13.0, 11.5 and 13.0 for 48, 72 and 72 h, respectively.

Out of 18 treatments (given in Table 2), three best pre-treatment conditions *i.e.* 2% H_2O_2 + 1% NaOH, *p*H 13, 72 h; 2% H_2O_2 + 1% NaOH, *p*H 13, 48 h and 2% H_2O_2 + 1% NaOH, *p*H 11.5, 72 h leading to maximum delignification and hemicellulose solublization *i.e.* 43.1, 41.3 and 40.1% weight loss and maximum reducing sugars production *i.e.* 504.85, 488.64 and 498.12 mg/g pre-treated bagasse, respectively were selected for the estimation of production potential of HMF from sweet sorghum bagasse (Table 4). HMF production potential was calculated on the basis of yield (40%) of HMF obtained from D-glucose as given in section 3.1. Maximum amounts of glucose *i.e.* 0.287, 0.286 and 0.298 g/g bagasse would produce 0.115, 0.114 and 0.119 g HMF/g bagasse, respectively. It has been reported that *in situ* isomerization of glucose to fructose with subsequent condensation to HMF is feasible in high yields (70-80%), by using lewis acid catalysts such as $CrCl_2$ and ionic liquids as solvents, thus paving the way to the use of renewable feed stock[8]. As the yield of HMF from fructose was found to be higher, the amount of HMF produced from sweet sorghum bagasse may be enhanced if glucose is first isomerized to fructose and then converted into 5-hydroxymethyl furfural.

Conclusion

Sweet sorghum bagasse could be a promising alternative for the production of many value-added chemicals like 5-hydroxymethyl furfural, 2,5-dimethyl furan, 2,5-furan dicarboxylic acid and its derivatives. Out of two different pathways selected for the production of 2,5- dimethyl furan, the pathway involving oxidation with PCC/CH_2Cl_2 followed by Wolf-Kishner reduction was found to be better. As the yield of 5-hydroxymethyl furfural from glucose was less than from fructose, therefore the strategy involving isomerization of glucose to fructose and then its conversion into 5-hydroxymethyl furfural and its derivatives needs to be further explored.

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