Egypt. J. Chem. **Vol. 66**, No. 11 pp. 53-61. (2023)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Recycling and chemistry of the lignocellulosic biomass for cotton stalks to primer value-added products

Nadia H. Metwally,[a] Amal S. Owis,[b] Faten M. El-Tohamy[b]

[a]*Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt*
[b]*Cotton Research Institute, Agricultural Research Center, Giza, Egypt*

Abstract

This study aims to recycle the lignocellulosic biomass (LB) of Egyptian cotton stalks as organic plant waste to produce a primer for value-added economic products. The cellulose content of Giza 86 and Giza 90 (32.37 % and 30.79 %), respectively, results in the conversion of promising raw materials into many economic products. The extracted cellulose was investigated by X-ray diffraction which confirms the efficient extraction process when compared to the X-ray spectrum to the standard sample. It was then depolymerized to glucose using molten $ZnCl_2$ in the presence of hydrochloric acid. Glucose was dehydrated to 5-Hydroxymethylfurfural (5-HMF) by a one-pot reaction using dimethylsulfoxide (DMSO) as a solvent and ferric chloride hexahydrate as a catalyst. The as-formed 5-HMF was then analysed by (FT-IR, HPLC, and ^{1}H & ^{13}C-NMR). The spectra of the prepared 5-HMF sample were compared with that of the spectra of the standard 5-HMF sample, and this comparison showed a quite parallelism between the prepared and the standard samples, confirming that 5-hydroxymethylfurfural was successfully produced.

Keywords: Cotton stalks, Lignocellulosic biomass, Cellulose, 5-Hydroxymethylfurfural (5-HMF) ;

1. Introduction

The agriculture sector in Egypt still plays an important role in the national economy, contributing 11.05 percent to Gross Domestic Product (GDP) and employing more than one-quarter of the labor force [1]. The prime sources of biomass waste in Egypt are agricultural waste (crop residues), followed by municipal solid waste, animal waste, and sewage waste [2]. The number of cotton bolls produced in Egypt in 2020/2021 is 891639.64 kantar per feddan according to CATGO, so the cotton stalk produced all over Egypt approaches a huge amount which is treated as an uneconomic waste [3]. Cotton stalks which, are produced in large amounts as a by-product, causing several problems such as its storage above the farmer's houses, which may cause fires when the wind blows or upon its disposal by burning, on the other hand, cotton stalks contain eggs and larvae of pink bollworm, which remain dormant until the following season, resulting in serious damages to the cotton crop [4]. Lignocellulosic biomass is the most abundant natural and renewable resource available for the enhancement and maintenance of industrial societies, and is essential for development of a sustainable global economy [5]. The term "lignocellulosic biomass" is defined as lignin, cellulose, and hemicellulose that form the plant cell wall. Strong cross-linked structures exist between these constituents and back draw occurs in the decomposition of this cell wall [6,7]. In general, most agricultural lignocellulosic biomass is composed of about 40-50% cellulose, 20-30% hemicellulose, and 10-25% lignin [5,8,9]. Cellulose is a fundamental structural component of plant cell walls and is responsible for mechanical strength. The hemicellulose macromolecules are mainly repeating polymers of pentoses and hexoses. Lignin contains three aromatic alcohols (coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol) that arise during biosynthesis and forms a protective cover for the other two constituents i.e., cellulose and hemicellulose [10, 11]. Cellulose is a complex

*Corresponding author e-mail: mnadia@sci.cu.edu.eg
Receive Date: 30 June 2022, Revise Date: 10 September 2022, Accept Date: 17 October 2022
DOI: 10.21608/EJCHEM.2022.148153.6409

carbohydrate composed of oxygen, carbon, and hydrogen, with several properties of cellulose depending on the degree of polymerization, chain length, and the number of glucose units comprising the polymer chain. Natural biopolymers as cellulose, hemicellulose, and lignin, showed antibacterial activities [12]. Cellulose is insoluble in water, weak acids, alkalis, and most organic solvents [13]. Lignin, a common plant biopolymer, is known to have antioxidant activity and its nanoparticles showed a significant power to inhibit bacterial growth over time [12]. Recently, industrial production of most chemicals relies on fossil-based feedstock [14]. Global consumption of crude oil and the effects of climate change induced by greenhouse gas emissions have resulted in valuable research efforts to innovate renewable and sustainable transportation fuels and industrial chemicals [9, 15]. Today, lignocellulosic biomass has obtained special importance as an energy resource due to its renewable nature [16]. The abundance of renewable biomass has the potential to be used to produce fuels and chemicals at low-cost.

Fig. 1. Converting cotton stalks into 5-hydroxymethylfurfural

2. Materials and Methods

Raw material:

This study was carried out on two Egyptian cotton stalks cultivars (*Gossypium barbadense L.*) Giza 86 and Giza 90. These cultivars were brought from the experimental fields of the Cotton Research Institute, Agricultural Research Center, Egypt season 2014.

Chemicals:

Ethyl alcohol, chloroform, sulphuric acid, formic acid, hydrogen peroxide, sodium hydroxide, zinc chloride dihydrate, hydrochloric acid, dimethylsulphoxide (DMSO), ferric chloride hexahydrate, and 5-hydroymethylfurfural standard reagent.

Bio-refinery includes sustainable processing of all types of biomass to many bio-based products and bio-energy employing efficient processes of production and valorization without producing waste [17]. Recently, the catalytic transformation of hexoses into furans (as one of the lignocellulosic biomass derivatives) is very interesting and the furanic products available with this strategy such as 5-hydroxymethylfurfural (HMF), 2,5-diformylfuran (DFF), 2,5-furandicarboxylic acid (FDCA), 2,5-bis(hydroxymethyl)furan (BHF), and 2,5-dimethylfuran (DMF) [18]. 5-Hydroxymethylfurfural (5-HMF) is an organic compound formed from the dehydration of certain sugars [19]. Molecule consists of a furan ring, with both aldehyde and alcohol functional groups [20]. 5-HMF is commonly produced by catalytic dehydration of fructose to achieve high conversion and selectivity, but this technique is limited by the high production costs and inherent backdraws caused by the limited availability of fructose [21].

All the following laboratory works were carried out in Cotton Seed Technology and Natural Products unit, Cotton Chemistry and Textile Fibers department, Cotton Research Institute (CRI), Agricultural Research Center (ARC), Giza, Egypt.

A. Chemical composition analysis of cotton stalks:

i. Moisture content determination [22]:

Thoroughly mix the sample and select a representative sample of 100 to 300 gram. Determine the mass of this sample, and spread it evenly on a large flat pan, and allow at least 24 hours for the sample to reach moisture equilibrium with the room air. At this time, stir occasionally to ensure that the entire sample is exposed to the maximum amount of air. Once the mass of the sample is constant, calculate the moisture removed during air drying as a percentage of the as-received mass. Place the sample in a container and record the mass to nearest 0.01 gram in a high-silica or porcelain evaporating dish fitted with a heavy-duty aluminum foil cover. The dish shall have a capacity of not less than 100 ml. Mix thoroughly the representative sample, place at least 50 gram of the test specimen in the container, immediately cover it with an aluminum foil cover, and record its mass to the nearest 0.01 gram. Dry uncovered at 105 °C for at least 16 hours or until the mass of the sample remains unchanged after drying for at least one hour. Remove from oven, cover tightly, cool in a desiccator, and record the mass.

ii. Wax content determination [23]:

Three to five grams of sample were placed in a large Soxhlet (50 x 250 mm) extractor, and then 250 ml of 95% ethanol was added to the extraction flask. After 6 hours of the extraction procedure, the sample was removed and the condenser was kept upon heating until part of the alcohol has passed over to the extraction compartment of the Soxhlet and only 75 to 85 ml of liquid remains in the extraction flask, then the extract has been allowed to cool, transferred after then to a 500 ml separatory funnel. The Soxhlet flask was washed with 5 ml portions of hot 95% ethanol, the ethanol to bring the final volume to 100 ml, and 100 ml of chloroform was added to the separatory funnel and mix thoroughly. Then 75 ml of water was added to the alcohol-chloroform solution and agitate to cause mixing and separation of two distinct layers. The chloroform layer was drawn off, and set aside in a 300 ml flask with a freshly added 50 ml portion of chloroform to the separatory funnel, agitate gently, and again allow the layers to separate. The wax is now practically completely in the chloroform layer. The separatory funnel was drained and discard the spent alcohol-water solution, without washing the funnel, the chloroform solution of wax back was poured in, about 100 ml of distilled water was added, shacked carefully, and allowed the two layers to separate. When the separation was complete, the chloroform layer was withdrawn and received in the same flask from which it was last removed. Next 5 ml of fresh chloroform was added sequentially to the separating funnel in two separate volumes, shucked well, to separate them, and each was withdrawn in turn into the flask containing the main body of chloroform solution. This should complete the transfer of the wax back into this flask. Chloroform was removed from the wax by placing it in a 100 ml beaker and evaporating it on a steam bath. After the waxy residue appeared to have dried, the beaker was cooled and weighed, then heated on a steam bath for another 30 minutes, cooled again, and weighed. If the weights were not constant, heating was repeated until two successive weightings agreed within 0.1% of the residue weight.

ii. Ash content determination [22]:

Determine the mass of a covered porcelain dish. Place a part of or the entire oven-dried test specimen from moisture determination in the dish and determine the mass of the dish and specimen. Remove the cover and place the dish in the muffle furnace. Gradually increase the temperature in the furnace to 750 °C and hold until the specimen is completely ashed (further heating until no change of mass). Cover with the retained aluminum foil cover, cool in a desiccator, and determine the mass.

B. Cellulose extraction and determination:

Cellulose was extracted according to two procedures [24] and [25] respectively:

1. The raw fibers were dewaxing for 6 hours in the soxhlet apparatus using 200 ml of 70% (v/v) ethyl alcohol. The fiber to solvent ratio was 1:10 (g L^{-1}). After thoroughly washing the collected fibers with distilled to remove traces amounts of alcohol, and drying, 10 g of dewaxed fibers were taken in a beaker and suspended in 100 ml of 10% sodium hydroxide, followed by 100 ml of 10% of H_2O_2. The beaker was covered with aluminum foil and autoclaved at 121°C, 1.5 bar for 1 hour. Fibers separated from the supernatant solution were thoroughly washed with double distilled water. The autoclaved fibers were dignified by soaking in a 1:1 (v/v) mixture of 20% formic acid and 10% hydrogen peroxide. The mixture was maintained at 85 °C in water bath for 2 hours, and after filtration, the graded fibers were collected. Fibers were first washed with 10% formic acid and repeated washings with distilled water were carried out. The extracted cellulose fibers were pale yellow. It was then treated with 10% hydrogen peroxide at 60 °C for 90 min. The pH was adjusted using sodium hydroxide (10%) solution. The resulting white suspension was filtered and washed several times. The insoluble cellulose was collected and the yield (w/w) was calculated [24].

2. Cotton stalk sample (50 gram) was extracted with ethanol– benzene (1:2 v/v) for 6 hours in soxhlet apparatus then dried at 45 ºC. The dried samples were heated in sodium chlorite solution [add 23.5 gram of sodium chlorite ($NaClO_2$) in 1000 ml of water containing 5 gram of glacial acetic acid] at 75-80 ºC for 5 hours to remove the lignin. This treatment was repeated twice and the solution was filtered. After filtration, the residual material was washed with distilled water until the chloride ions were removed, and treated with ethyl alcohol to give holocellulose (hemicellulose and cellulose). To obtain the hemicellulose and cellulose fractions, holocellulose was treated with 500 ml NaOH 10% (w/v) for 4 hours at 25 ºC with occasional stirring then filtered. The residue was again treated with 250 ml. NaOH 10% (w/v) for 3 hours at 80-90 ºC, filtered and washed with water, ethanol, acetone, ether, and air dried. This fraction contained the cellulose [25].

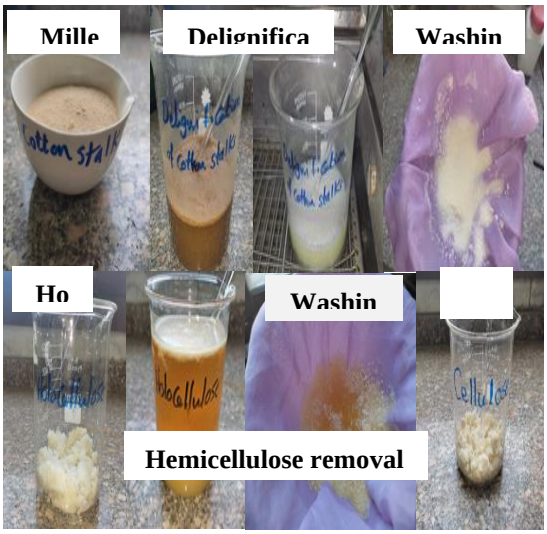

Fig. 2. Delignification of cotton stalks

C. Synthesis and characterization of 5-hydroxy-methylfurfural [26]:

First, 0.1gram cellulose, and 2.0 gram $ZnCl_2$ $2H_2O$ were mixed homogeneously in a 50 ml flask, and heated to 95 ±°C to a molten state. Next, 0.6 mL of 1 mol/L HCI solution was added droplet in 45 seconds, and stirred at 95 ±°C for different times to degrade the cellulose. Some of the samples were separated from the mixture at different times and were cooled down to room temperature for analysis. The above mixture obtained after cellulose depolymerisation was used directly as the feedstock for the preparation of HMF. Briefly, 4 mL of DMSO and 1.24 mmol of catalyst were added directly to the reaction system at room temperature, and it was heated up to the reaction temperature for various times under reflux condensation. Finally, the system was cooled, diluted with distilled water, and subjected to FT-IR, HPLC, ^{1}H NMR, and ^{13}C NMR measurements.

3. Results and Discussion

A. Chemical composition:

Cotton stalk chemical composition was analyzed for the two cultivars Giza 86 and Giza 90. The results showed that Giza 86 had higher in the content of moisture, ash and lipids, while Giza 90 cultivar had higher in the content of wax and organic matter extracted by benzene-ethanol (2:1) mixture. Statistical analysis [27] showed significant difference between the two cultivars for moisture, ash and lipids, but not for wax and organic matter.

Table 1. Cotton stalk chemical composition

Cultivar	Moisture %	Wax %	Ash %	Organic matter %	Lipids %
Giza 86	11.83	1.31	5.245	10.21	0.90
Giza 90	9.95	1.62	4.13	11.29	0.86
LSD (0.05)	0.2278	1.165	0.1787	0.3159	0.09

The results of the two cellulose extraction methods showed that procedure [24] gave higher yields of cellulose than procedure [25] for both Giza 86 and Giza 90 cultivars. However the procedure [25] have environmental and economical advantages over procedure [24] in that it uses eco-friendly dilution reagents, and consumes less time and energy. Statistical analysis [27] of the cellulose results showed significant differences between the two cultivars for both methods [24] and [25].

Table 2. Cellulose percentage according to the two methods [24] and [25]

cultivar	Cellulose % *	Cellulose % **
Giza 86	29.10	32.37
Giza 90	23.41	30.79
LSD (0.05)	0.3574	0.4853

* Acc. to method [24].
** Acc. to method [25].

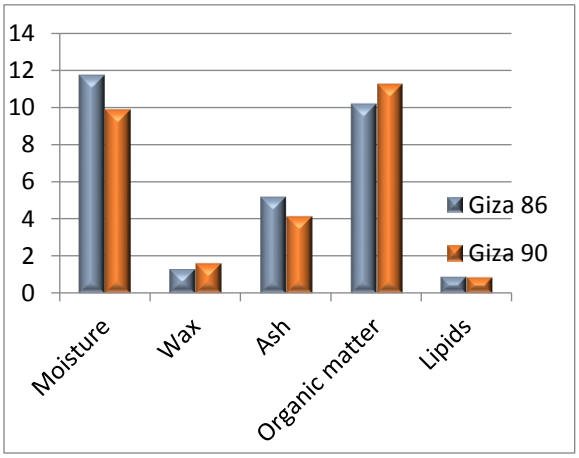

Fig. 3. Diagram of the chemical composition of cotton stalk

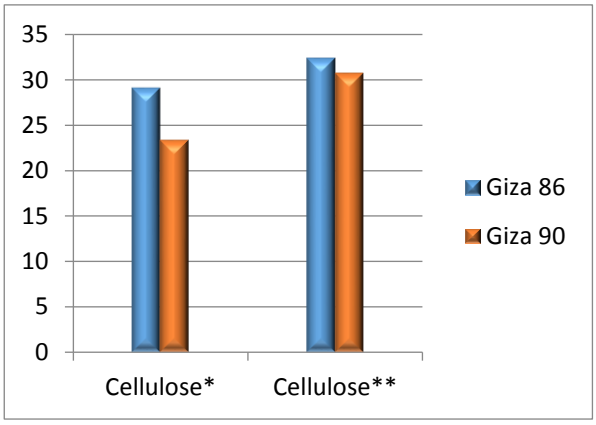

Fig. 4. Diagram of the percentage of cellulose in cotton stalk, (cellulose*) acc. to [24] and (cellulose**) acc. to [25]

B. Physical analysis:

i. X-RAY diffraction (XRD):

The extracted cellulose samples of Giza 86 (Fig. 4) and Giza 90 (Fig. 5) cultivars were examined on a Philips X-ray diffraction equipment model PW/1710 with monochromator, Cu-radiation (λ=1.542 Å) at 40 K.V., 35 m.A. and scanning speed 0.02º/sec. were used. The reflection peaks between 2Θ = 2º and 60º, corresponding spacing (d, Å) and relative intensities (I/Iº) were obtained, the diffraction charts and relative intensities are obtained and compared with ICDD files, obtained diffraction chart of both extracted cellulose samples were checked against the chart of standard cellulose sample (Fig. 6) [28], and it was found that they had the same trend and enclosed in the same range.

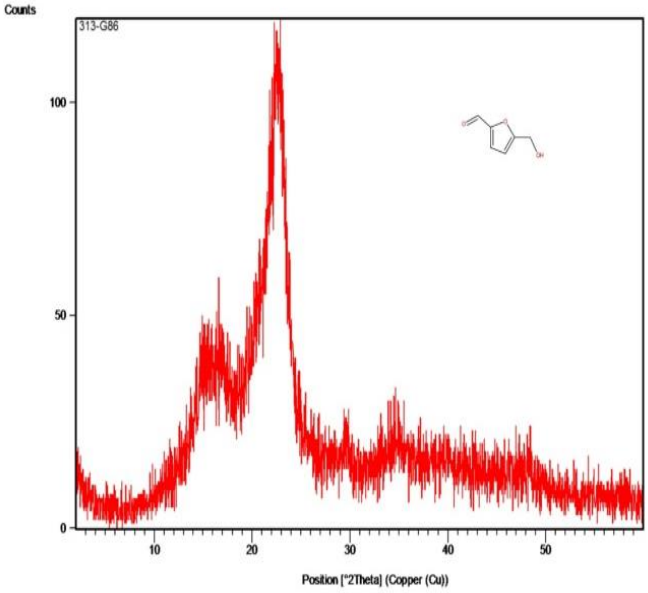

Fig. 5. XRD of cellulose for Giza 86

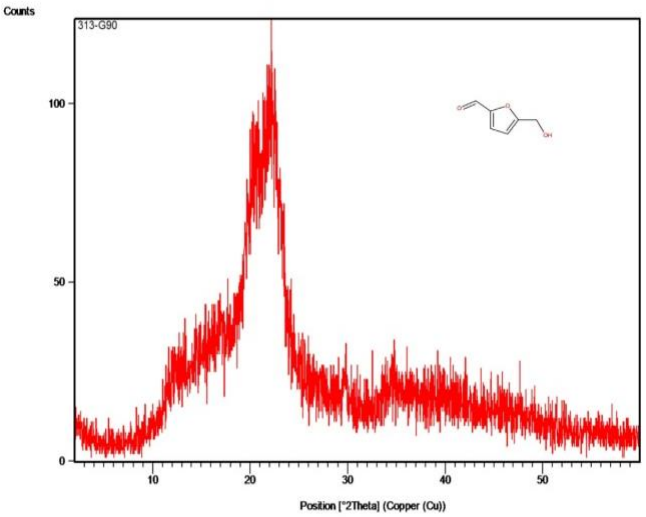

Fig. 6. XRD of cellulose for Giza 90

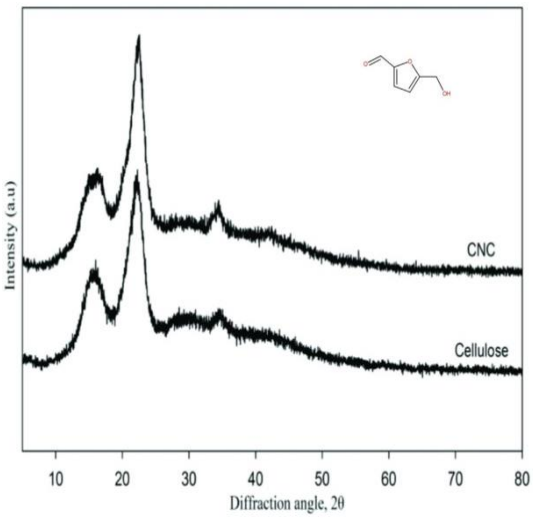

Fig. 7. XRD of cellulose sample

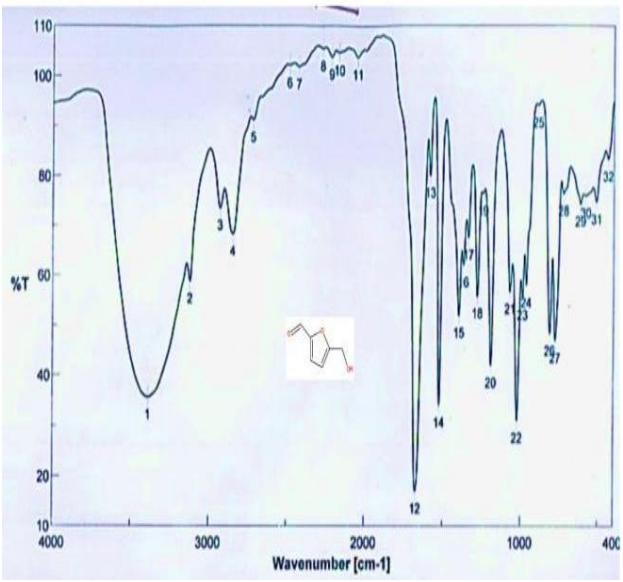

Fig. 8. FT-IR of standard 5-HMF

ii. Fourier Transform Infra-Red analysis (FT-IR):

The FT-IR analysis was carried out in the spectral range from 4000 cm^{-1} to 400 cm^{-1} without any treatment. The FTIR spectrum of the prepared 5-HMF (Fig. 8) showed characteristic peaks suggesting the presence of 5-HMF, with strong broad peak at 3399.89 cm^{-1} being the stretching vibration of the intermolecular hydrogen bonded alcohol, the peak at 1671.98 cm^{-1} refers to the stretching vibration of the aldehyde group, the peak at 1402.00 cm^{-1} refers to the bending vibration of a methylene group, and the peak at 1020.16 cm^{-1} refers to the stretching vibration of the ether linkage. Comparison of FT-IR spectrum of the prepared 5-HMF sample (Fig. 8) with that of the standard 5-HMF sample (Fig. 7) showed considerable parallelism between the prepared and the standard samples, confirming the successful formation of 5-hydroxymethylfurfural.

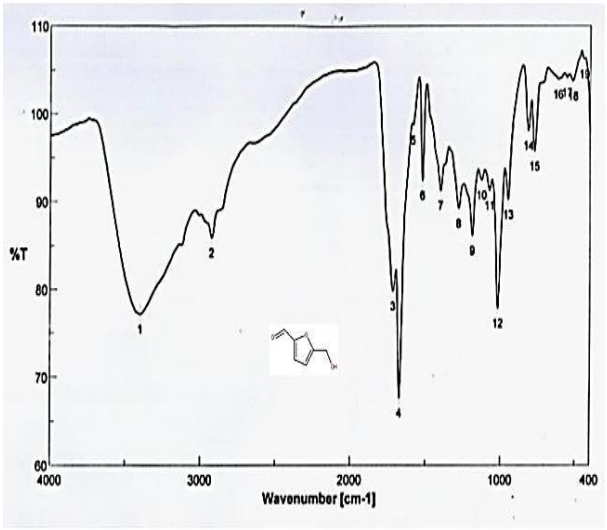

Fig. 9. FTIR spectra for prepared 5-HMF

iii. HPLC analysis

The HPLC analysis was carried out to optimize the formation of 5-hydroxymethylfurfural (5-HMF), the 5-HMF curve of the standard (Fig. 9) was compared with the prepared 5-HMF (Fig. 10), showing that 5-HMF efficiently synthesized and separated.

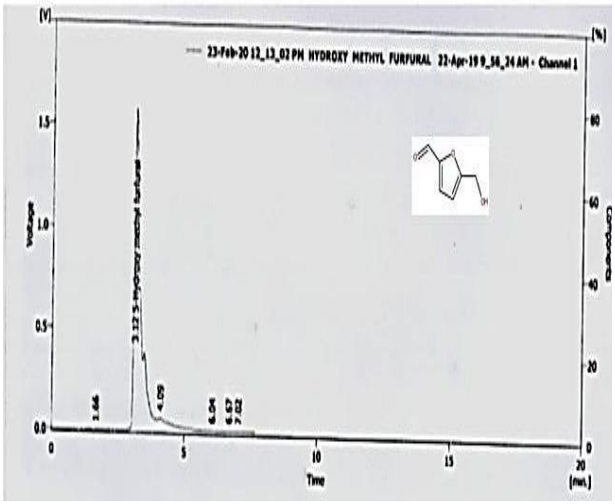

Fig. 10. HPLC for standard 5-HMF

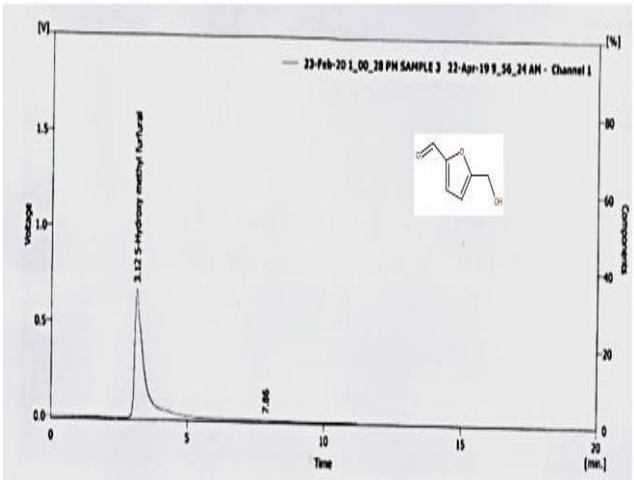

Fig. 11. HPLC for prepared 5-HMF sample

Table 3. Results of the standard

	Reten. Time [min]	Response	Amount [mg/ml]	Amount [%]	Peak Type	Compound Name
1	1.657	14.065	0.000	0.0		
2	3.123	25510.140	0.294	100.0	Ordnr.	5-Hydroxymethylfurfual
3	4.090	2615.104	0.000	0.0		
4	6.040	94.730	0.000	0.0		
5	6.673	130.008	0.000	0.0		
6	7.023	173.495	0.000	0.0		
	Total		0.294	100.0		

Table 4. Results of the 5-HMF sample

	Reten. Time [min]	Response	Amount [mg/ml]	Amount [%]	Peak Type	Compound Name
1	3.123	17534.953	21.013	100.0	Ordnr.	5-Hydroxymethylfurfual
2	7.857	138.048	0.000	0.0		
	Total		21.013	100.0		

iv. NMR analysis

The ^{1}H NMR spectrum of the prepared 5-HMF was carried out and the spectrum showed a singlet signal at δ = 4.15 ppm corresponding to the methylene protons. In addition, a broad signal at δ = 5.5 ppm due to the hydroxyl proton, along with two doublet signals at δ = 5.5 with coupling content J = 1.65 and 2.16 Hz due to the aryl protons. There was also a singlet signal at 9.55 ppm owing to aldehyde proton. ^{13}C NMR analysis also confirmed the structure of 5-HMF, which presented a characteristic signals at 56.40, 110.15, 124.92, 152.20, 162.62 and 170.44 (Fig. 14 and 15). Comparison of the charts of the prepared 5-HMF (Fig 14 and 15) with those of the standard sample 5-HMF (Fig. 12 and 13) showed that they were almost identical, confirming the formation of 5-hydroxymethylfurfural.

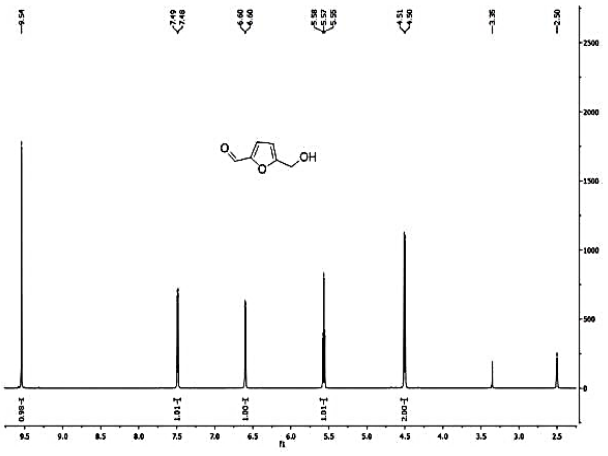

Fig. 12. [1]H NMR spectra of standard 5-HMF

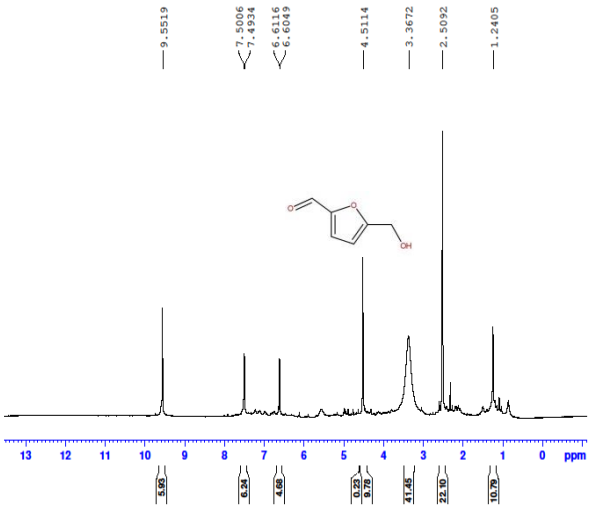

Fig. 14. [1]H NMR spectra of the prepared 5-HMF

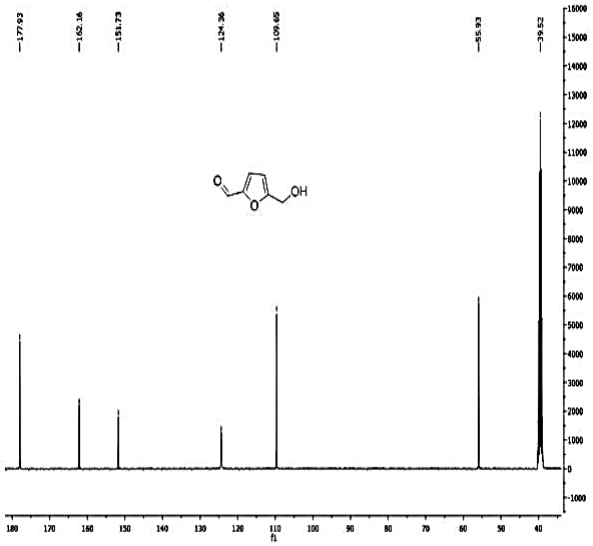

Fig. 13. [13]C NMR spectra of standard 5-HMF

4. References

[1] World Development Indicator. (2019).

[2] Said N., EL-Shatoury S. A., Diaz L. F., Zamorano M. (2013) "Quantitative appraisal of biomass resources and their energy potential in Egypt" Renewable and Sustainable Energy Reviews 24:84–91.

[3] Cotton Arbitration and Testing General Organization (CATGO).

[4] Amal S. Owis, A. F. M. Abdel Wahab, El-Etr M., (2010). "Recycling of cotton stalk with rice straw to compost as friendly technology to the environment" Agric. Chem. And Biotech. J., 1 (1), 41-52.

[5] Kumar, P., Barrett, D. M., Delwiche, M. J., and Stroeve, P. (2009). "Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production" Ind. Eng. Chem. 48, 3713-3729.

[6] Da Costa Sousa L., Chundawat S. P. S., Balan V., Dale B. E. (2009). "Cradle-to-grave" assessment of existing lignocellulose pretreatment technologies. Curr. Opin. Biotechnol. 20, 339-347.

[7] Himmel, M. E., Ding, S. Y., Johnson, D. K., Adney, W. S., Nimlos, M. R., Brady, J. W., et al. (2007). "Biomass recalcitrance: engineering

plants and enzymes for biofuel production" Science, 315, 804-807.

[8] Iqbal, H. M. N., Ahmed, I., Zia, M. A., & Irfan, M. (2011). "Purification and characterization of the kinetic parameters of cellulose produced from wheat straw by Trichodermaviride under SSF and its detergent compatibility" Advances in Bioscience and Biotechnology, 2 (3), 149-156.

[9] Malherbe, S., Cloete, T. E. (2002). "Lignocellulose biodegradation: fundamentals and applications" Reviews in Environmental Science and Biotechnology, 1, 105-114.

[10] Clavo-Flores. F. G., and Dobado, J. A. (2010). "Lignin as renewable raw material" Chem. Sus. Chem. 3 (11), 1227-1235.

[11] Jiang, G., Nowakowski, D. J., and Bridgwater, A. V. (2010). "A systematic study of the kinetics of lignin pyrolysis" Thermochimica Acta. 498 (1), 61-66.

[12] Ali, M., Abdel-Moein, N., Owis, A., Ahmed, S., and Hanafy, E. (2021). "Preparation, Characterization, Antioxidant and Antimicrobial Activities of Lignin and Eco-Friendly Lignin Nanoparticles from Egyptian Cotton Stalks" Egypt. J. Chem. 65, 703–716.

[13] Amal Saber Owis (2021). Cotton Facts and Secrets "Natural Color, Cultivation, Chemistry and Finishing", (handbook), The Egyptian National Library and Archives, Deposit No. (23328) and ISBN: 9789779094286. Pp 264.

[14] Serrano-Ruiz J. C., Luque R., Sepúlveda-Escribano A. (2011) "Transformations of biomass-derived platform molecules: from high added-value chemicals to fuels via aqueous-phase processing" Chem Soc Rev 40, 5266-5281.

[15] Solomon B. D. (2010). "Biofuels and sustainability" Ann. N. Y. Acad. Sci. 1185, 119-134.

[16] Asgher, M., Ahmad, Z., and Iqbal, H. M. N. (2013). "Alkali and enzymatic delignification of sugarcane bagasse to expose cellulose polymers for saccharification and bio-ethanol production" Ind. Crop. Prod. 44, 488-495.

[17] De Jong E., Jungmeier G. (2015). "Biorefinery concepts in comparison to petrochemical refineries" Industrial Bioref and White Biotechnol. Elsevier, Amsterdam, 3-33.

[18] Tong, X., Ma, Y., Li, Y. (2010) "Biomass into chemicals: Conversion of sugars to furan derivatives by catalytic processes" Appl. Catal. A Gen. 385, 1–13.

[19] Rosatella, A. A., Simeonov, S. P., Frade, R .F. M., Afonso, C. A. M. (2011) "5-Hydroxymethylfurfural (HMF) as a building block platform: biological properties, synthesis and synthetic applications" Green Chem. 13, 754.

[20] Huber, G. W.; Iborra, S.; Corma, A. (2006). "Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering" Chem Rev. 106, 4044-4098.

[21] Agarwal, B., Kailasam, K., Sangwan, R. S., and Elumalai, S. (2018). "Traversing the history of solid catalysts for heterogeneous synthesis of 5-hydroxymethylfurfural from carbohydrate sugars: a review" Renew. Sust. Energ. Rev. 82, 2408-2425.

[22] ASTM D 2974-87 Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils.

[23] Conrad, C. M., (1944). "Determination of Wax in Cotton Fiber "A New Alcohol Extraction Method" Ind. Eng. Chem. anal. 16, 245.

[24] Nazir M.S., Wahjoedi B. A., Yussof A. W., Abdullah M. A. (2013) "Eco-friendly extraction and characterization of cellulose from oil palm empty fruit bunches" bioresources 8 (2), 2161-2172.

[25] Chahal, D.S., Moo-Young, M., and Dhillon, G.S. (1979). "Bioconversion of wheat straw and wheat straw components in to single-cell protein" Canadian J. of Microbiology 25, 793-797.

[26] Bin L., Yi Z., and Li-feng Y., (2016). "Preparation of 5-Hydroxymethylfurfural from Cellulose via Fast Depolymerization and Consecutively Catalytic Conversion" 26, 355-360.

[27] Anonymous. (2009). Statistica 9: supporting 32-bit and 64-bit computing. StatSoft. Tulsa, Okla., USA.

[28] Wan H. W., Ishak A., Suria R.,Mohd C. I. (2018) "Gamma irradiation-assisted synthesis of cellulose nanocrystal-reinforced gelatin hydrogels" Nanomaterials 8, 749.