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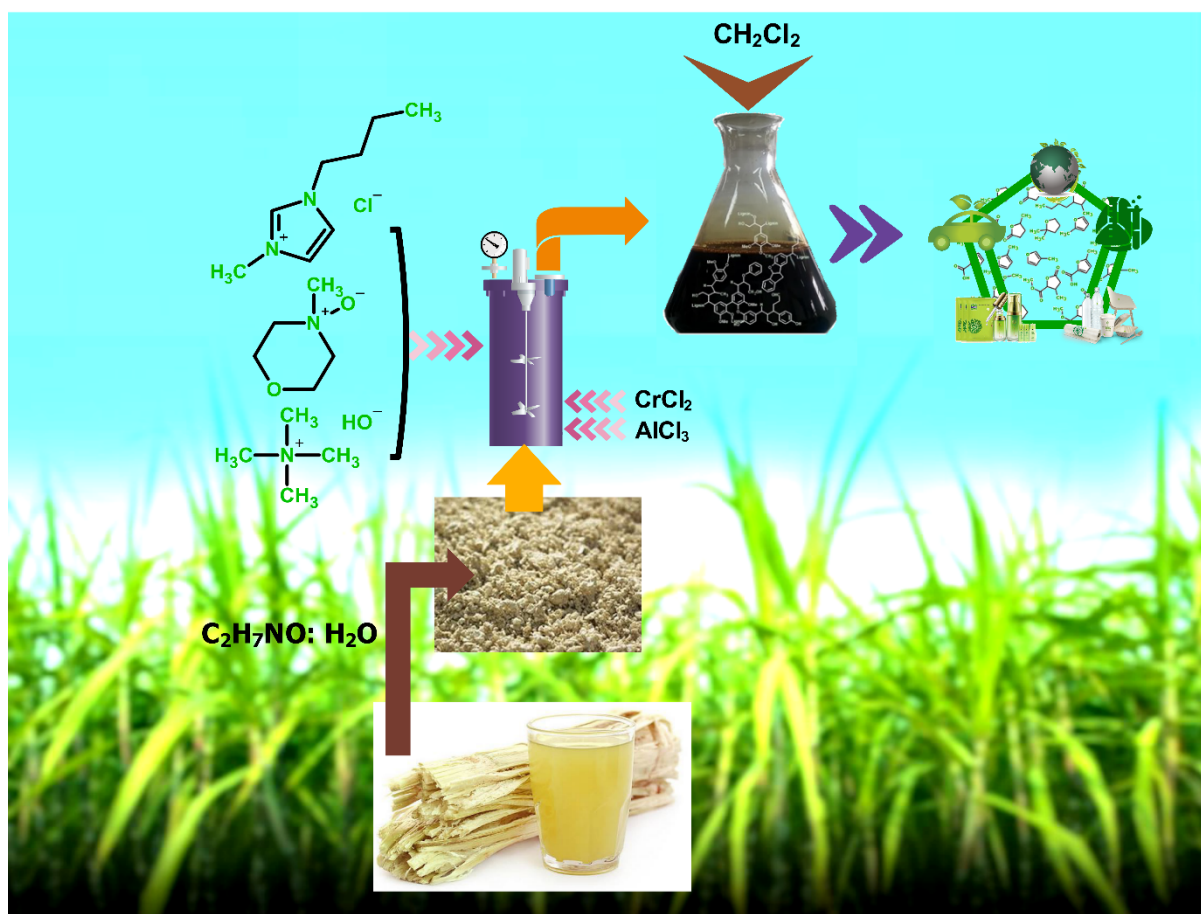
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Graphical abstract



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Abstract

The applications of lignocellulosic wastes to produce a wide variety of products, including biochemicals, biomaterials, and biofuels, can be an effective solution for utilizing these valuable waste materials. In this study, the production of furan building blocks from bagasse fibers was investigated by treating unbleached fibers with NMMO, [Bmim]Cl, and TMAH at different temperatures using AlCl₃ and CrCl₂ as the catalysts. The resulted liquors were extracted with CH₂Cl₂ to obtain furan rich fraction. Analysis of extracted fractions with GC/MS indicates the production of various furanic compounds due to catalytic solvolysis with different solvents at elevated temperatures. 2(3H)-furanone and 2-methyl-THF were the main products of catalytic treatment of bagasse fibers with NMMO. Treatment by [Bmim]Cl resulted in 2,5-dihydro furanone as the dominant product at elevated temperatures. Furan carboxylic acid methyl ester and 2, 5-furan dicarboxylic acid dimethyl ester were the main TMAH reaction products with unbleached fibers. The results indicate that the type of solvent affects the solvolysis rate and dehydration of cellulose to furanic compounds. Moreover, increasing the temperature led to an increase in the formation of the furanic compounds.

Keywords: Bagasse; Biorefinery; Furan; Building blocks; Furan carboxylic acid; methyl furan

Abbreviations

MF	Methyl furan
FA	Furanic acid
NMMO	n-methyl morpholine oxide
[Bmim]Cl	1-butyl-3-methyl imidazolium chloride
TMAH	Tetramethylammonium hydroxide
AlCl₃	Aluminum Chloride (III)
CrCl₂	chromium chloride (II)
HMF	Hydroxymethyl furfural
DMF	Dimethyl furan
FDCA	Furan-2,5-dicarboxylic acid
FF	Furfural
FCA	Furan carboxylic acids
PTA	Terephthalic acid
DMTHF	3-methyl-tetrahydrofuran
MFCA	Methylfuran-2-carboxylic acid
GC/MS	Gas chromatography and Mass spectrometry
LAC	1-hydroxy-3,6-dioxabicyclo [3.2.1] octan-2-one
LG	Levoglucosan

1. Introduction

There is no doubt that fossil fuel sources are being depleted due to increased industrialization. As a result, global warming, which is an extraordinary phenomenon, leads to increased concern about greenhouse gas emissions. Its consequences have directed technology and science towards sustainable production of chemicals and energy from indigenous bioresources. In 2018, worldwide consumption of energy reached more than 584 exajoules (EJ), of which 84% of that consumption was obtained from fossil fuels [1] (Fig. 1).

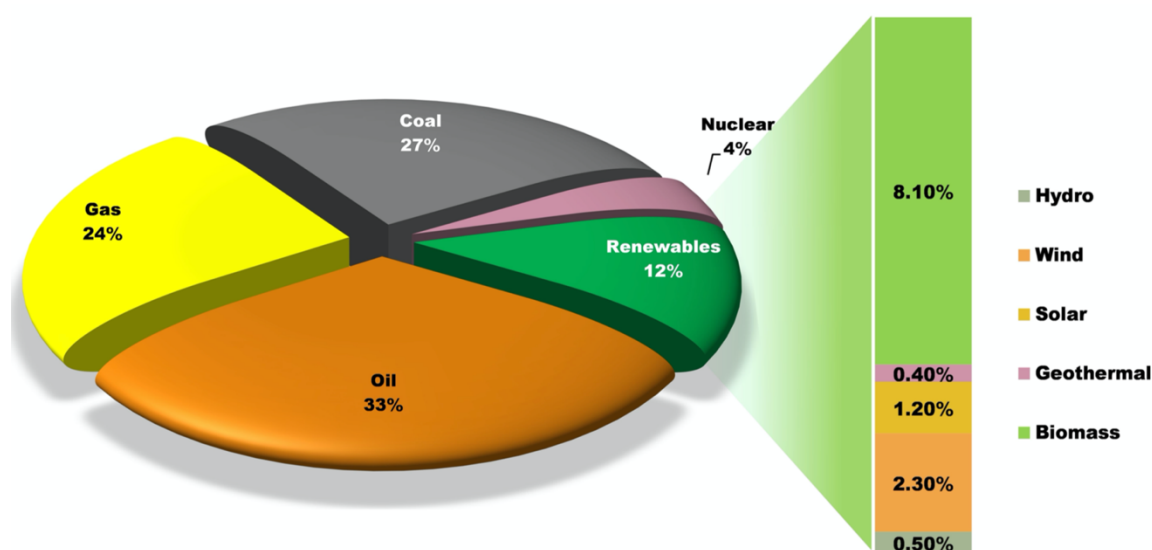


Fig. 1. World energy profile consumption in 2018

Besides producing most of the transport fuels, crude oil is used to produce 95% of all carbon-containing chemicals utilized in our society [2]. About 10% of the total amount of crude oil is used to produce industrial chemicals[3]. The necessity of a renewable source of carbon to purposely re-build the chemical industry for replacing fossil-based chemicals is one of the significant concerns of today's society. For this reason, research tends to shift towards the development of new technologies for the conversion of renewable and natural resources of carbon into sustainable energy and chemicals. Concerning the availability, low cost, and environmentally friendly production; in the meantime, lignocellulosic biomass is one of the suitable oxygenated carbon sources that could be used to produce liquid fuels and valuable biochemical intermediates such as alcohols, aldehydes, ketones, and carboxylic acids[4].

Typical lignocellulosic biomass contains around 40-50 wt.% cellulose, 20-40 wt.% hemicellulose, and 10-40 wt. % lignin [5], and the content of each component varies with the type of biomass [6]. Thus, lignocellulosic biomass contains a wide range of ready to use

polymeric compounds, including polysaccharides and lignin, with a variety of functional groups and molecular weight such as phenolics, aromatics, furans, ketones, alcohol, acids, sugars, ethers, esters and aldehydes [4]. The main products of depolymerisation of cellulose are acids, alcohols, and anhydrosugars. However, the cleavage of β -1, 4-glycosidic bonds contributes largely to the formation of furans and laevoglucose[7]. Furans are volatile cyclic compounds which resulted from cellulose degradation and are used in the production of resins, lacquers and agrochemicals[8]. Furans have the potential to be converted into a wide variety of high value-added chemicals to reduce the dependency on petroleum-based chemicals[9, 10]. The furan derivatives including the hydroxymethylfurfural (HMF) and furfural (FF), Methyl furan (MF), Dimethyl furan (DMF), Furan-2,5-dicarboxylic acid (FDCA), Furan carboxylic acids (FCA), 3-methyl-tetrahydrofuran (DMTHF), and Methylfuran-2-carboxylic acid (MFCA).

Furans have wide applications in pharmaceuticals because of their biological activities. The furan derivatives showed interesting biological activity in many bio-based products such as antioxidant[11], anti-inflammatory[12], antibacterial[13], antiviral[14], insecticidal[15], and antifungal[16] properties. They are considered as the green substituents to replace fossil-based fuels and materials [17]. Bozell and Petersen's report in 2010 named Furfural, 5-hydroxymethyl-furfural and furan dicarboxylic acid as target structures in the top 10 compounds that could be generated from carbohydrates [18]. Reviews of previous findings on different furan production are listed in Table 1. Furans dominantly were produced from lignocellulosic wastes, cellulose and hemicelluloses, monosaccharides, wood, and non-wood raw materials through the catalytic hydrolysis-dehydration process by using acidic salts, organic/inorganic acids, and solid acids catalysts[19, 20]. The production of furfural (FF), hydroxymethyl furfural (HMF), and methyl furans (MF) were the main purposes of the conducted research[21]. The novelty of this work is the use of organic solvents for the production of furanic compounds using in bleached fibers. The yield of the generated furans was reported as the function of temperature in most of the studies.

Table 1. A summary of previous research on furan compounds production from different feedstocks

Feedstock	Catalyst	Method	Product	Ref.
Hemicellulose	Ru–Re/biochar	Hydrolysis ¹	1,4-BD and THF	[22]
Bio-derived furans	HZSM-5	Diels-Alder cycloaddition	MF	[23]
Fructose	Nb ₂ O ₅	fructose dehydration	5-HMF	[24]
Xylose	supported Ni	Hydrodeoxygenation ³	2-MF and FF	[25]
Cellulose	NaY	Pyrolysis	Furan, 2-MF, 3-MF,	[26]
Olive mill solid waste	-	Anaerobic digestion	HMF and FF	[27]
Fructose, inulin and MCC	Pd, Pt, Ir, Ni, Ru	Hydrolysis	2,5-DHMF	[28]
Monosaccharides and cellulose	H ₃ PO ₄ and NaOH	Hydrolysis-dehydration ⁴	HMF, FF	[29]
Fructose	Ionic liquid- Ru/C	Dehydration	DMF and DMTF	[30]
Seaweed biomass	Solid acid KHSO ₄	Autoclave treatment	HMF	[31]
Glucose	Ga and Sn zeolite Y catalyst	Dehydration	HMF	[32]
	ZnCl ₂ /HCl and AlCl ₃ /HCl	Dehydration	HMF	[33]
	-	Hot Compressed Water	HMF	[34]
cellulose, glucose, and fructose	functionalized zeolites	Dehydration	HMF	[35]
Cellulose		Dehydration	HMF	[36]
High fructose corn syrup	Amberlyst-15	Dehydration		[37]
Hexose sugars	H ₂ SO ₄ , Formic acid	Dehydration		[38]
Cellulose	ZnCl ₂ ·nH ₂ O	Biphasic batch system		[39]
Lignocellulose	ChCl/MIBK	Biphasic batch system		[40]
Cellulose, corncob, wheat straw	TiO ₂ , TiOSO ₄ , TiN and GaN	Catalytic fast pyrolysis		[41]
Cellulose	Alkali metal bromide	Hydrolysis in formic acid	5-HMF and FMF	[42]
Cellulose	Na/Fe solid acid	Catalytic pyrolysis		[43]
Xylose	Zn doped CuO nanoparticles	Dehydration		[44]
Sugarcane bagasse	phosphoric acid	Delignification	HMF and FUR	[45]
Poplar-wood fiber	Boric acid	Pyrolysis	FF	[46]
Sunflower seed hull	Pd/biochar	Pyrolysis/hydrogenation	Furfuryl alcohol	[47]
Lignocellulose	Cu–Al/C catalysts, 4Cu–2Al/C	catalytic pyrolysis	2-MF, FF and furan	[48]
5-HMF	MnO _x and Fe ₂ O ₃	Oxidation	FFCA	[49]
HMF	MeOH	Catalytic oxidation	FDCA	[50]
Glucose	AlCl ₃	Deep eutectic solvent	HMF, AMF, CMF, EMF	[51]
HMF		Oxidation	FDCA	[52]
Biomass-derived 5-HMF	Cu–Al ₂ O ₃	Calcination and reduction		[53]

Among the furans, the production of hydroxymethylfurfural (HMF) and furfural (FF) from monosaccharides and cellulose has been well studied in the literature [33, 54–56]. Stepwise dehydration reaction of glucose and xylose in lignocellulosics led to HMF FF building blocks production in a Lewis-Bronsted acid-catalyzed system. HMF and FF could be further converted to furan precursors, which can be used as a green chemical intermediate for the forming of a wide variety of oil-based commodity chemicals. For example, many high-value-added building blocks and intermediates could be achieved from chemical processing of HMF through oxidation, reduction, amination, rehydration, and alkylation reactions, as it is schematically represented in Fig. 2 [57, 58]. HMF can be produced by the conversion of cellulose in water and ionic solvents [59]. Although cellulose swelling in ionic liquids and water-miscible organic solvents such as NMMO and TMAH was well discussed in many studies [60, 61], production of furans from lignocellulosics in these solvent systems was not reported yet. Interruption of

Louis, MO). 1-Butyl-3-methylimidazolium chloride ([Bmim]Cl) was laboratory prepared with the reaction of equimolar amounts of methyl imidazole and chlorobutane (Aldrich, St. Louis, MO) under reflux for 72 h at 60 °C and a reaction time of 15 seconds. [Bmim]Cl was purified through the discarding of unreacted moieties upon vigorous shaking with ethyl acetate. The obtained chemicals were of analytical grade and were used without any further purification.

2.1 Preparation of unbleached fibers

Delignification of depithed bagasse was performed by mono-ethanol amine (MEA): H₂O (v: v, 75:25) in a laboratory-scale reactor at 170 °C for 120 minutes to obtain the holo-cellulose rich fibers.

2.2 Fibers reaction with solvents

The catalytic experiments were performed in a 25 mL Parr stirred reactor (stainless steel). Air-dried fibers (500 mg) were mixed with laboratory-grade n-methyl morpholine oxide (NMMO), tetramethylammonium hydroxide (TMAH) and 3-methyl-imidazolium chloride ([Bmim]Cl) (solvent: fiber, 20:1, g: g). Aluminum chloride III (1 mmol) chromium chloride II (1 mmol) were added as the catalysts to the reaction mixture, and the reactor was heated at 170, 200, 220, and 240 °C using preheated oil. The reaction mixture was mixed thoroughly by an agitator. The air within the reactor was evacuated using a vacuum pump just before the heating process. At the end of run time (60 min), the reaction was quenched by cooling the reactor in an ethylene glycol bath at 0 °C. Analytes were diluted with methanol (10 mL), and the unreacted fibers and solid catalysts were separated through a centrifuge at 8000 rpm. The obtained liquors were further filtered through a 0.22 µm syringe filter to discard the suspended solids. Microwave heating of fibers with [Bmim]Cl ionic liquid was done in a flask by a laboratory microwave device at 400 watts for 3 minutes. Furans were solvent extracted from the obtained liquors with dichloromethane before analysis with gas chromatography and mass spectrometry (GC/MS).

2.3 Gas chromatography and Mass spectrometry (GC/MS)

The analysis of obtained extracted liquors from treatments with different solvents at various temperatures was performed using an Agilent technologies 6890 N gas chromatograph equipped with HP-5MS capillary column (30 m × 0.25 mm × 0.25 mm) coupled to a 5973 N mass selective detector (Agilent Technologies, Santa Clara, CA, USA). The oven temperature was adjusted from 40 °C for 1 min, increased to 280 °C at 8 °C/min, kept at 280 °C for 10 min. Helium gas (He) was used as carrier gas at a 1 ml/min flow rate. All detected chemicals were recognized by comparison with the NIST and Wiley libraries.

3. Results and Discussion

3.1 Solvolysis of bagasse fibers at high temperatures

3.1.1 Treatment with NMMO

The results obtained from GC/MS of NMMO treatment of fibers at various temperatures are presented in Table 2. The corresponding GC-FID chromatogram of separated components is illustrated in supplementary materials (Fig. S-1). The Main identified compounds in the liquors from catalytic NMMO treatment at different temperatures are presented in Table 2. According to Table 2, 2(3H)-furanone and 2-Methyltetrahydrofuran (2-methyl-THF) are the main furanic components that were formed during the NMMO solvolysis. Furanone comprised 2.8 and 2.8 % of the identified compounds at 170 and 200 °C, respectively. The ratio of the furanone was decreased by raising the temperature to 240 °C. The amount of 2-methyl-THF was increased from 0.8 to 6.0% as the result of increasing the temperature from 170 to 200 °C and declined to 0.28% by increasing the temperature to 240 °C. The wide swelling and partial dissolution of the fibers in the NMMO at 170 °C resulted in the formation of heterocyclic compounds such as cyclopentanone with a relative abundance of 2.5. However, increasing the temperature led to a decrease in cyclopentanone abundancy in NMMO.

It has been reported that NMMO could increase the swelling of cellulosic chains, and rising the reaction temperature led to the dissolution of the cellulose[62, 63]. Although the reaction of the cellulose with NMMO has not been explained yet, the strong interactions between anionic N-O in NMMO with hydroxyl groups in cellulose lead to degradation of intramolecular hydrogen bonds of cellulose and disincorporation of cellulose chains within NMMO. A low degree of polymerization and branched hemicelluloses' backbone leads to fast dissolution in the NMMO even at 170 °C. Formation of methylated furans after dehydration of hydrolyzed sugars may occur due to the reaction with methyl groups of NMMO [64].

Table 2. Main compounds identified by GC/MS in liquor obtained from the solvolysis of bagasse fibers in NMMO, [Bmim]Cl and TMAH (T₁, T₂, T₃, T₄ and MW are the reaction temperatures at 170, 200, 220, 240 °C and microwave conditions, respectively)

Solvent	Compound	Relative abundance				
		T ₁	T ₂	T ₃	T ₄	MW
NMMO	2(3H)-furanone	2.8	2.8	1.9	1.2	-
	3-Buten-2-one	1.3	1.6	-	-	-
	Cyclopentanone	2.5	1.9	-	-	-
	Acetaldehyde-hydroxy	0.3	-	-	-	-
	2-Methyltetrahydrofuran (2-methyl-THF)	0.8	6.0	1.2	0.3	-
	Adipic acid	0.5	0.1	-	-	-
	1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	-	15.0	-	-	-
[Bmim]Cl	1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	95.7	89.1	59.5	54.1	49.8
	Acetaldehyde-hydroxy	-	-	0.4	-	-
	Dimethyldihydro furanone (DMDH-furanone)	-	-	13.4	12.2	7.0
	Levoglucosan	-	-	-	-	1.0
TMAH	2(3H)-furanone	1.9	2.2	1.4	1.0	-
	Succinic acid	1.1	-	-	-	-
	1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	7.5	5.8	0.4	-	-
	2,5-dihydro-2,5-dimethoxy Furan (DMDF)	3.3	2.2	-	-	-
	Furan carboxylic acid (FCA), methyl ester	1.0	-	-	0.5	-
	Acetaldehyde-hydroxy	0.9	-	-	-	-
	2,5-Furandicarboxylic acid (FDCA), dimethyl ester	2.5	2.7	1.1	0.5	-
	Maleic acid	0.5	0.6	-	-	-
	3-Buten-2-one	-	-	-	2.3	-
	Cyclopentanone	-	-	-	5.9	-
Adipic acid	0.5	-	-	0.4	-	

3.1.2 Treatment with [Bmim]Cl

The results obtained from GC/MS of [Bmim]Cl treatment of fibers at various temperatures are presented in Table 2. The corresponding GC-FID chromatogram of separated components is illustrated in supplementary materials (Fig. S-2). The results of GC/MS analysis of the obtained compounds by treatment with ionic solvent indicate the production of methyl-bearing furans at different temperatures. Dimethyldihydro furanone, the dominant furan product, was formed at 220 °C with an amount of 13.4%. By increasing the temperature to 240 °C and fast solvolysis at microwave conditions, the amount of furanone was decreased to 12.2 and 7.0%, respectively.

Formation of 1-hydroxy-3,6-dioxabicyclo [3.2.1] octan-2-one (LAC) and levoglucosan (LG) during solvolysis with ionic liquid indicate the hydrolysis and dehydration of polysaccharides. The use of ionic liquids in new cellulose processing and materials technologies is a topic that has attracted interest in recent years [65]. The strong hydrogen bonds of polysaccharides on the one hand and the unique properties of ionic liquids, on the other hand, raise the interest in the use of ionic liquids for cellulose dissolution [66, 67]. It has been reported that the treatment with ionic liquids facilitates the depolymerization of cellulose due to the comprehensive unfolded structure and can be carried out under moderate conditions. Therefore, dehydration of sugars at high temperatures quickly happened to result in the formation of different furans. Moreover, Imidazolium salts, methylated at C-2, have been proposed frequently as cellulose modification mediums solvents[68, 69]. The methyl group in [Bmim]Cl can be deprotonated to facilitate side reactions such as furan methylation[70]. There are few possibilities for rehydration and decomposition of the produced furans to byproducts [71]. During the fiber treatment at elevated temperatures, oxidation conditions may promote the oxidation reaction.

3.1.3 Treatment with TMAH

The identified compounds by GC/MS in catalytic treatment of bagasse fibers with TMAH are presented in Table 2. The corresponding GC-FID chromatogram of separated components is illustrated in supplementary materials (Fig. S-3). As demonstrated in Table 2, the catalytic solvolysis products of fibers with TMAH are mainly including 2 (3H)-furanone, furan carboxylic acid methyl ester, 2,5-furan dicarboxylic acid dimethyl ester and 2,5-dihydro-2,5-dimethoxy furan. The results indicate that catalytic solvolysis of fibers with TMAH at high temperatures is a practical approach for producing methyl-bearing furanics by enhancing the conversion of sugars. Methyl esterified furans, including FCA methyl ester and FDCA dimethyl ester, were formed with a relative abundance of 1.0 and 2.5% at 170 °C, respectively. The highest amount of FDCA was determined at 200 °C. The further raising of temperature led to a decrease in FDCA relative abundance.

Moreover, 2,5-dihydro-2,5-dimethoxy furan was produced at 200 °C with an amount of 2.2% due to fibers' treatment with TMAH. TMAH is widely used as a thermally assisted methylation reagent in gas chromatography[72, 73]. Thermally assisted methylation (thermochemolysis) has previously been used in other studies to elucidate polymers structures, such as lignin [74] and other biomacromolecules [75]. Moreover, the TMAH was used to facilitate the chemical degradation of different polymers to produce methylated compounds[72].

3.2 The effect of solvents on the formation of furan compounds

The formation of furans due to glucose dehydration was well discussed in the literature [76, 77]. According to the obtained products, it seems that the solvent's ability to swell fibers significantly influences cellulose reaction initiation. The abundance of furanic compounds is increased at the rate of TMAH > [Bmim]Cl > NMMO. The solvents used in this study are known to have swelling and dissolving cellulose structure [62, 67, 78].

Treatment of raw fibers with TMAH led to a couple of different methyl and carboxyl bearing furans indicating that the solvolysis ability is not the sole determinative parameter in cellulose conversion. It is known that TMAH is used as a methylating/hydrolyzing agent with a phase transfer catalyst activity [79]. The proposed phase transfer function of TMAH on produced furans is represented in Fig. 3. The TMAH mediated dehydration of polysaccharides in the presence of AlCl_3 and CrCl_2 as catalysts usually occur in the aquatic phase. Since the formation of different furans from monosaccharides proceeds through the FF and HMF intermediates, the production of aliphatic acid such as adipic and maleic acids could be due to the undesired rehydration of FF and HMF [80, 81]. Moreover, the formation of methyl esterified FCA and FDCA indicates the synchronous oxidation and methylation of intermediates due to reaction with TMAH [82–84] (Fig. 3). Meanwhile, the high relative abundance of methylated furans due to in situ methylation of furanic compounds in the organic phase of TMAH indicates that the products were preserved from oxidation at the extraction phase [74].

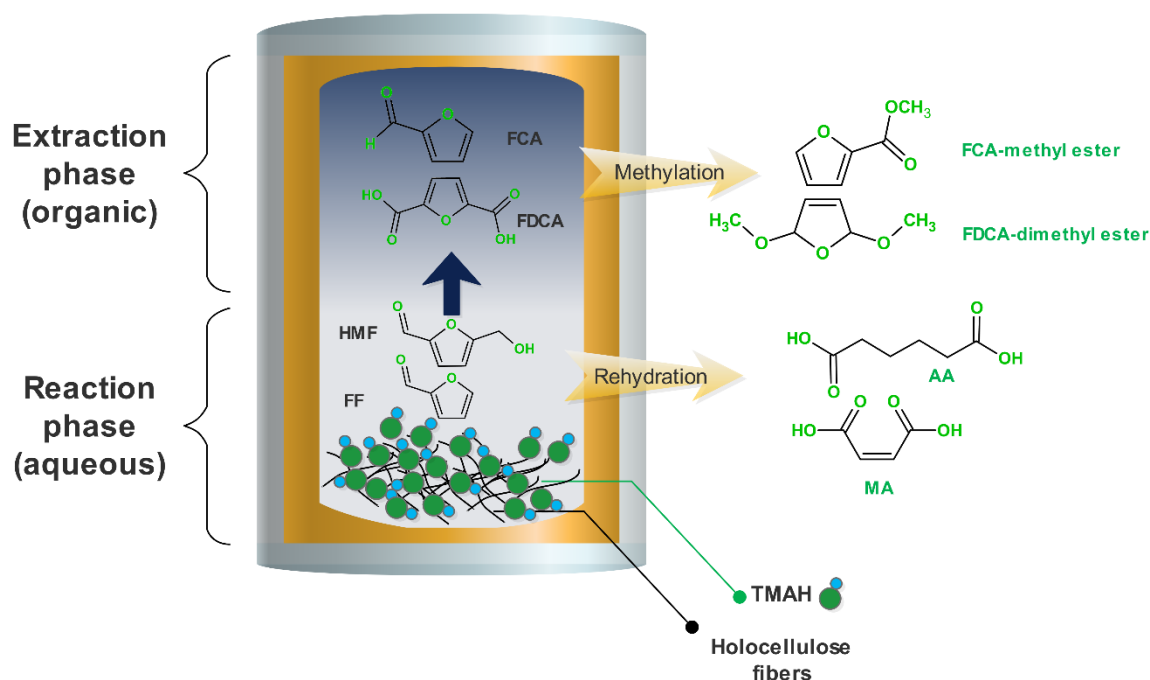


Fig 3. Schematic representation for the biphasic in situ reaction-extraction of 5-hydroxymethylfurfural and furfural during treatment of fibers with TMAH

3.3 The effect of solvolysis temperature on the formation of furan compounds

The influence of temperature on the relative abundance of furan compounds and the total peak area of identified products by GC/MS is presented in Fig 4. The amount of most generated furans was increased and then was decreased at solvolysis temperatures over 200 °C. Obviously, methyl-THF, furanone, and 3,5-DMF exhibit the highest relative abundance at 200 °C in solvolysis with NMMO and TMAH, respectively (Fig. 4a and 4c). DMDH-Furanone shows a maximum amount at 220 °C with fibers' treatment with [Bmim]Cl (Fig. 4b). The identified compounds' total peak area was also increased from 170 to 220 °C in solvolysis with NMMO and TMAH, while the peak area of identified compounds was increased from 170 to 240 °C with the highest amount at microwave conditions (Fig. 4d, 4e, and 4f). Considering both the peak area of total compounds as a whole and for generated furan compounds, it leads to a finding that the maximum temperature of 200 °C is suitable for the production of furans with catalysts. At temperatures 170-200 °C, cellulose may not be wholly depolymerized under solvolysis conditions; thus, the amount of oligosaccharides/monosaccharides is relatively low to proceed with the dehydration reactions. Accordingly, at temperatures above 200 °C, the rapid transformation of monosaccharides hinders the process of furan generation, or condensation of furans may occur.

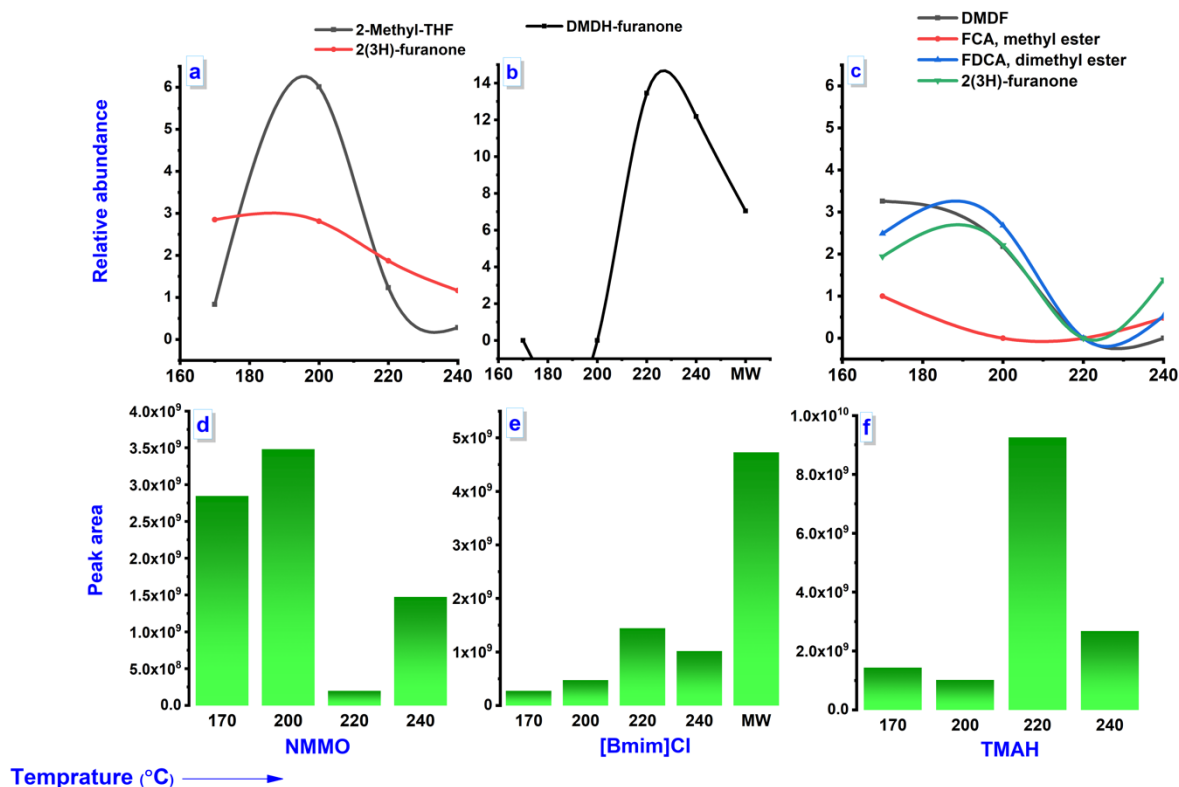


Fig. 4. The effect of temperature on the relative abundance of furans and total peak area of identified compounds in different solvents

3.4 The effects of catalysts on furan formation

According to the obtained results, the proposed stepwise reaction of cellulose and xylan's catalytic solvolysis is shown in Fig. 5. As shown in Fig. 5, the catalytic transformation of holo-cellulose is proceeding in multistep. Briefly, the depolymerization of cellulose and xylan is happening due to the swelling and partial dissolution in swelling solvents, leading to the concurrent generation of monomeric sugars and oligosaccharides in the presence of AlCl_3 and CrCl_2 as catalysts. Oligosaccharides will undergo ring-opening reactions and then rearrangement and cyclization reactions or alternatively by converting LG and LAC through isomerization and dehydration reactions to generate different furans.

It seems AlCl_3 supports the cracking of LG, and led to the formation of 1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one (LAC) and furan compounds including, 3(2H)-furanone, 2-methyl-THF, dimethyldihydro-furanone, and dimethylfuran carboxylic acid methyl ester. In this context, AlCl_3 rather than CrCl_2 can accomplish the rapid depolymerization of cellulose. In contrast, CrCl_2 promotes the formation of furans from

intermediates. The catalytic character of metal chlorides is mostly associated with the Lewis and Brønsted acidity, both of which can support the hydrolysis reaction of cellulose to glucose, isomerization of glucose and dehydration of fructose at different stages. The Brønsted acids are ideal for accelerating the hydrolysis of cellulose into monosaccharides and the dehydration of fructose.

On the other hand, Lewis acid can bind to the hydroxyl oxygen atoms in glucose and support glucose's isomerization into fructose [85, 86]. Noticeably, Al^{3+} appeared as a Brønsted acid in the used cellulose swelling solvents method and enhanced cellulose's depolymerization [87]. In the subsequent steps after cellulose disincorporation, Cr^{2+} presented more effectively as the stronger Lewis acid in converting intermediates than Al^{3+} . Therefore, co-catalyst $\text{CrCl}_2\text{-AlCl}_3$ can be regarded as a bi-functional catalyst.

Therefore, the critical step in furan formation is the isomerization of glucose to fructose, subsequently the dehydration of fructose that is catalyzed by chromium ions through stabilizing of anionic sugar. The isomerization process occurs in the presence of the Cr^{+2} complex by stepwise hydrogen relocation from C_2 to C_1 carbon of glucose. The self-organization of the catalytic chromium species at this step is controlled by the more efficient stabilization of the negative charge of the intermediate by the interface with more than one Cr^{+2} Lewis acid [88, 89]. It has been reported that CrCl_2 -catalyzed glucose dehydration in $[\text{Bmim}]\text{Cl}$ leads to a ring-opening reaction that is an essential step in the self-organization of such a Cr–chloride–glucose complex with a second $[\text{CrCl}_4]$ [88] ion into a binuclear Cr complex that stabilizes the intermediates and transition state for glucose isomerization. Cyclopentenone with 5-carbon rings might have been formed by ring-opening, cyclization, dehydration, C-C bond breaking, and rearrangement of chain intermediates containing multifunctional groups.

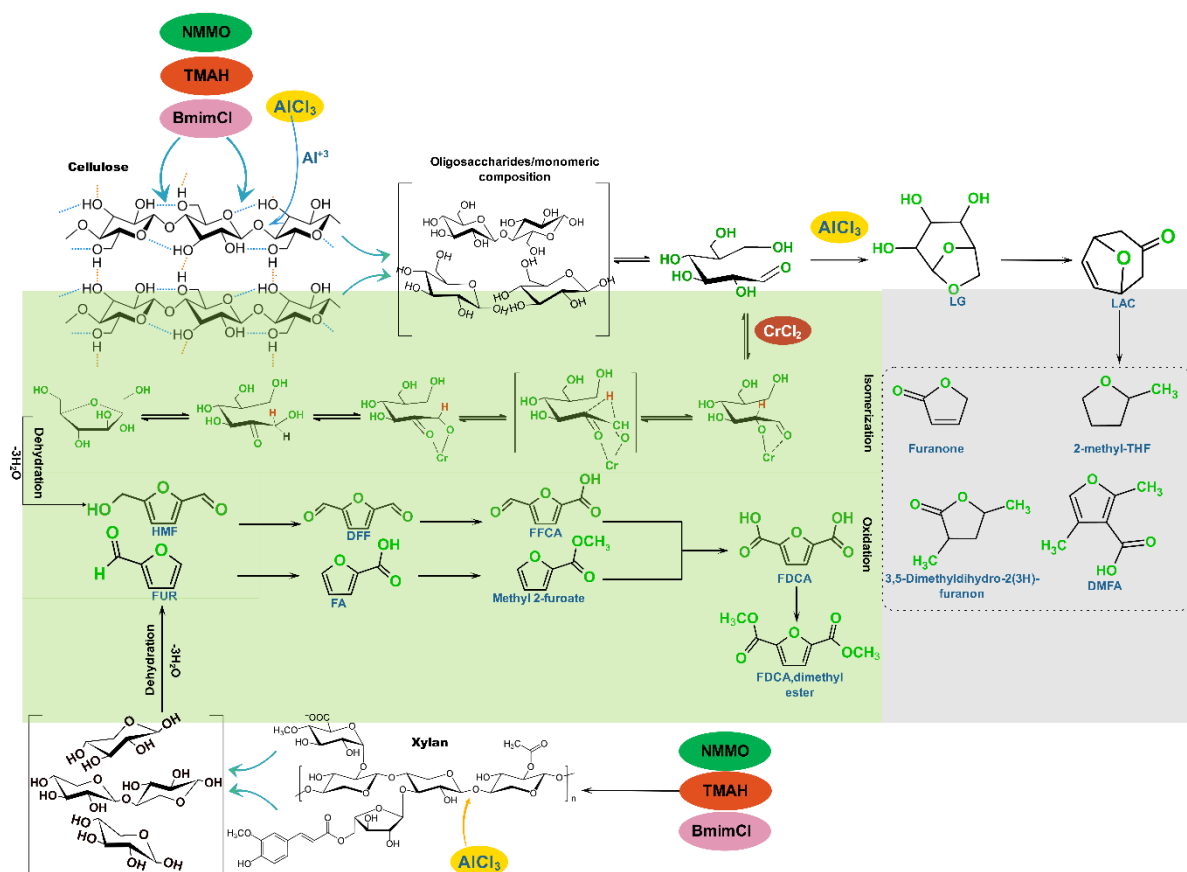


Fig. 5. Proposed reaction pathway of formation of furans (HMF, DFF, FFCA, FDCA, MF and FA), from cellulose and xylan

4. Conclusions

Lignocellulosic biomass is a renewable and sustainable energy resource for carbon that is readily available in the environment. The utilization of lignocellulosic biomass has proven as an efficient solution for the production of biofuels and value-added chemicals. In this study, the potential of unbleached fibers as substrates for different furan production has been investigated in cellulose swelling media, including NMMO, TMAH and ionic liquid [Bmim]Cl in the presence of catalysts. The catalytic mechanism of cellulose depolymerization and transformation of the intermediates to furans in the presence of swelling media and $\text{CrCl}_2\text{-AlCl}_3$ have been elucidated by GC/MS analysis of the products. The process of cellulose transformation has been realized to be done in three stages, including depolymerization, isomerization, and dehydration. Both CrCl_2 and AlCl_3 offer advantages in different stages. AlCl_3 primarily develops the first reaction rate, whereas CrCl_2 mainly improves the rate of the

second and third reactions, leading to the improvement of the total reaction rate. In each reaction medium, due to the nature and the ability of the solvent, the reaction temperature has various influences on the degree and amount of cellulose depolymerization and conversion rate to furan. The ratio of methyl-bearing furans was considerably high in treating fibers with NMMO, [Bmim]Cl and TMAH. The relative abundance of produced furans generally was increased by increasing the reaction temperature up to 200 °C for NMMO and TMAH, while the amount of generated furans was at its maximum rate at 220 °C. It has been found that using TMAH as the solvolysis solvent leads to the formation of FCA and FDCA methyl ester furans.

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Supplementary data

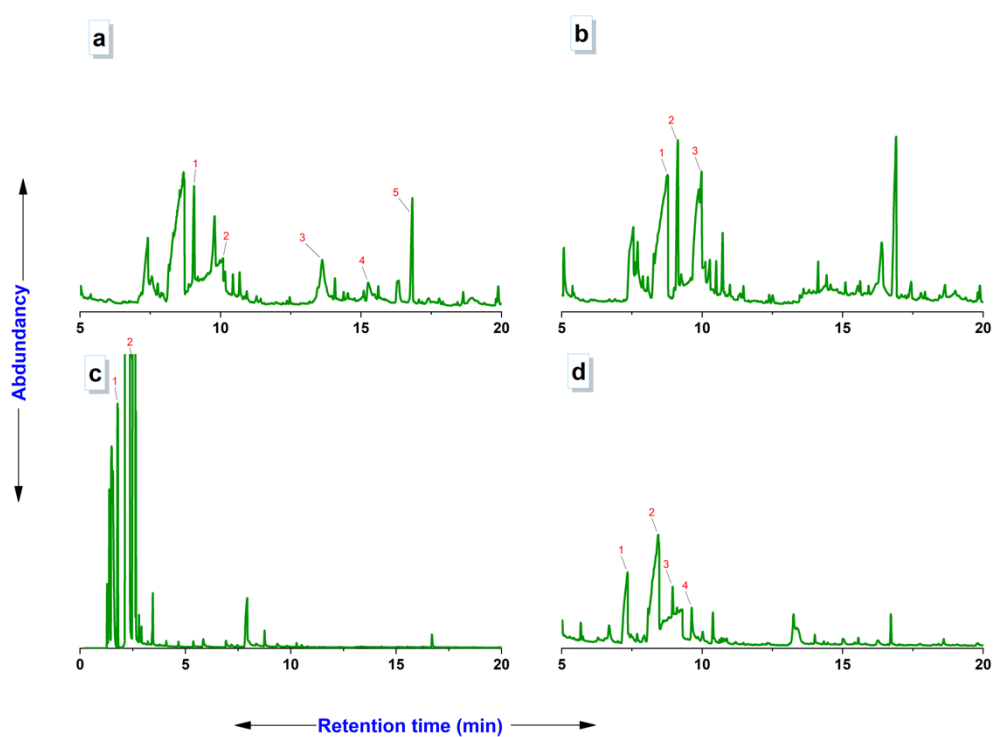


Fig.S-1. GC-FID of extracted liquor of fiber treatments with NMMO. a,b,c and d refer to treatment temperatures at 170,200,220 and 240 °C, respectively.

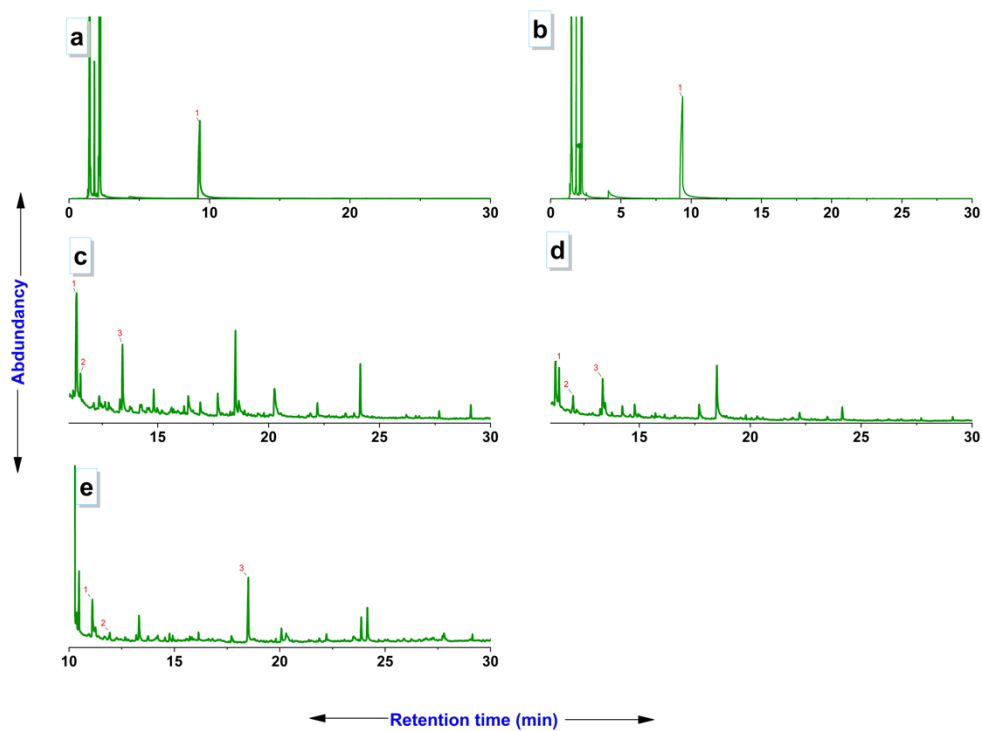


Fig.S-2. GC-FID of extracted liquor of fiber treatments with [Bmim]Cl. a,b,c,d and e refer to treatment temperatures at 170,200,220,240 °C and microwave conditions, respectively.

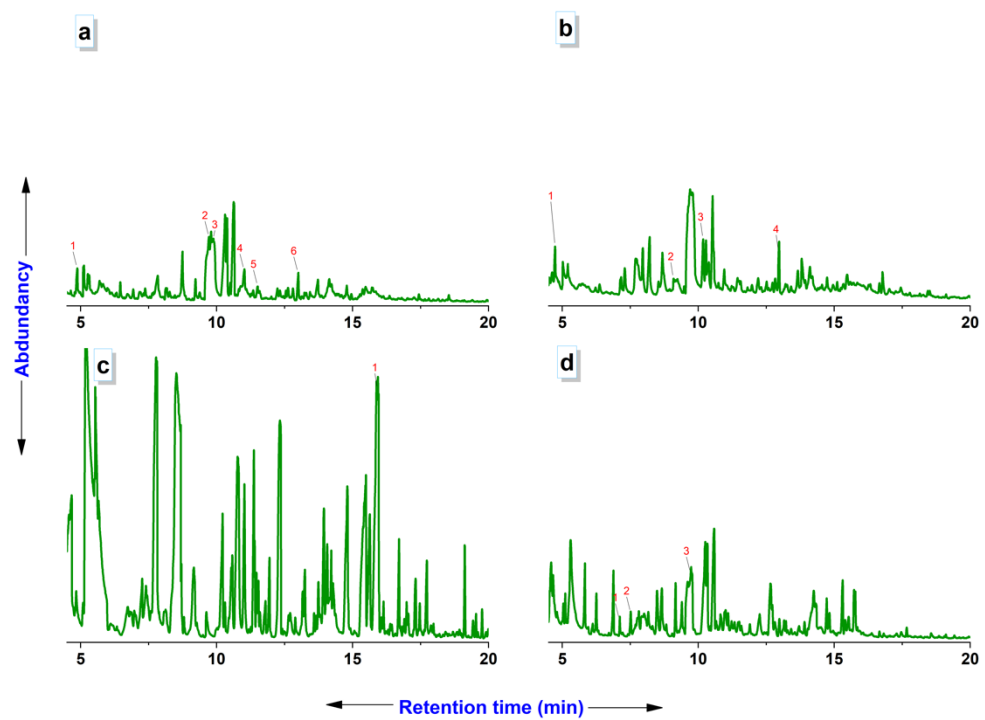


Fig.S-3. GC-FID of extracted liquor of fiber treatments with TMAH. a,b,c and d refer to treatment temperatures at 170,200,220 and 240 °C, respectively.