Review Article

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Separation procedures in the identification of the hydrogenation products of biomass-derived hydroxymethylfurfural

Abstract: Lignocellulosic biomass is considered an attractive and most abundant renewable carbon feedstock. Hydroxymethylfurfural (HMF) is one of the platform molecules obtained from biomass. HMF transformation in the reductive atmosphere allows to obtain numerous value-added molecules with applications in several recently emerged sectors, e.g. biofuels and biopolymers. This process is still intensively investigated, and more efficient, stable and sustainable solutions are envisaged. Therefore, the choice of efficient analytical methods is of great importance. This review covers the methodologies used for the analysis of HMF hydrodeoxygenation, including chromatographic and spectrometric methods. Techniques such as gas chromatography, high-performance liquid chromatography, Fourier transform infrared spectroscopy, nuclear magnetic resonance, and mass spectrometry are mentioned as well in this review.

Abbreviations

2-MF – 2-methylfuran
2-MTHF – 2-methyltetrahydrofuran
5-MF – 5-methyl furfural
5-MFA – 5-methylfurfural alcohol

BHMF – 2,5-bishydroxymethylfuran
BHMTHF – 2,5-bis(hydroxymethyl)tetrahydrofuran
BPMF - 2,5-bis(isopropoxymethyl)-furan
DCM – dichloromethane
DFF - 2,5-diformyl furan
DMF – 2,5-dimethylfuran
DMSO – dimethylsulfoxide
DMTHF – 2,5-dimethyltetrahydrofuran
EFA - mono-ether-furfural alcohol
EMMF - ether 2-(ethoxymethyl)-5-methylfuran
FA – furfural
FFMF - (5-formylfuran-2-yl)methyl formate
FID – flame ionization detector
FOL - furfuryl alcohol
GC – gas chromatography
GVL – γ-valerolactone
HA - 2-hexanol
HD – 2,5-hexanedione
HMF – 5-hydroxymethylfurfural
HMFCA - 5- hydroxymethyl-2-furancarboxylic acid
HT - hexanetriol
MFM - 5-methyl-2-furanmethanol
MIBK - methyl isobutyl ketone
MTHFA – 5-methyltetrahydrofurfuryl alcohol
NMR - nuclear magnetic resonance
TCD – thermal conductivity detector
THF - tetrahydrofuran
THF2A - tetrahydro furfural
THFA - tetrahydrofurfuryl alcohol

1 Introduction

Lignocellulosic biomass is considered the most abundant source of renewable carbon. Taking into account the depletion of the fossil fuel reserves, biomass constitutes a very attractive sustainable carbon feedstock. In the last decade, we could observe an increasing interest in the development of bio-based processes allowing to reach
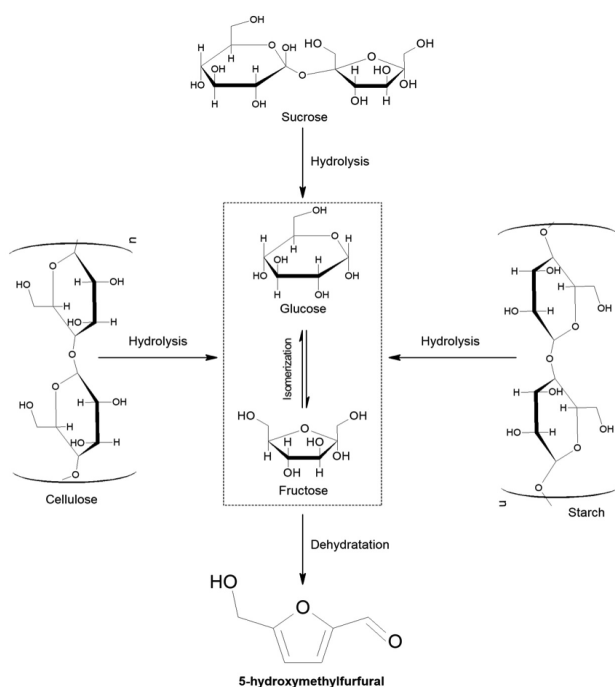
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high yields of newly emerged products like biofuels or various platform molecules [1-5]. Those processes provide new, more advanced functionality of biomass-derived raw materials, which is often allowed by precisely tailored oxygen content [6].

Following this, 5-hydroxymethylfurfural (HMF) has since the last decade of the 19th century been considered a valuable platform molecule, which is broadly illustrated in excellent reviews on this topic [7-10]. It is obtained from lignocellulosic biomass via a multi-step reaction, with acid hydrolysis of lignocellulose being the first step, followed by dehydration of glucose or fructose in the presence of acid catalysts (Scheme 1). Due to the higher selectivity, fructose is considered as the preferred source allowing to obtain high HMF yield. [11].

Thanks to the high functionalization of HMF, i.e. both hydroxyl and carbonyl groups in its structure, it possesses a high potential to be catalytically transformed to multiple industrially relevant products of both oxidation [12,13] and reduction reactions [7]. Particularly its hydrodeoxygenation provides a series of added-value molecules possessing a wide range of applications. Among the products of the HMF reductive transformation (Scheme 2) there are 2-methyltetrahydrofuran (2-MTHF), known as an appealing eco-friendly aprotic ether solvent and biofuel additive, 2,5-bishydroxymethylfuran (BHMF), a potential substrate for biopolymer production [14,15], or 2,5-dimethylfuran (DMF), a biofuel [16], among others.
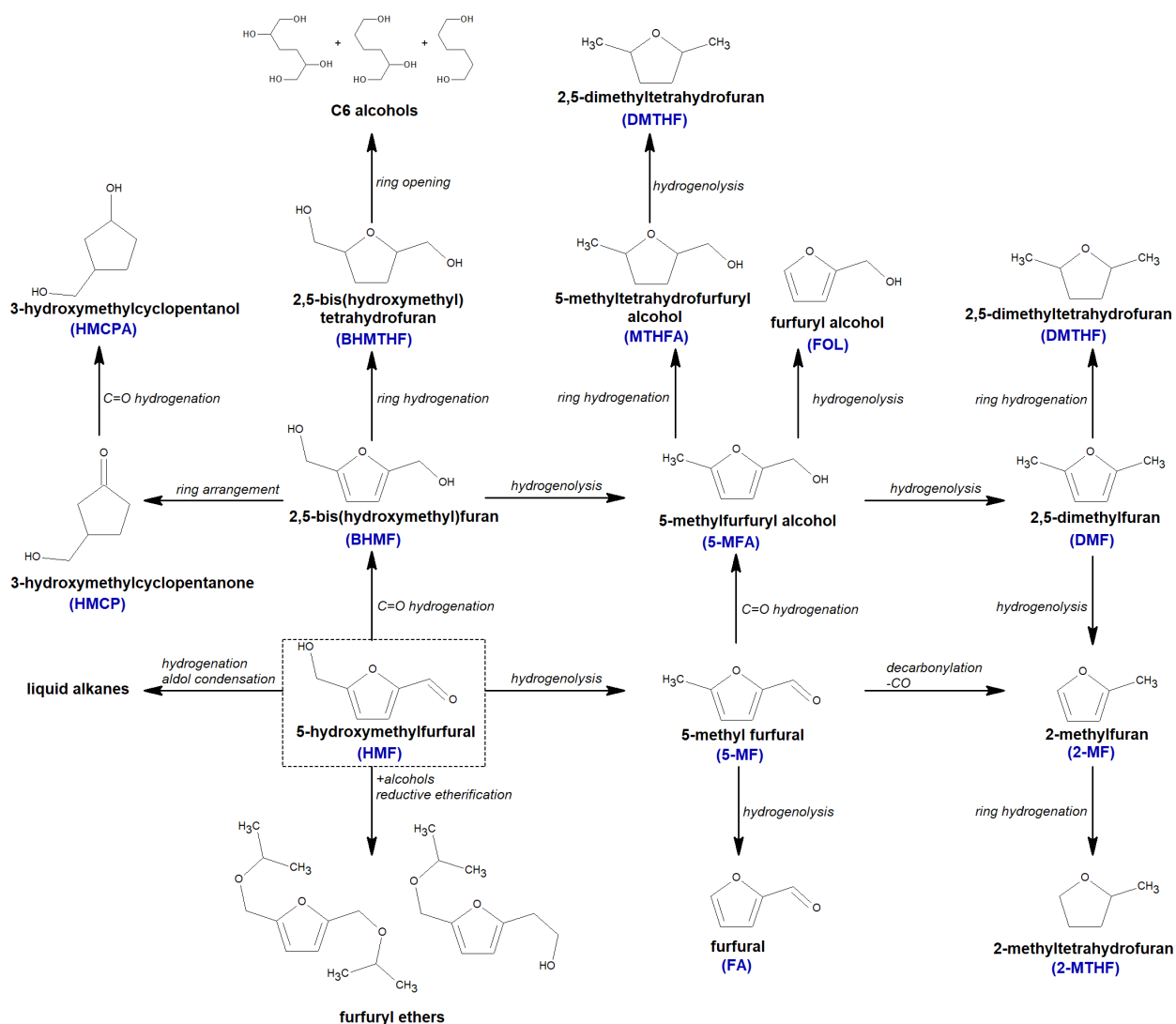

Scheme 1 Synthesis of HMF from biomass.

As illustrated in Scheme 2, HMF transformation in the reductive atmosphere involves several processes like hydrogenation of the C-O bond, hydrogenation of the furan ring, C–O hydrogenolysis, or polymerization. The selectivity of this reaction strongly depends on the reaction conditions, including the catalyst used [8]. This process is still intensively investigated, and more efficient, stable and sustainable solutions are envisaged. The vast potential of this reaction is however partly overshadowed by analytical difficulties which are often faced by researchers. The bottlenecks are associated with the closure of the carbon balance for all reaction products, their separation and identification.

HMF hydrodeoxygenation products can be of high complexity. Therefore, specific, comprehensive, and robust analytical methodologies need to be used in order to understand the transformation pathways of this process and to work out new, more efficient solutions. This review concentrates on presenting various analytical methods and their potential, as to the best of our knowledge the analytical challenges of this process are omitted in most of the papers. Although high-resolution chromatographic techniques are fundamental for the characterization of HMF value-added reaction products, they are not exclusive. This work provides an overview of the current state of the art, the main challenges that still need to be addressed, and improvements concerning more robust, sustainable and efficient separation processes.

2 HMF separation from cellulose/sugars

The most conventional methods of HMF synthesis include acid-catalyzed dehydration of monosugars obtained from biomass. HMF is obtained from fructose rather than glucose because the ring structure of glucose is more stable and therefore fructose reacts faster [17]. Water is usually used as a reaction solvent, although unfortunately it accelerates the consecutive side reactions and consumes HMF. It is worth noting that the formation of HMF by sugar dehydration is a complicated process due to the possibility of many side reactions. As a result of decomposition of fructose in water at high temperatures, isomerization, dehydration or condensation products may be formed. That is why the process is usually carried out in a biphasic system in order to extract HMF from the aqueous phase or aprotic organic solvents like dimethylsulfoxide (DMSO). The used organic solvent reduces the HMF degradation and the formation of by-products such as soluble polymers or humines, among others [18]. The most commonly used solvents include ethyl

Scheme 2 Conversion of HMF to valuable chemicals.

acetate, diethyl ether, and ionic liquids or methyl isobutyl ketone (MIBK) [19-22]. In literature, there are also numerous examples of efficient use of biphasic systems for direct HMF production from sugars. Biphasic system MIBK/H_2O together with different zeolite catalysts was used for the HMF production and its efficiency was much higher in comparison to water only [23,24]. Biphasic THF/H_2O systems modified with NaCl together with $FePO_4$ and NaH_2PO_4 as catalysts show a potential as an efficient solvent system as well [25]. Advanced approach related to the design of a biphasic reactor system composed of the aqueous phase modified with DMSO, combined with an organic extracting phase composed of MIBK–2-butanol mixture or dichloromethane (DCM) was shown by the group of Dumesic. By using the modified conditions tuned for the specific feedstock this reactor allows to obtain HMF with good selectivities at high conversions, independently of the feedstock [26].

Another approach includes environmentally friendly solvents like 2-MTHF, γ-valerolactone (GVL) or 1-butanol are considered as good bio renewable, sustainable alternative solvents, as they are effective, stable, and reasonably cheap [27].

3 Analytical techniques used for the analysis of HMF conversion products

HMF hydrodeoxygenation has been continuously explored in the literature. In order to avoid side reactions, the selectivity to the main products is tuned by the change of reaction conditions (temperature, pressure, hydrogen source, solvent) and the use of proper catalysts. A large group of catalysts is based on noble metals (Pd, Au, Pt, Ru) [7,8]. Non-noble metal-based catalysts are more

appealing due to lower cost and availability, but harsher experimental conditions are generally required in their presence [28]. Electro- and photo-assisted approaches to catalytic hydrogenation are examples of a greener methodology found in the literature. Competitive side reactions, which are often co-catalyzed by the same system or are also sensitive to the experimental conditions, are however difficult to avoid. In turn, this requires complex analytical systems. This section is divided into two parts and will be related to the analysis of the reaction products by gas and liquid chromatography, Fourier transforms infrared spectroscopy and nuclear magnetic resonance spectroscopy.

4 Gas and liquid chromatography

For several decades, gas chromatography (GC) has been one of the most popular techniques for the detection, identification and separation of volatile and semi-volatile analytes, in complex, including biomass-related samples [29,30]. GC usually concentrates on the volatile organic species with lower polarity and lower boiling point (<350°C) [31].

Different detectors are applied in GC analysis due to the different resolutions and sensitivities to specific molecules. For instance, GC–MS is rather established as a semi-quantitative tool, for which the limitation is additionally related to its lack of capability of direct analysis of nonvolatile or polar compounds.

In the case of highly polar analytes, a derivatization step is usually required in order to increase both volatility and thermal stability of the analyzed species. This procedure can increase the detector response by incorporating functional groups which lead to higher detector signals and in consequence to improved GC separation performances [32,33]. Multiple derivatization reactions like silylation, alkylation, or acylation can be used to mask the polar functional groups [34].

Several different derivatizing procedures are used in the case of the HMF analysis. They are mostly based on the formation of silylated derivatives with the use of different reagents. Among the derivatizing reagents examined, N,O-bis-trime- thylsilyltrifluoroacetamide (BSTFA) provided very good deri- vatization yields, while those examples are usually limited to food analysis [35].

The strong advantage of GC-MS is related to the high reproducibility of the generated mass spectra using electron impact ionization (EI). EI is a hard ionization process that results in the production of very reproducible mass spectra independently of the instrument used – in consequence, it allows the use of broad EI-mass spectral libraries [36]. EI fragmentation can be however sometimes too powerful and extensive so that softer ionization techniques such as chemical ionization (CI) can enhance the detection of molecular ion-based species.

Flame ionization detectors (FID) are most commonly used. Due to their broad detection limits, they can measure organic substance concentration at very low (10^{-13} g/s) and very high levels, having a linear response range of 10^7 g/s. Here the analysis strongly depends on the column choice and methodology applied, as the separation depends on the interaction of the substances with the stationary phase in the chromatography column. One of the important features of GC column is the kind of its active phase. Interaction between solutes and stationary phases decides about the separation of different solute molecules. For typical stationary phases like polysiloxanes and polyethylene glycols, three factors are crucial: dispersion, dipole-dipole interaction and hydrogen bonding interaction. The presence of the dipole-dipole interaction can enhance the separation of solutes like in the case of polyethylene glycols phase. The stationary phases that undergo dipole-dipole interactions also undergo hydrogen bonding interactions that also strongly influence the separation. The latter interaction is present when there is hydrogen bonding between the solute molecules and the stationary phase. Another key issue is the column polarity, which can strongly affect the separation of the solutes. For the molecules of similar volatility, higher retention time is obtained for the molecules possessing similar polarity to the polarity of the stationary phase [37]. In the broad range of presented examples (Table 1), FID was the most commonly used and high-polarity columns (like WAX) with the polyethylene glycol polymer phase were often applied. They are known to be good in the separation of many nonhalogenated organics, free C1-C26 fatty acids, alcohols, diols including glycols, and many other chemicals with different nature. When it comes to the subject of this review, the product identification efficiency depends on many factors, of which one of the most important is the selectivity of HMF hydrodeoxygenation reaction and therefore the number of products to analyze, and their difference in volatility. There are some limited examples where only one GC detector was used for analysis (FID) [38,39] and for selective reactions with the presence of only a few products (HMF, DMF, BHMF, 5-MFA) without many impurities it proved fully sufficient, practically allowing to close the carbon balance of the reaction [40-42]. However, where a wide range of by-products is present, FID is

Table 1 GC analysis of the reaction products of HMF hydrodeoxygenation with the use of polar columns

Detector	Column	Internal standard	Typical GC operating conditions and additional comments	Hydrogen source for HMF conversion	Carbon balance analysis	Reaction products to be analyzed	Reference
FID	DB-WAX capillary column (30.0m×250 μm×0.25 μm)	Tridecane	The injector temperature 250 °C, and the column temperature was increasing from 100 to 150 °C with a ramp rate of 5 °C min⁻¹.	Hydrogen	Up to around 4% of non-identified products	HMF, DMF, BHMF, 5-MFA, others mainly include DMTHF, tetrahydrofuran (THF) and C-C cracking products.	[38,39]
FID MS	DB-WAXetr (FID) DB -WAX and non-polar HP-5MS (MS)	n-propylbenzene	For the analysis of GC and GC-MS, the initial column temperature was set to 40 °C and kept for 2 min, then, the column temperature was elevated to 100 °C at 5 °C min⁻¹ and kept for 2 min, after the temperature was further elevated to 250 °C at 10 °C min⁻¹ and kept for 4 min	Methanol, ethanol, n-propanol, i-propanol, n-butanol, sec-butanol Isopropanol, hydrogen	From 2% to 20% of non-identified products	HMF, BHMF DMF, 5-MF, BHMF, MFM (5-methyl-2-furanmethanol), 2-MF, 5-MF, HA, FOL, MFM	[52-58]
FID MS	DB-WAXetr column (30 m × 250 μm × 0.25 μm)(FID) and non-polar TR-5 MS (15 m × 250 μm × 0.25 μm) (MS)	no	For GC-MS and GC analyses the initial column temperature was 40 °C held for 4 min, followed by heating at a rate of 10 °C min⁻¹ to 360 °C with a hold time of 2 min.	Isopropanol	From around 8% to 24% of non-identified products	HMF, BHMF, 2,5-bis(isopropoxymethyl)-furan (BPMF)	[59-60]
FID MS	DB-WAXetr 60 x 0.25 mm i.d., 0.25 μm film thickness capillary column was employed in both cases.	no	¹H and ¹³C NMR used as complementary technique	Hydrogen	100% identified products	HMF, BHMF	[36]
FID	HP-Innowax, capillary column 30 m x 0.25 mm, 0.25 μm film thickness	no	-	1-Propanol Hydrogen	Up to around 5%-56% of non-identified products	HMF, DMF, DMTHF, HA, HD, 2-hexanone	[48,61,84]
FID MS	HP-Innowax capillary column (30 m x 0.25 mm, 0.25 μm film thickness (FID) HP-Innowax column (MS)	Cyklohexanone		Hydrogen; n-butyl alcohol; 1-propanol; Ethanol; toluene	Up to around 5%-35% non-identified products	HMF, DMF, HD, 2-MF, 5-MF, MTHFA, DMTHF, HA, HD, mono-ether-furfural alcohol (EFA) and 2-hexanone	[43-49]
FID MS	Wax pillar column (film thickness: 0.25 μm, internal diameter: 0.25 mm, length: 30 m)	no	The temperature of the vaporization chamber: 250 °C, the temperature of the column: maintained at 50 °C for 3 min and then increased to 250 °C at 10 °C min⁻¹	Hydrogen	Most of the products are identified. Between 10-75 % of non-quantified products	HMF, 5-MF, DMTHF, BHMF, 2,5-diformyl furan (DFF)	[65]

Detector	Column	Internal standard	Typical GC operating conditions and additional comments	Hydrogen source for HMF conversion	Carbon balance analysis	Reaction products to be analyzed	Reference
FID MS	1.SUPELCO-WAX 10 capillary column (30 m × 0.32 mm × 0.25 µm)(FID) 2.HP-5MS column (MS)	Tridecane	injector = 270 °C; T_{FID} = 280°C; flow(N_2) = 1 mL min⁻¹. The following method was used: 40 °C for 2 min, 20 K min⁻¹ ramp to 260 °C and hold for 3 min.	Hydrogen	Up to around 10% of non-identified products	HMF, DMF, BHMF, DMTHF	[42]
FID MS	TC-WAX or a slightly polar - Inert Cap 5 capillary column was used for the separation (FID)	no	-	Hydrogen	Up to around 16% of non-identified products	HMF, THFA, FOL, tetrahydro furfural (THF2A), BHMTHF, BHMF, THFA	[62]
FID	CP-Wax 57 CB	1-heptanol	Injection volume 1.0 mL, inlet temperature 250°C, detector temperature 250°C, split flow 50 ml min⁻¹, column flow 1.5 ml min⁻¹ He. The initial column temperature was 50°C (5 min) with a temperature rise of 12°C min⁻¹ and a final temperature of 200°C (30 min).	Hydrogen, 1-butanol, 1-phenyloethanol, 2-phenyloethanol, 1-phenyl-1-propanol, 3-phenyl-1-propanol	-	HMF, BHMF, 5-MFA, DMF, DMTHF, BHMTHF	[50]
FID	β-dex column (length 30 m, diameter 225 µm, film thickness 0.25 µm)	no	The temperature of the GC injector was fixed at 513 K with the column detector at 533 K. The oven temperature was set at 363 K for 6 min followed by heating (10 K min⁻¹) up to 443 K and finally this temperature was kept for 30 min.	Hydrogen,	Up to around 1% of non-identified products	HMF, BHMF, DMTHF, DMF	[41]
FID	DM-FFAP capillary column	Toluene	-	-	Up to around 10% of non-identified products	HMF, DFF, BHMF	[63]
FID	Restek RTX-1701 mid polarity capillary column 60 x 0.25 mm i.d. and 0.25 µm film	Toluene or decane	The temperature of the injector and detector were set at 250°C and 285°C, respectively. The programmed temperature starts from 40°C (10 min) and is then increased up to 250°C with a heating rate of 10 °C min⁻¹.	Hydrogen, Ethanol, isopropanol, 2-methyltetrahydrofural, cyclopentyl methyl ether, methyl isobutyl carbinol	Up to around 21% of non-identified products	HMF, DMF, DMTHF, MFM, 5-MF, ether 2-(ethoxymethyl)-5-methylfuran (EMMF), BHMF, BHMTHF, HD, 1,2-hexanediol	[64]

often combined with MS detector or NMR spectroscopy analysis, which allow the structure confirmation [42-48] and therefore more complete detection. This combined technique allows to nearly fully identify and quantify all reaction products [40,46,49]. An interesting example of analysis is described in the work of Chimentão et al. [41] with the use of GC-MS equipped with a β-dex column containing permethylated β-cyclodextrin embedded in an intermediate-polarity stationary phase. Those types of phases are recommended for analysis of chiral compounds like ketones, alkanes, alkenes, alcohols, acids, ethers, etc. Performing the mass spectrometry allowed to compare the mass spectral patterns (m/z) of the compounds in the reaction mixture. The most intense peaks in the mass spectrum (notably m/z: 97 and 126 for HMF, 128 and 97 for BHMF, 56 and 41 for DMTHF, 96 and 95 for DMF) allowed to identify HMF and the reaction products [41]. Analytics was as well established in detail way in the work of Gyngazova et al. [50]. The study focused on understanding the reaction kinetics of HMF hydrogenation. Thanks to the identification of products (2-MF, 5-MFA, DMTHF, BHMF, BHMTHF and 2-MTHF) in a presence of different solvents by GC-FID with CP-Wax 57, the authors [50] understand the reaction network and explained that it proceeds via the hydrogenation of HMF aldehyde group to form BHMF and the subsequent conversion of BHMF to 5-MFA, followed by its to DMF. Side reactions include the formation of BHMTHF and DMTHF. The proposed analysis did not allow however to close the carbon balance. This could be caused by polymeric side reaction products in the reaction mixture which could not be analyzed by the current device [50].

Also, in the work of Li et al., a very detailed GC-MS analysis did not allow to close the carbon balance [57]. When THF was used as a solvent, different unidentified peaks with high molecular weights of ca. 200-250 could be identified in the GC-MS spectrum. Only HMF dimer with a molecular weight of 190 was identified, suggesting that a polymerization catalyzed by the Lewis acidity of the Fe catalysts can take part. Therefore, it was concluded that the Lewis-acid-catalyzed polymerization formed humins and other polymers, that could not be identified by GC-MS.

The side products resulting from HMF polymerization products during the hydrogenation reaction were however analyzed in the work of the group of Sun et al. [65] thanks to the use of fluorescence spectrometer. In this work, the reaction network was examined in detail and the liquid reaction products were analyzed with a GC–MS with a Wax pillar column. GC-MS spectra allowed to identify the majority of the products, although not all were analyzed in the quantitative manner [65]. Among the factors that

increase the number of by-products, the authors included side reactions like polymerization, dehydration and the furan ring opening, that can be co-catalyzed by the presence of acid/basic sites in the used catalyst.

On the other hand, there are several examples where non-polar or low-polarity columns, like HP-5, or AB-5 with (5%-phenyl)-methylpolysiloxane, or CP-Sil 5 containing 100% dimethylpolysiloxane phase, are used (Table 2). Those columns are quite popular for general purposes in a broad range of applications. Their advantage is the high temperature limit. When a small number of reaction products were observed [66], the carbon balance was nearly fully closed. Of course, typical internal standards (e.g. tetradecane, tridecane, or naphthalene) were often used to improve the quantitative analysis of the products. Typically, an MS detector with EI ionization or even liquid chromatography was used for improved analysis [67,68].

A very interesting example is provided in the work of Hu et al. [69] showing a detailed analysis of by-products provided by the use of GC-FID with HP-5 column, with confirmation of the DMF structure by GC-MS and NMR and FT-IR. Moreover, the authors established a detailed separation procedure of DMF from the by-product mixture (2,5-hexanedione (HD), 2-hexanol (HA), FOL and tetrahydrofurfuryl alcohol (THFA)) based on distillation and fractionation. This allowed to obtain 98.9% purity of the final product (DMF). Additionally, the structure of all the reaction products was confirmed by GC-MS analysis, which allows to propose a plausible mechanism of the reaction [69].

In order to increase the sustainability aspect, the reaction is frequently performed with internal hydrogen source like formic acid. In this case for closing the carbon balance, it is obligatory to use a thermal conductivity detector (TCD) for analyzing the gaseous substances, like in the work of Zhang et al. [67] and Yu et al. [68]. Three GC detectors FID, MS, TCD were used for the analysis of the HMF conversion products in the hydrogenation with Ni-Fe catalysts with the use of different solvents. Besides the typical reaction products HMF, BHMF, 5-methyl-2-furanmethanol (MFM), DMF, and DMTHF, as well as the starting material, the authors identified different ethers, products of decarbonylation and ring-opening product, and humins [68].

In some cases, the presence of large amounts of non-analyzed products is related to several factors. Firstly, often the research focuses only on the key molecules obtained in high yield [84], whereas the analysis of side products is omitted. Another reason is the complexity of the analysis itself. In the HMF valorization under hydrogen atmosphere, the by-products are of similar

Table 2 GC analysis of the reaction products of HMF hydrodeoxygenation with the use of non-polar or low polarity columns

Detector	Column	Internal standard	Typical GC operating conditions and additional comments	Hydrogen source for HMF conversion	Carbon balance analysis	Reaction products to be analyzed	Ref.
FID	HP-5 capillary column, 30.0 m × 320 μm × 0.25 μm	Tetradecane, Tridecane, or Naphthalene	Injector port temperature, 250 °C; detector temperature, 300 °C; and oven temperature, starting at 60 °C and rising to 230 °C at 20 °C min⁻¹	Hydrogen or Formic acid	Up to 41% of not identified products	HMF, DMF, 5-MF,5- MFA, BHMF, DMTHF FA, BHMTHF, MTHFA	[70-73]
FID	HP-5 capillary column	Naphthalene	Injector and detector temperatures of 240 and 280 °C, respectively; oven temperature programmed from 60°C (keeping for 1 min) to 100 °C at a rate of 5°C min⁻¹, then raised to 270°C (keeping for 2 min) at a rate of 10°C min⁻¹ HPLC- UV used as a complementary technique	Hydrogen	Up to around 25% of non-identified products	BHMF	[74]
FID MS	HP-5 capillary column (30 m × 0.32 mm × 0.25 μm)	Tridecane	Initial column temperature of 40°C was held for 2 min, and then, the temperature was ramped at 5 °C min⁻¹ until 100 °C was reached and held for 2 min; after that, the temperature was ramped at 10 °C min⁻¹ until 250 °C was reached and held for 2 min.	Hydrogen Formic acid, hydrogen, 2-propanol	Up to around 7-36%	HMF, DMF, 2-MF, 5-MF, BHMF, 5-MFA, HD, FOL, HA, THFA, 2,5-hexanediol	[69,75,76]
FID MS TCD	HP-5 capillary column (30 m × 0.32 mm × 0.25 μm) (FID) HP-5 capillary column (MS) Porapak Q column (3 m × 3 mm) (TCD)	no	-	Hydrogen, n-butanol	Up to around 20% of non-identified products –	1. HMF, DMF, DMTHF, BHMF, 5-MFA 2. Others 3. Gaseous products	[68]
FID MS TCD	KB-5 capillary column (30.0 m × 0.32 μm × 0.25 μm) (FID) 30 m HP-5 (0.25 mm internal diameter) (MS) Agilent 7890A - CP-7429 (TCD)	no	Injector port temperature 533 K, column temperature and initial temperature 323 K (3 min), gradient rate 10 K min⁻¹, final temperature 493 K (2 min), (FID) Column temperature was maintained at 333 K for 15.2 min (TCD)	Methanol	Up to around 66% of non-identified products	HMF, DMF	[67]

Detector	Column	Internal standard	Typical GC operating conditions and additional comments	Hydrogen source for HMF conversion	Carbon balance analysis	Reaction products to be analyzed	Ref.
FID MS	HP-5MS capillary column (0.25 mm in diameter, 30 m in length)	Dodecane		Hydrogen	Up to around 4% of non-identified products	HMF, DMF, DMTHF, 5-MFA	[66]
FID	HP-5MS collumn	Naphthalene	The GC oven was held at a controlled temperature of 303 K for 1 minute and then increased to 358 K with a temperature gradient of 10 K min^{-1}. This temperature was held for 2 minutes and then increased to 423 K with a temperature gradient of 10 K min^{-1} and hold for 10 minutes	Hydrogen 2-propanol	-	HMF, DMF, FOL, 5-MF, 5-MFA, DFF	[77,78]
FID	GC AB-5 capillary column with dimension of 30 m x 0.25 mm x 0.5µm	-	The initial oven temperature was held at 50 °C and increased up to 180 °C with the ramp of 10 °C min^{-1}, and further increased up to 280 °C with the ramp of 5 °C min^{-1} and hold for 2 min.	2-propanol Hydrogen	Up to around 25%-39% of non-identified products	HMF, DMF, BHMF, 5-MFA, FOL, 2-MF	[79,80]
FID MS	CP SIL 5 CB column (60 m, i.d. = 0.32 mm, Film = 5 µm) FID) CP-WAX 57 CB (25 m, ID = 0.25 mm)(MS)	-	-	Butan-2-ol, hydrogen	Up to around 30% of non-identified products	HMF, 2-butanone, 5-MF, 2-(sec-butoxymethyl)-5-methylfuran, hydroxymethyl furfural ether), dihydroxymethyl furan ether, dihydroxymethyl furan diether	[81]
FID MS	CP Sil 8 CB capillary column (30 m length, 0.25 mm diameter)	n-decane	-	Hydrogen	Up to around 20% of non-identified products	HMF, DMF, BHMF, MFA, DMTHF	[82]
FID MS	1. GC FID DB-5 capillary column of dimension 0.25 mm ID x 0.25 µm x 30 m 2. GC-MS 30 meter DB-5 capillary column (250 µm i.d. x 0.25 µm film thickness)	-	1. Injection volume 1.0 mL, inlet temperature 250°C, detector temperature 250°C, and a split ratio 1:5. The initial column temperature was 50°C (2 min) with a temperature rise of 10°C min^{-1} and the final temperature was 300°C 2. The initial column temperature was set at 35°C (for 3 min) and programmed to 280°C at 10.0°C min^{-1}. The flow rate was typically set at 1 mL min^{-1}. The injector temperature was set at 250°C.	Hydrogen	Up to around 10% of non-identified products	1. HMF, DMF, BHMF, 2. MTHFA, HD	[83]

chemical properties, particularly volatility, which can make the analysis difficult. Additionally, by-products are present in small quantities in comparison to the main reaction product. On the other hand, side reactions lead to various kinds of products, e.g. polymers or C1-C2 compounds present in the gas phase. The C1 products can also be formed when another, the more sustainable hydrogen source is used, e.g. formic acid. Its non-selective decomposition can produce CO and CH_4 [85] that even in small quantities can poison the catalyst used for the HMF hydrodeoxygenation. This requires the use of complex analysis tools, including several techniques.

Liquid chromatography is more frequently used for the analysis of the compounds possessing lower vapor pressure, lower thermal stability and higher polarity or samples where water was used as a solvent. However, its limitations include the lower resolution or sensitivity of the columns to different impurities related to the catalyst leaching to the reaction solvent. Various HPLC detectors have been used for analyte characterization. Detectors based on the absorption of light in the ultraviolet and visible ranges are the most common, as they respond to a wide variety of compounds with satisfactory sensitivity. The same holds for the photodiode array detector (PDA) since besides producing a typical chromatogram it can deliver the UV/VIS scan of every component.

There are some examples shown in Table 3 of HPLC analysis with the use of standard UV-VIS or PDA detectors, that typically were performed with a gradient of two solvents [86,87]. Due to the complexity of the reaction mixture, this analysis was usually limited to the identification of two reaction products [86]. Otherwise, examples, where HPLC with UV-VIS is a dominant analytical technique, are scarce. More typically, the UV-VIS detector was used in combination with other techniques. The refractive index detector (RID) thanks to its simplicity of analysis is often applied. It has a broad range of analyzed products but does not respond well to very low concentrations of measured samples, cannot be used in a gradient of solvents and as a result does not allow to provide information about the reaction products obtained with the lower yield.

However, when combined with UV-VIS and additionally GC, GC-MS and LC-MS [93,94], it allows to nearly close the carbon balance of obtained products.

The use of LC-MS combined with GC-MS and H[1] NMR was described in the work of Sun et al. and allowed to describe and understand the reaction mechanism of MF formation which occurred via esterification and hydrogenolysis, rather than decarboxylation reaction [91].

The potential of RID is often used for the analysis of sugars that are the HMF precursors or reaction impurities or by-products [94,95]. For complementarity of analysis it is often combined with GC [94] or with MS detector, allowing broader identification of the products [83]. A detailed study concerning analytical procedures of hydrogenolysis of 5-hydroxymethylfurfural towards 5-methylfurfural is shown by Sun et al. [91] who present clear examples of HPLC-MS of HMF, FFMF ((5-formylfuran-2-yl)methyl formate and 5-MF and GC-MS of the HMF over hydrogenation products, combined also with NMR analysis. HPLC with UV-VIS also clearly shows that the product distribution was worked out elegantly. The authors however concentrated mainly on the main reaction product 5-MF, limiting the analysis of other products to the qualitative aspect. To complete the overview, the analysis of C1 gaseous products of the formic acid decomposition would be desirable.

Besides the necessary complete analysis of gaseous or liquid products formed during the hydrodeoxygenation of HMF, we would like to emphasize that an extended analysis of the reaction products might also request to investigate the deposition with a time of solid or polymeric carbonaceous products at the surface of the catalyst. Indeed, while this might help in closing the carbon balance, this also influences the catalytic performance with potential impact on both conversion and selectivity patterns, as well as on stability and reusability issues. Whether academic or industrial investigations are concerned, it is worth keeping always in mind that the criteria for selecting the adequate analytical tool should include the analysis time. Indeed, due to the high number of products with close functions, the analysis might remain time-consuming when a good chromatographic product separation is desired.

5 Fourier transform infrared spectroscopy (FTIR) and Nuclear magnetic resonance spectroscopy (NMR)

Another technique worth describing is Fourier transform infrared spectroscopy (FTIR), which is frequently applied in the qualitative and quantitative analysis of organic substances [30]. The mid-infrared region is particularly used to reveal the presence of various functional groups in molecules, thanks to their characteristic absorption bands. Bands around 3050 cm^{-1} are commonly attributed to C-H stretching vibrations indicating the presence of aliphatic hydrocarbons. Bands around 3300–3400 cm^{-1} correspond to O-H stretching vibrations suggesting the presence of carboxylic acids or alcohols. Bands in the region of 1450

Table 3 HPLC analysis of the reaction products of HMF hydrodeoxygenation

Detector	Column	Eluent	Other complementary techniques	Hydrogen source for HMF conversion	Carbon balance	Reaction products to be analyzed by HPLC	Ref.
PDA	Eclipse XDB-C18 (4.6mm×250 mm, 5 μm) (reversed-phase HPLC)	Acetonitrile/0.4% $(NH_4)_2SO4$ solution (10:90, v/v) with the flow rate of 0.6 mL min⁻¹.	-	-	Up to around 18 % of non-identified products	HMF, BHMF 5- hydroxymethyl-2-furancarboxylic acid (HMFCA) retention times of HMFCA, BHMF and HMF were 6.1, 8.3 and 9.9 min,	[86]
RID UV (280 nm)	Aminex HPX-87 H (Bio-Rad, Richmond, CA)		GC-FID (BHMF; HP-5 column (30m×0.320mm×0.25 μm) using naphthalene as internal standard) GC-MS (by-products)	Polymethylhydrosiloxane (PMHS)	Up to around 23% of non-identified products	HMF	[94]
UV	Bio-Rad Aminex HPX-87 H pre-packed column	Diluted solution of H_2SO4 (0.0005 M) in water		Hydrogen, Methanol	Up to around 34% of non-identified products	HMF, BHMF, BHMTHF	[88]
UV RID	Shodex Sugar SH-1011 103 (300 ×8 mm)	H_2SO_4 (0.005 M) water solution and a flow rate of 0.5 mL min⁻¹ Column temp 50°C	LC-MS	Hydrogen	Up to around 2% of non-identified products	UV detector (284 nm) for determination of HMF Refractive index (RI) detector for determination of BHMF, DHMTHF and hexanetriol (HT)	[93]
RID	Shodex SP0810	Water Column temp 30°C/50°C	GC-MS	1-butanol	Up to around 65% of non-identified products	BHMF, 5-MF, DMF, 2,5-dimethyl-2,3-dihydrofuran	[95]
RID	C18 column		GC-FID DB-wax capillary column (Other products analyzed: 5-MF, 5-methyl-2-furanmethanol, ring-opening rearrangement products, etherification products)	Hydrogen, ethanol	Up to around 43% of non-identified products	HMF, BHMF	[89]
RID	Aminex HPX 87-H (Bio-Rad) with Sugar SH1011 (Shodex)	0.5 mM H_2SO_4 column temp 85°C	LC-MS	surface-adsorbed hydrogen atoms are generated electrochemically from water or proton reduction,	-	HMF, DHMF, DHMTHF, 2,5-dimethyl-2,3-dihydrofuran	[90]

Detector	Column	Eluent	Other complementary techniques	Hydrogen source for HMF conversion	Carbon balance	Reaction products to be analyzed by HPLC	Ref.
UV (250 nm)	C18 column (4.6 mm inner diameter)	methanol/ water gradient was used as eluent (A: 30% methanol; B: 90% methanol; linear gradient from 100% A to 100% B in 5 min.)	GC-FID AT 6890 N gas chromatograph equipped with a 30 m DB-1 column and a flame ionization detector (FID)	2-propanol, hydrogen	Up to around 20 % of non-identified products	HMF, (E)-4-[5-(hydroxymethyl)furan-2-yl]but-3-en-2-one, (1E, 4E)-1,5-bis[5-(hydroxymethyl)furan-2-yl]penta-1,4-dien-3-one	[87]
UV (265 nm)	C18 column	1‰ aqueous acetic acid solution and pure acetonitrile. The volume ratio of them was 80:20. Column temp 30°C	GC-MS DB-35MS column	Formic acid	-	HMF, MF	[91]
IR	Hi-Plex H		GC-FID with Suprawax 280 capillary column DMF and other products in the liquid product stream	Hydrogen	Up to around 80% of non-identified products	HMF	[97]
IR	Hi-Plex H		GC-FID with Suprawax 280 capillary column DMF and other products in the liquid product Stream	1-butanol, hydrogen	Up to around 80% of non-identified products	HMF	[96]
PDA (284 nm for the identification of HMF) and (223 nm for the identification of BHMF)	Cortecs T3 2.4 μm (4.6 x 100 mm)	Gradient elution in three steps: isocratic conditions for 6 minutes, with eluent composed of CH_3CN/H_2O 10/90 v/v ratio; gradient elution for 5 minutes until a CH_3CN/H_2O 50/50 elution ratio was obtained; gradient elution for 4 minutes until a CH_3CN/H_2O 70/30 elution ratio was obtained. The flow rate was 0.7 mL min^{-1}. Column temp 30°C	GC-MS capillary column HP5, composed by (5%-Phenyl)-methylpolysiloxane. ESI-MS	surface-adsorbed hydrogen atoms are generated electrochemically from water or proton reduction,	-	HMF, BHMF	[92]

Table 4 NMR analysis of the reaction products of HMF conversion.

Technique	NMR as Prevailing analytical technique	Other complementary techniques	Hydrogen source	Reaction Products to be analyzed	Analytical Device	Solvent for analysis	Typical shifts δ/ppm	Ref.
^{1}H NMR	yes	No	surface-adsorbed hydrogen atoms are generated electrochemically from water or proton reduction,	BHMF	^{1}H NMR frequency 400 MHz	90% H_2O and 10% D_2O. Acetonitrile was used as an internal standard	HMF peaks at 9.37, 7.45, and 6.59 ppm. BHMF peaks at 6.28 ppm.	[99]
^{1}H NMR	yes	No	surface-adsorbed hydrogen atoms are generated electrochemically from water or proton reduction,	BHMF	^{1}H NMR frequency 400 MHz	90% H_2O and 10% D_2O	HMF peaks at 9.36, 7.45, and 6.59 ppm. BHMF peaks at 6.24 and 4.45 ppm	[98]
^{1}H NMR	yes	HSQC HPLC GC-MS ^{13}C-NMR	surface-adsorbed hydrogen atoms are generated electrochemically from water or proton reduction,	HD DMF 5-MF	^{1}H NMR frequency 400 MHz	90% H_2O and 10% D_2O 0.2 M sulfate buffer solution (pH 2.0)	(HMF peaks at 9.35, 7.43, and 6.57 ppm. HD peaks at 2.71 and 2.12 ppm. HHD peaks at 4.31, 2.78, 2.59, and 2.24 ppm. 5-MF peaks at 9.21, 7.40, 6.32, and 2.32 ppm.	[100]
^{1}H NMR ^{13}C NMR	no				^{1}H NMR 400 MHz, ^{13}C NMR 100 MHz	CDCl$_3$	^{1}H NMR HMF peaks at 7.34 (s, 2H), 9.86 (s, 2H); ^{13}C NMR 119.23 (2C), 154.23 (2C), 179.24 (2C).	[101]
1H NMR	no	GC	hydrogen	DMF	500 MHz	CDCl$_3$	Np	[102]
^{1}H NMR ^{13}C NMR	no	GC-MS GC-FID	hydrogen	HMF and 1-hydroxyhexane-2,5-dione (HHD) in order to obtain HHD/HMF molar ratio	-	-	-	[103]

and 1600 cm^{-1} show C=C stretching vibrations indicating the presence of aliphatic or aromatic structure. Finally, bands at 1600 and 1800 cm^{-1} are attributed to the presence of C=O groups, whereas bands between 1000 and 1100 cm^{-1} are assigned to C-O stretching vibrations which can indicate the presence of e.g. ethers, alcohols or carboxylic acids.

In the HMF hydrodeoxygenation there are only very limited examples of the application of this method [96,97] and additionally, they are supported by other techniques like GC. HPLC with IR detector was used for HMF determination whereas all other products of hydrogenolysis of HMF were analyzed by GC (Table 4).

Carbon ^{13}C NMR and hydrogen ^{1}H NMR allow both qualitative and quantitative analysis of chemical structures. They are however used marginally, and their potential is mainly used for confirmation of the structure functionality and purity rather than the analysis of the reaction product range. The existing examples where this technique is used solely for following the reaction performance are limited to the analysis of one reaction product [98].

The concentration of HMF and BHMF, the product of its electrochemical or photoelectrochemical hydrogenation in water was estimated thanks to hydrogen NMR by the group of Roylance et al. [98] and Zhang et al. [99]. The measurements were performed using acetonitrile as an internal standard, and 90% H_2O and 10% D_2O were used as a solvent. ^{1}H signal originating from water was removed by the water suppression method. Then the respective ^{1}H NMR peaks allowed to determine the selectivity to the main reaction product and the HMF conversion. The identification of other possible reaction products was however omitted.

Another interesting example where the NMR technique was efficiently exploited for analysis was also used in the case of electrochemical reduction of HMF to HD, a hydrated derivative of DMF, which can be used for the production of terephthalic acid for polyethylene terephthalate (PET) [100]. Here the analysis of other main reaction products was also performed. In all those examples water was used as a reaction medium, often with the presence of inorganic salts working as a buffer, which could be potentially problematic for other chromatographic techniques.

6 Conclusions and future outlook

Conversion of HMF is a process of constantly growing interest. It is a difficult reaction from an analytical point of view due to the variety of formed products. Numerous analytical approaches have already been developed. Most of the studies however concentrate only on the most important reaction products, omitting the analysis of by-products. Information about the detailed product contributions therefore of high interest, as understanding all side reactions that can occur allows improving the whole process. The precise analysis includes a combined approach using several techniques. Gas chromatography coupled with various detectors (TCD, FID, MS) is the most frequently used method and allows both qualitative and quantitative understanding of most of the products. FTIR and NMR analyses additionally provide information on the functional groups and types of chemical bonds, which allows to complete the picture of reaction network and product distribution.

Besides the necessary complete analysis of gaseous or liquid products formed during the hydrodeoxygenation of HMF, we would like to emphasize that an extended analysis of the reaction products might also request to investigate on the deposition with time of solid or polymeric carbonaceous products at the catalyst surface, as well as to implement on-line product analysis. Indeed, while this might help in closing the carbon balance, this also influences the catalytic performance with potential impact on both conversion and selectivity patterns, as well as on stability and reusability issues. Whether academic or industrial investigations are concerned, it is worth keeping always in mind that the criteria for selecting the adequate analytical tool should include the analysis time. Indeed, due to the high number of products with close functions, the analysis might remain time-consuming when a good chromatographic product separation is desired. We believe that that information presented in this current review can also shed the light on the selection of adapted chromatographic techniques for other similar biomass-derived molecule hydrogenation processes.

Further, the continuous improvement of the analytical tools played a role – and is still expected to do so in the future – in the progress obtained in the last decades both from fundamental and applied points of view, notably by allowing faster and more sensitive detection of the large variety of the HMF hydrogenation side-products view.

Acknowledgments

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