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Catalytic upgrading of biomass derived furans

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ABSTRACT

The current interest in biomass derived renewable furan derivatives furfural and 5-hydroxymethylfurfural commonly known as biofurans is due to their ready accessibility through dehydration of abundant cellulosic biomass derived monosaccharides. However, an upgrading to more stable compounds is an essential step for these materials in many sustainable fuel and chemical industry applications due to their instability and facile polymerization to humins. The aim of this article is to cover all aspects of catalytic upgrading reactions of biofurans, especially focusing on the developments in the last five years. The importance of this class of renewable feedstocks, preparation from monosaccharides as well as the diversity of possible transformations are discussed in the introduction sections of this review. The recent advances in catalytic reductions and oxidations of biofurans at CHO, OH functional groups, in ring system as well as rearrangements to form more stable value-added derivatives are reviewed. In addition, recently developed catalytic methods in carbon number upgrading of biofurans through condensation reactions and further conversions to renewable synthetic fuel range molecules are discussed in the article.

1. Introduction

Cellulosic fraction of biomass is an abundant renewable feedstock and the most widely distributed natural polymeric material on earth. In recent times an increased effort has been made to utilize this cellulosic fraction of biomass for the production of fuels and chemicals as renewable alternatives to petroleum based resources (Tong et al., 2010). The lignocellulosic biomass mainly consists of cellulose, hemicellulose and lignin. There are several approaches in processing cellulosic fraction and one of the most extensively explored routes involves the catalytic transformations of cellulose and hemicellulose in a series of steps including hydrolysis of the polysaccharides to monosaccharides followed by dehydrations. This route leads to substituted furan compounds with an aromatic system and these compounds are commonly known as biofurans. Furfural (F) and 5-hydroxymethylfurfural (HMF) are the most common biofurans formed in the dehydration of pentose and hexose respectively. The main drawback of these important furan aldehydes is their instability as these compounds polymerizes to humins during storage as well as darkens due to air oxidations. The widely adopted method to get around these problems is conversion of furan aldehydes to their more stable derivatives or other stable value added chemicals (Kabbour and Luque, 2020). As a promising biobased platform chemical, furfural can be further converted into a variety of C4 and C5 chemicals such as furfuryl alcohol (FA), cyclopentanol (CPL), cyclopentanone (CPO), levulinic acid (LA), γ-valerolactone (GVL), tetrahydrofuran (THF), and succinic acid (SA) (Li et al., 2016). Similarly, C6 aldehyde HMF can be upgraded to value added chemicals such as: 2,5-furandicarboxylic acid (FDCA), and 2,5-dimethylfuran (DMF), levulinic acid (LA), formic acid, 2,5-bis(hydroxymethyl)furan (BHF), and 2,5-diformylfuran (DFF) (Boisen et al., 2009). These building block chemicals play important roles in multiple industries. For example, CPO is used as a precursor for fragrances, manufacture of insecticides and pesticides (Fan et al., 2019). LA is widely used as a precursor for pharmaceuticals, plasticizers and synthesis of fuel additives (Badgujar et al., 2020). GVL can be used in perfume and flavor industries due to its herbal flavor and it is also considered as a renewable fuel and a green solvent (Zhang, 2016). FDCA is widely used in polymer industry for the production of polyesters, polyurethanes, and polyamides (Terzopoulou et al., 2020; Cousin et al., 2018). The aim of this article is to review the recent developments in the catalytic upgrading of these important biobased furans.

2. Biobased furans from lignocellulosic materials

The acid catalyzed hydrolysis followed by dehydration of monosaccharides is the widely used technique for producing these biobased

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furans from polysaccharides. The general reaction pathways for this acid catalyzed production of F (**1**) from hemicellulose and HMF (**2**) from cellulose are outlined in Fig. 1 (Luo et al., 2019; Tong et al., 2010). In the traditional biomass utilization processes, multiple steps are involved, including pretreatment to disrupt the rigid structure of the biomass, hydrolysis to breakdown the polysaccharides into simple sugars, followed by the fermentation or further sugar conversions. However, in the case of biofuran production from biomass these multiple steps can be achieved as a "one-pot" process as well.

A large variety of biomass forms: polysaccharides, monosaccharides as well as acid catalysts have been used to produce furfural or HMF. For example, Marcotullio and De Jong (2010) have reported the use of 50 mM aq. HCl at 200 °C for the preparation of furfural from xylose with a yield of 81 % and over 90 % selectivity. Similarly, another group has used 0.05 M sulfuric acid at 170 °C for only 15 min for the conversion of xylose to furfural with a yield of 80 % (Gallo et al., 2013). Antal et al. (1990) has shown that HMF can be prepared with a 53 % yield by dehydration of fructose using sulfuric acid as the catalyst at 250 °C. On the other hand, the selective conversion of glucose to HMF is more difficult; where only a 42 % yield and 53 % selectivity could be achieved in acid catalyzed dehydration of glucose to HMF in DMSO at 170 °C (Chheda et al., 2007). The lower yield in using glucose is likely due to the difficulty in isomerization of glucose to fructose; which is an essential step before dehydration to HMF. Generally pentoses are converted to F in higher yields in comparison to the conversion of hexoses to HMF and this could be due to the relatively higher stability of F as well (Tong et al., 2010).

The direct use of polysaccharides such as xylan and glucan as starting material is also possible in the preparation of biofurans; nevertheless, there can be a small loss in yield in this approach. For instance, It was reported that a 36.5 % yield in preparation of furfural from polysaccharide xylan and a 38.3 % yield in using the monosaccharide xylose under similar reaction conditions, 0.1 M HCl as the catalyst at 180 °C for 30 min (Yemiş and Mazza, 2011). It is also worth noting that the use of acid catalysts such as sulfuric, nitric, phosphoric, formic and acetic acids resulted significantly decreased yields in comparison to hydrochloric acid under similar conditions (Yemiş and Mazza, 2011). An acidic ionic liquid with a combination of ionic liquid and acidic properties is one of the most promising catalysts for the direct conversion of cellulose or glucose to HMF under relatively mild conditions (Amarasekara and Razzaq, 2014; Li et al., 2009; Su et al., 2009; Zhou et al., 2013). The pairing of metal ions with ionic liquids is also a well documented approach in achieving higher yields of HMF from cellulose. In this case, the metal ions and in particularly transition metals are believed to coordinate with oxygen atoms in the carbohydrate and acting as a co-catalyst. For example, the use of metal ion containing ionic liquids catalysts such as, ethyl methyl imidazolium chloride ([EMIM]Cl) paired with $CuCl_2$ or $CrCl_2$ as the catalyst, is known to give HMF directly from cellulose in 55 % yield at 120 °C in a one-pot process (Su et al., 2009).

The direct use of lignocellulosic biomass as the starting material can add another layer of complications as the typical percentage composition of biomass by dry weight is: 35–50 % cellulose, 20–35 % hemicellulose, and 20–30 % lignin (Lynd et al., 2002; Balat and Balat, 2009; Amarasekara, 2013). In general, it is difficult to achieve selectivity towards an individual furan product, furfural or HMF through the direct production of biofurans from raw biomass. However, furfural yield is normally higher than HMF yield, even though the major polysaccharide is cellulose in most biomass materials. Furthermore, several researchers have noticed the relative ease of the hydrolysis of hemicellulose fraction during the first phase of acid catalyzed degradation processes of various biomass forms in aqueous media. For instance, in an experiment using biomass forms: triticale straw, wheat straw, and flax shives, with 0.1 M HCl catalyst at 180 °C, Yemis and Mazza have reported the formation of 46, 48 and 72 g of furfural per 100 g hemicellulose fraction in the first 30 min. (Yemiş and Mazza, 2011). However, during the same period the HMF yields were less than 3 g/100 g cellulose for all three biomass forms. This significant difference in ease of hydrolysis is most likely due to the more organized rigid crystalline structure of cellulose in comparison to the hemicellulose structure (Deng et al., 2018).

Secondly, in addition to HMF, furfural can also be formed from the dehydration of hexoses as a secondary product (Asghari and Yoshida, 2010). The large-scale economical production of HMF and furfural from biomass are still challenging problems and additional efforts are needed regarding the choice of solvent and catalysts. Then there are recent advancements in producing HMF in decent yields from cellulose under moderate conditions using complex catalyst - solvent systems. For example, It was reported that using *N,N*-dimethylacetamide containing lithium chloride (DMA-LiCl) as the solvent, 10 % $CrCl_3$ and 10 % HCl with 60 % [EMIM]Cl as the catalyst, produced HMF and furfural with a yield of 48 % and 34 % respectively at 160 °C after 2 h from corn stover (Binder and Raines, 2009). However, the use of an expensive solvent, complex catalyst system and practical problems in recycling the catalyst are major issues in scaling up of this process. In summary, the direct production of biofurans from lignocellulosic biomass is achievable in fewer processing steps with several advantages compared to other fermentation based biomass utilization methods, as there are no restrictions from bioactivity inhibitors (Deng and Aita, 2018a, b). However, the selectivity of target product needs to be carefully controlled by the selection of proper solvent, catalyst systems and reaction conditions to simplify the downstream purification process.

3. Catalytic reductions of biofurans

After obtaining F and HMF from lignocellulosic materials, further upgrade biofurans can be achieved through different pathways. The reductive transformation to more stable derivatives is the most widely

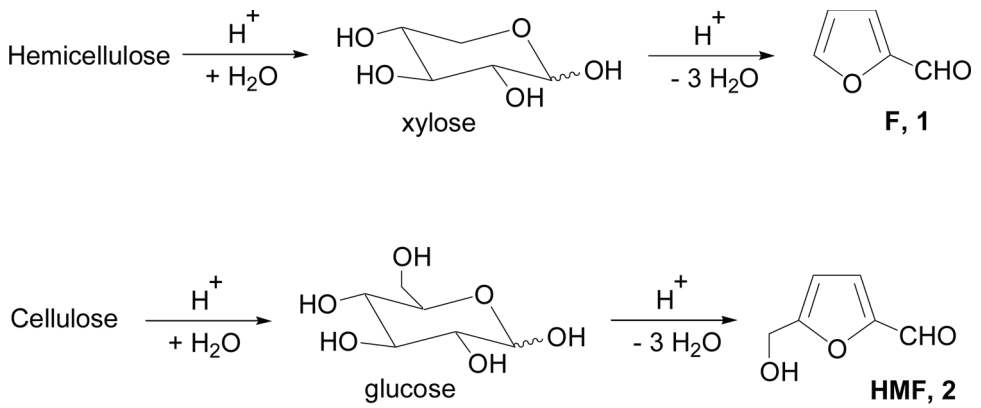

Fig. 1. Reaction pathways for the production of biofurans furfural (F, **1**), 5-hydroxymethylfurfural (HMF, **2**) from hemicellulose and cellulose fractions in biomass.

studied approach of upgrading the two common biofurans. The use of hydrogen gas as the H source is the more common approach; nevertheless transfer hydrogenation has become a competitive route as well in recent years. The reductions can be basically divided into two groups: reductions in the ring and reduction in the peripheral CHO and OH groups. Then there are examples in reducing both the ring and attached groups. Some of the common reduced derivatives of interest are furfural alcohol, tetrahydrofurfuryl alcohol, methyl tetrahydrofuran and dimethyl tetrahydrofuran with numerous applications in chemical and polymer industry (Kabbour and Luque, 2020). Catalytic reduction of furfural to furfural alcohol is the most widely studied of all these reactions; noble metals (Chen et al., 2016; Wu et al., 2016; Dohade and Dhepe, 2017) as well as non-noble metal catalytic systems such as Ni/Fe phosphates (Kurchenko et al., 2018), Fe/Ni-SiO_2 (Shi et al., 2019b), Fe-Ni alloy (Putro et al., 2017a; Putro et al., 2017b), and Fe(NiFe)O_4-SiO_4 nano catalyst (Halilu et al., 2016), have been used in this transformation. Both noble and non-noble metal catalysts perform extremely well, achieving almost 100 % yield of furfuryl alcohol in most cases. For example, Mayo et al. (2020) reported the use of Pd(II) and Pt (II) complexes as catalysts, with a 99 % yield of furfuryl alcohol using ethanol as solvent at 140 °C, 20 bar H_2 for 10 h (Table 1, entry 1). On the other hand, a 99 % yield of furfuryl alcohol could be achieved under similar conditions using an iron(II) based catalyst as well (Table 1, entry 12) (Shi et al., 2019a). The hydrodeoxygenation leading to 2-methylfuran is also known with Ni/C (Jaatinen et al., 2017), Pt-Co and Ni-Fe bimetallic catalysts (Wang et al., 2018). Furan ring reduction together with complete reductive deoxygenation of the aldehyde function to produce 2-methyl tetrahydrofuran is also possible with Pd (Turtabaev, 2004; Chatterjee et al., 2014), Cu-Pd/ZrO_2 (Pasha and Puttaramegowda, 2006), Rh (He et al., 2003), Ni (Connor and Adkins, 1932). In another example Liu et al. have reported a two-step process for the conversion of furfural to 2-methyl tetrahydrofuran. In the first stage furfural was converted into 2-methylfuran over a Co-based catalyst and a second step with a Ni-based catalyst was then used to reduce to 2-methyl tetrahydrofuran (Liu et al., 2020). Then the reductive ring opening of the furan ring to produce 1,2-pentanediol is also known with the use of Fe-Co-Ni alloy as the catalyst (Xia et al., 2019). Similarly, reductive transformations of HMF were also possible with noble as well as non-noble metal catalysts. For example, Zhang et al. (2020a) reported the use of Zr/Ca based catalysts, where 2,5-furandimethanol yield reached 84 % in isopropyl alcohol medium at 190 °C, after 10 h (Table 2, entry 1). Subsequently even higher 94 % yield of 2,5-dimethylfuran was reported using Cu/Al_2O_3 catalyst, at 423 K, 20 bar H_2 for 10 h (Table 2, entry 13) (Esteves et al., 2020). Some additional selected recent examples of reductive transformations of furfural and HMF are summarized in Tables 1 and 2.

While furfural and HMF can be transformed into a variety of C4, C5 and C6 chemicals, one particularly worth noting reaction is the production of cyclopentanone (CPO) and its derivatives in aqueous conditions. These chemicals are building blocks in multiple industries including energy, food, medicine, cosmetics, and pesticide (Ohyama et al., 2014; Ramos et al., 2017; Xia et al., 2016) Currently, these chemicals are mainly produced via petrochemical pathways under harsh conditions, such as catalytic ketonization of adipic acid with barium hydroxide at elevated temperature (Jia et al., 2019; Tang et al., 2019; Wang et al., 2017). Therefore, there are great potentials for biobased pathways for the production of renewable CPO and its derivatives from biomass derived furfural and HMF.

The conversion of furfural to CPO has been reported using various metal catalysts in aqueous medium at elevated temperatures. Fang et al. (Fang et al., 2015) reported the use of Ru nanoparticle catalyst to achieve 96 % CPO selectivity with 99 % furfural conversion under a H_2 atmosphere, 4.0 MPa at 160 °C for 2.5 h. Similarly, it was reported that with the use of 5 % Pt/C as catalyst, a 76.5 % yield of CPO could be achieved after 30 min reaction under H_2 at 80 bar and at 160 °C (Hronec and Fulajtarová, 2012). It is worth noting that solvent played a key role in selectivity in these reactions; aqueous condition favored a 76 % yield of CPO and CPL, while a butanol solution resulted in less than 1 % yield of CPO and CPL, however gave a mixture of furfuryl alcohol and 2-methyltetrahydrofuran in a 88 % combined yield under similar conditions (Hronec and Fulajtarová, 2012). Comparable results of over 90 % CPO selectivity have been reported using Pd or Au based catalysts, hydrogen atmosphere and at elevated temperatures as well (Hronec et al., 2012, 2013; Zhang et al., 2016a).

Although competitive yield and selectivity could be achieved with the use of noble metal catalysts, the major drawback is the high cost of

Table 1
Selected examples of reductive transformations of furfural (F, **1**).

Entry	Catalyst, reaction conditions	Product(s), Yield(s)	Reference
1	Pd(II) and Pt(II) complexes, ethanol, 20 bar H_2, 140 °C, 10 h	furfuryl alcohol, 99 %	(Moyo et al., 2020)
2	Fe, Cr - MOFs, Me_2CHOH, NaOH, 100 °C, 15 h	furfuryl alcohol, 99 %	(Sebastiao et al., 2014)
3	Zr -nanohybrid, Me_2CHOH, 140 °C, 4 h	furfuryl alcohol, 98 %	(Schmidt et al., 2005)
4	Mg-Cu, H_2, Me_2CHOH, 100 °C, 4 MPa, 3 h	furfuryl alcohol, 98 %	(Llop Castelbou et al., 2017)
5	Ru-chitosan, HCO_2H, THF, 120 °C, 1.5 h	furfuryl alcohol, 99 %	(Dohade and Dhepe, 2017)
6	$ZrCO_3$, Me_2CHOH, rt → 80 °C, 7 h	furfuryl alcohol, 99 %	(Dohade and Dhepe, 2017)
7	Hf-imidazoledicarboxylic acid, s-BuOH, 130 °C, 2 h	furfuryl alcohol, 99 %	(Dohade and Dhepe, 2017)
8	Hf-imidazoledicarboxylic acid, Me_2CHOH, 120 °C, 1 h	furfuryl alcohol, 99 %	(Chen et al., 2016)
9	Zr-heteropoly acid, Me_2CHOH, 120 °C, 1 h	furfuryl alcohol, 99 %	(Wu et al., 2016)
10	Hf-MOFs, Me_2CHOH, 120 °C, 2 h,	furfuryl alcohol, 99 %	(Kurchenko et al., 2018)
11	Cu(I)-Cu(0), CuNPs@ZIF-8, H_2, EtOH, 140 °C, 2 MPa, 3 h	furfuryl alcohol, 99 %	(Xia et al., 2019)
12	Fe(II) hydride complex, HCO_2^- •Na^+, H_2O, 80 °C, 1 h	furfuryl alcohol, 99 %	(Shi et al., 2019a)
13	Hf-phenylphosphonate, Me_2CHOH, 120 °C, 2 h	furfuryl alcohol, 98 %	(Putro et al., 2017b)
14	Ru-Triphos, H_2, rt → 120 °C, 30 bar, 9 h	furfuryl alcohol, 100 %	(Wang et al., 2018)
15	Cu-SiO_2, H_2, 210 °C, 5h	2-methylfuran, 95 %	(Putro et al., 2017a)
16	Ni-Cu/Al_2O_3. HCO_2H, Me_2CHOH, 210 °C; 7 h	2-methylfuran, 92 %	(Jaatinen et al., 2017)
17	$Cu(NO_3)_2$, $Ni(NO_3)_2$ - C: TiO_2, H_2, 200 °C, 35 bar, 8h	2-methylfuran, 91 %	(Abu-Dief et al., 2016)
18	Cu-Co/Al_2O_3. H_2, Me_2CHOH, 220 °C, 40 bar, 5 h	2-methylfuran, 87 %	(Halilu et al., 2016)
19	MgO catalysts, MeOH, 380 °C	2-methylfuran, 83 %	(Yu and Chen, 2015)
20	Co modified Mo_2C, H_2, 323 K	2-methylfuran, 80 %	(Chieffi et al., 2014)
21	Cu-Pd, Me_2CHOH, 220 °C, 4 h	2-methylfuran and 2-methyltetrahydrofuran total yield: 83.9 %	(Pasha and Puttaramegowda, 2006)
22	Pt -Pd, Me_2CHOH, 493 K, 35 bar, 5 h	furfuryl alcohol, 16 %; tetrahydrofurfuryl alcohol 32 %; 2-methylfuran, 14 %; 2-methyltetrahydro-furan, 18 %; tetrahydrofuran 20 %	(Turtabaev, 2004)

Table 2
Selected examples of reductive transformations of 5-hydroxymethylfurfural (HMF, **2**).

Entry	Catalyst, reaction conditions	Product(s), Yield(s)	Reference
1	Zr/Ca, isopropyl alcohol, 190 °C, 10 h	2,5-furandimethanol, 84 %	(Zhang et al., 2020a)
2	10 % Ni with hydrothermal carbon, 1.5 MPa H_2, 2 h, 180 °C	2,5-furandimethanol, 88 %	(Zhang et al., 2020b)
3	Zr organic-inorganic nanohybrid, Me_2CHOH, 140 °C, 4 h	2,5-furandimethanol, 99 %	(Schmidt et al., 2005)
4	Ru/$MnCo_2O_4$, H_2, MeOH, 100 °C, 8.2 MPa, 16 h	2,5-furandimethanol, 99 %	(Hashemi and Beni, 2000)
5	Ru complex Me_2CHOH, 82 °C	2,5-furandimethanol, 99 %	(Beisekov et al., 1993)
6	CuNPs@ZIF-8, H_2, EtOH,140 °C, 2 MPa, 3 h	2,5-furandimethanol, 99 %	(Xia et al., 2019)
7	Biocatalyst - *Daucus carota* and *Brassica oleracea* extract	2,5-furandimethanol, 99 %	(Petri et al., 2018)
8	Biocatalyst - coconut (*Cocos nucifera L.*) water	2,5-furandimethanol, 99 %	(Amarasekara et al., 2020)
9	Cu- hydrotalcite, H_2, MeOH, 513 K, 1 MPa, 1.5 h	2,5-dimethylfuran, 98 %	(Chatterjee et al., 2014)
10	Co-Cu/N-graphene-Al_2O_3, H_2, THF, 400 °C, 2 MPa, 24 h	2,5-dimethylfuran, 99 %	(Biradar et al., 2014)
11	Pd, H_2, CO_2, H_2O, 80 °C, 10 MPa, 2 h	2,5-dimethylfuran, 100 %	(Chang et al., 2016)
12	$Cu(NO_3)_2$, $Ni(NO_3)_2$, H_2, THF, 220 °C, 4 MPa, 12 h	2,5-dimethylfuran, 94 %	(He et al., 2003)
13	Cu/Al_2O_3, 423 K, 20 bar H_2, 10 h.	2,5-dimethylfuran, 94 %	(Esteves et al., 2020)
14	NiCoTi, 200 °C and 1.5 MPa H_2, 6 h	2,5-dimethylfuran, 96 %	(Ma et al., 2020)
15	Ru/ZSM-5, 180 °C, ethanol, 3 h, 250 psi H_2	2,5-dimethylfuran, 98 %	(Feng et al., 2020)

the catalyst. Recent research has revealed the promising use of mixtures of non-noble metal catalysts with comparable results. For instance, Guo et al. (Guo et al., 2014) reported the use of an alloy catalyst, Cu-Zn-Al (Cu/Zn molar ratio 0.5) and achieved 62 % yield of CPO from furfural, under a H_2 atmosphere at 4 MPa, and 150 °C for 6 h. Furthermore, the catalyst could be recycled for five times with good stability. Likewise, a few other Cu based catalysts are known to be effective, including Cu-Co (Li et al., 2015), Cu-Al_2O_3 (Ramos et al., 2017), Cu-Ni/C (Wang et al., 2016), Cu-ZrO_2 (Zhang et al., 2018), Cu-Ni-Al (Zhu et al., 2014). The Ni-Fe bimetallic catalytic system is another promising non-noble metal system. In this case a catalyst produced from $Ni(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_2{\cdot}9H_2O$ was used with a SBA-15 support, producing CPO in 90 % selectivity from furfural in aqueous medium at 160 °C (Jia et al., 2019). In another instance, Astuti et al. (Astuti et al., 2020) reported the formation of CPO and CPL in 68 % combined yield from furfural using Ni-Fe bimetallic catalytic system on a Ti_2O support and at 170 °C. In general, non-noble metal catalytic systems require elevated temperatures, higher hydrogen pressure, and longer reaction times in comparison with noble metal catalysts, in order to achieve comparable yield and conversion rates.

The possible furfural reduction pathways and products leading to cyclopentanone (**7**) and cyclopentanol (**8**) are shown in Fig. 2. In the initial step furfural is generally catalytically hydrogenated to furfuryl alcohol (**3**); if the solvent is alcohol based, further hydrogenation is favored, leading to tetrahydrofurfuryl alcohol (**4**). Whereas in aqueous environment, furfuryl alcohol (**3**) can get rearranged to intermediate products such as 4-hydroxy-2-cyclopentenone (**5**) and 2-cyclopentenone (**6**). These intermediates may be further reduced to cyclopentanone (CPO, **7**) and cyclopentanol (**8**) in the presence of metal catalysts (Hronec et al., 2014b; Jia et al., 2019).

Similar to furfural, HMF can be catalytically transformed to cyclopentanone derivative 3-hydroxymethyl cyclopentanone (HCPN) in aqueous media under a hydrogen atmosphere at elevated temperatures. In this case the use of Pd/Cu loaded metal-organic framework was used as the catalyst, producing HCPN from HMF in 99.5 % conversion and 90.9 % selectivity in water at 150 °C, under H_2 at 4.0 MPa for 24 h (Deng et al., 2019). The study further reported that the comparable conversion of furfural to CP could be achieved in a shorter time of 12 h. (Deng et al., 2019). In another example, Ohyama et al. (Ohyama et al., 2016) demonstrated the use of acidic metal oxides such as: Ta_2O_5, ZrO_2, Nb_2O_5, TiO_2, Al_2O_3, CeO_2, La_2O_3 as catalysts for the same transformation. Furthermore, among these metal oxide catalysts, Ta_2O_5 performed particularly well for the conversion of HMF to HCPN in 82 % yield, under H_2, at 140 °C, 3.0 MPa for 12 h. In addition, the use of Au nanoparticles, Cu-Al_2O_3 and Co-Al_2O_3 as catalysts is also known for the HMF ring rearrangement in aqueous medium (Ohyama et al., 2014; Ramos et al., 2017). The proposed HMF ring rearrangement reaction pathway is shown in Fig. 3. In the initial step aldehyde group in HMF (**2**) can get reduced to give 2,5-bis(hydroxymethyl)furan (BHMF, **9**). Then a opening in the furan ring followed by a dehydration and hydrogenation provides 1-hydroxy-3-hexene-2,5-dione (**10**) intermediate. A subsequent hydrogenation of this dione may give 1-hydroxyl-2,5-hexanedione (**11**) intermediate. Next, intramolecular aldol condensation of **11** can give rise to 3-hydroxymethyl-(2, 3, or 4)-cyclopentenone (HCPEN, **13**). On the other hand, intramolecular aldol condensation of **10** could produce 4-hydroxy-4-hydroxymethyl-2-cyclopentenone (HHCPEN, **12**). Furthermore, catalytic hydrogenation of HCPEN, **13** may result 3-hydroxymethylcyclopentanone (HCPN, **14**) as the final product (Kong et al., 2018; Ohyama et al., 2014, 2016).

In comparison of these ring rearrangement reactions of HMF and furfural, HMF generally requires more demanding conditions, such as complicated catalytic systems and prolonged reaction times. In furfural ring rearrangement, water is acting as the proton source or the acid and in general complicated acid-base catalysts are not required in the CPO

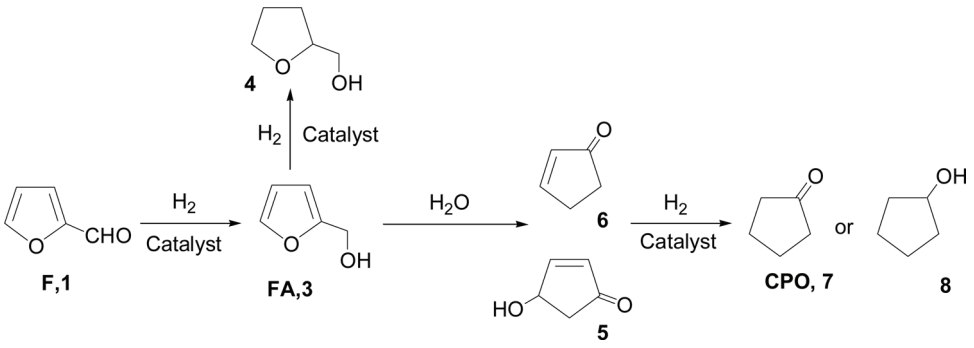

Fig. 2. The possible furfural reduction pathways leading to cyclopentanone (CPO, **7**) and cyclopentanol (**8**).

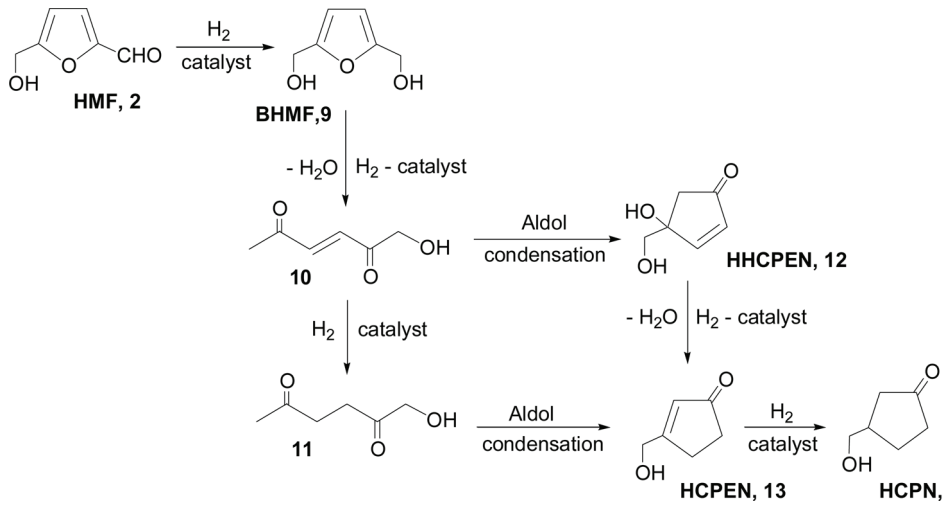

Fig. 3. The proposed HMF ring rearrangement reaction pathways leading to 3-hydroxymethylcyclopentanone (HCPN, **14**).

production from furfural via ring rearrangement pathway (Hronec et al., 2014b; Yang et al., 2013). Whereas in HCPN production from HMF, acid-base catalysis may play a significant role in reducing the energy requirements of the ring rearrangement reaction (Ohyama et al., 2014, 2016).

In summary, catalytic reductive conversions of biofurans have broad possibilities in terms of product variations. Building block chemicals such as furfuryl alcohol, DMF, CPO, HCPN, etc., play significant roles in multiple industries. Both noble and non-noble metal catalysts were reported to be highly effective, while multifunctional catalyst design requires further investigation.

4. Catalytic oxidations of biofurans

Oxidative transformations are the second approach in conversion of biofurans to stable compounds. These transformations can be broadly classified as oxidations of peripheral groups −OH, CHO and furan ring oxidation/opening transformations. The oxidation of F and HMF functional groups can be used to produce relatively more stable oxidation upgrades furoic acid, furan 2,5-dialdehyde and 2,5-furandicarboxylic acid (FDCA).

The oxidation of furfural to 2-furoic acid can be achieved in practically quantitative yields by using a variety of Au, Cu or Mn based catalysts under fairly mild conditions as shown in entries 1,3,4 and 6 in Table 3 (Ferraz et al., 2018; Yu et al., 2018; Hayashi et al., 2017b; Liu and Li, 2016). The bifunctional HMF can give a range of products depending on the oxidation reagents and the conditions used. The oxidation of $-CH_2OH$ provides 2,5-diformylfuran (DFF) as shown in entries 1–9 in Table 4; whereas the oxidation of both groups $-CH_2OH$ and −CHO to acid groups leads to FDCA, as shown in representative entries 13–17 in Table 4. A wide variety of Mn, Cd, Fe, Cu and Rh based catalysts have been used for the production of DFF from HMF (Amarasekara et al., 2008; DiMeglio et al., 2019; Hong et al., 2019; Wei et al., 2019; Chatterjee et al., 2017; Kong et al., 2018). For example, the use of Ru/C catalyst resulted in a 95.8 % yield of DFF at 383 K and 2.0 MPa O_2 pressure in toluene, where in the same study, other tested catalysts including Pt, Pd, and Au produced poor selectivities towards DFF (Nie et al., 2013). Mn and vanadium-based catalysts are the popular choice in oxidation of HMF to DFF (Kong et al., 2018). Noble metal catalysts are widely reported for the oxidative conversion of HMF to FDCA (Table 4, entries 12 and 15–17). For instance, the bimetallic Au–Cu catalysts supported on TiO_2 was used to convert HMF into FDCA in 99 % yield (Pasini et al., 2011). A number of other similar catalysts such as Pt (Ait Rass et al., 2013), Pd (Zhang et al., 2015) and Ru (Gao et al., 2018) are also reported as highly effective in the oxidation of HMF to FDCA. In addition, non noble metal system, MnO_2 in aqueous $NaHCO_3$, under an oxygen atmosphere at 100 °C, is also known to oxidize HMF to FDCA in good yields (Hayashi et al., 2017a).

Then ring fragmentation with oxidation can be used to prepare a number of compounds such as: 2(5 H)-furanone, succinic anhydride and maleic acid. A variety of metal catalysts can be used in this application

Table 3
Selected examples of oxidative transformations of furfural (F, **1**).

Entry	Catalyst, reaction conditions	Product(s), Yield(s)	Reference(s)
1	Au, O_2, 110 °C, 26 bar, 2 h	2-furoic acid, 100 %	(Ferraz et al., 2018)
2	Oxidized graphene (N,P, Co-doped), O_2, t-BuOOH, H_2O, 60 °C, 12 h	2-furoic acid, 96 %	(Yang et al., 2019)
3	Cu-inorganic/organic-ligand supported, Na_2CO_3, H_2O O_2, 50 °C, 12 h	2-furoic acid, 99 %	(Yu et al., 2018)
4	MnO_2, $NaHCO_3$, O_2, H_2O, 100 °C, 1 MPa, 24 h	2-furoic acid, 99 %	(Hayashi et al., 2017b)
5	Biocatalyst - *Deinococcus, wulumuqiensis*, H_2O, 35 °C, 12 h	2-furoic acid, 99 %	(Cang et al., 2019)
6	Cu-1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium,O_2, 100 °C, 1Atm., 24 h	2-furoic acid, 99 %	(Liu and Li, 2016)
7	N-heterocyclic carbene (NHC), Dabco, O_2, THF, rt, 1 Atm., 16 h	2-furoic acid, 99 %	(Khatana et al., 2018)
8	Fe(III), O_2, H_2O, 50 °C, 8 h	2-furoic acid, 99 %	(Yu et al., 2017)
9	Amberlyst-15, H_2O_2, H_2O, 353 K, 24 h	succinic acid,74.2 %; fumaric acid, 0.1 %; maleic acid, 11.0 %; furoic acid, 1.9 %	(Choudhary et al., 2012; Choudhary et al., 2013)
10	SO_3H-cyclodextrin carbon, H_2O_2, H_2O	succinic acid,80 %	(Maneechakr and Karnjanakom, 2017)
11	Graphene oxide, H_2O_2, H_2O, 70 °C	succinic acid,88.2 %	(Zhu et al., 2019)
12	SO_3H-polymer, H_2O_2, H_2O	succinic acid,80 %	(Saleem et al., 2017)
13	$Mg(OH)_2$, H_2O_2, H_2O	2(5 H)-furanone,44.8 %; succinic acid,38.0 %	(Xiang et al., 2016)
14	SO_3H-polybenzoxazine, H_2O_2, H_2O	succinic acid,93 %	(Thubsuang et al., 2020)
15	N-doped carbon, H_2O_2, H_2O, 70 °C	maleic acid, 61 %	(Van Nguyen et al., 2020)

Table 4
Selected examples of oxidative transformations of 5-hydroxymethylfurfural (HMF, **2**).

Entry	Catalyst, reaction conditions	Product(s), Yield(s)	Reference
1	Mn(III)–salen, NaOCl, pH 11.3 phosphate buffer–CH_2Cl_2 biphase system, 23 °C	2,5-diformylfuran, 89 %	(Amarasekara et al., 2008)
2	MnO_2, O_2, PhMe, 25 °C, 1 bar, 6 h	2,5-diformylfuran, 100 %	(Ke et al., 2019)
3	CdS, O_2, UV light, MeCN, 24–48 h	2,5-diformylfuran, 100 %	(DiMeglio et al., 2019)
4	$Fe(NO_3)_3$, O_2, 50 °C, 1 atm	2,5-diformylfuran, 99 %	(Hong et al., 2019)
5	$Cu(NO_3)_2$, O_2, MeCN,H_2O, 80 °C, 8 h	2,5-diformylfuran, 99 %	(Wei et al., 2019)
6	Rh, CO_2, 150 °C, 8 MPa	2,5-diformylfuran, 100 %	(Chatterjee et al., 2017)
7	Mn-Co, O_2, MeCN, 80 °C, 1 bar	2,5-diformylfuran, 97 %	(Ke et al., 2020)
8	Cu-2,2,6,6-tetramethylpiperidin-oxyl-MOF, O_2, DMSO, 120 °C, 0.34 MPa, 3 h	2,5-diformylfuran, 96 %	(Lin et al., 2019)
9	V_2O_5, carbon, O_2, DMSO, 120 °C, 9 h	2,5-diformylfuran, 99 %	(Zhao et al., 2018)
10	Biocatalyst - *Deinococcus, wulumuqiensis*, H_2O, 35 °C, 12 h	5-hydroxymethylfuroic acid, 99 %	(Cang et al., 2019)
11	Fe (III) porphyrin-polymer support, O_2, H2O	2,5-furandicarboxylic acid, 85 %	(Saha et al., 2013)
12	Au-TiO_2, light, Na_2CO_3, H_2O, 30 °C, 8h	5-hydroxymethylfuroic acid, 95 %	(Zhou et al., 2017)
13	Co-Zn-lignin, O_2, H_2O, 85 °C, 1 bar, 8h	2,5-furandicarboxylic acid, 100 %	(Zhou et al., 2019)
14	Mn_2O_3-MOF, $NaHCO_3$, O_2, H_2O, 100 °C, 1.4 MPa, 24 h	2,5-furan dicarboxylic acid, 99 %	(Bao et al., 2020)
15	Pt, O_2, H_2O, 120 °C, 7.7 bar, 22h	2,5-furandicarboxylic acid, 99 %	(Liguori et al., 2019)
16	$RuCl_3$, O_2, H_2O, 120 °C, 1 MPa, 24 h	2,5-furandicarboxylic acid, 100 %	(Gao et al., 2018)
17	Pt nanoparticles, Fe_3O_4-C, Na_2CO_3, O_2, H_2O, 90 °C, 4 h	2,5-furandicarboxylic acid, 100 %	(Zhang et al., 2016b)

and Cu or Au based catalysts are well known in oxidation of furfural to more stable furan-2-carboxylic acid with oxygen as the oxidant (Ferraz et al., 2018; Liu and Li, 2016). Conversion to more stable levulinic acid is also reported with the use of Cu-doped niobium phosphate (Fang et al., 2019) and water soluble Ru based catalyst (Gupta et al., 2015). In another example Amarasekara and Okorie have recently shown that 1-(3-alkylsulfonic)-3-methylimidazolium chloride acidic ionic liquids (**15**, Fig. 4) can be used as a metal-free catalyst in the hydrogen peroxide oxidation of biofurans (Amarasekara and Okorie, 2018). In this case, HMF was converted to succinic anhydride in 90–92 % yield by oxidation with 30 % hydrogen peroxide using 10 mol % 1-(3-alkylsulfonic)-3-methylimidazolium chloride acidic ionic liquid catalysts at 60 °C for 14 h. The acidic ionic liquid catalyst could be reused for four catalytic cycles without appreciable loss in catalytic activity. On the other hand oxidation of furfural (F, **1**) under similar ionic liquid catalyzed conditions produced a mixture of three products: 2(5 H)-furanone (**16**), succinic anhydride (**17**) and maleic acid (**18**) in 68, 8 and 12 % yields respectively as shown in Fig. 4. (Amarasekara and Okorie, 2018). Additional selected recent examples of catalytic oxidations of F and HMF are shown in Tables 3 and 4 respectively.

The most significant oxidation product from biofurans is FDCA, which is one of the twelve most valuable platform chemicals produced from biomass, as listed in a priority list prepared by the US Department of Energy (Kong et al., 2018). The oxidations of both alcohol and aldehyde groups in HMF are required to produce FDCA. A list of catalysts and reaction conditions used for this transformation is outlined under entries 13–17 in Table 4. The use oxygen gas as the oxidant together with noble metal catalysts such as Au, Pt and Ru is common in this relatively easily scalable transformation (Zhou et al., 2017; Liguori et al., 2019; Gao et al., 2018; Zhang et al., 2016b).

The majority of catalysts applied in biofuran upgrade reactions are solid metal or metal oxide catalysts with major advantages in the ease of reusability. In most cases, simple filtration and wash is enough to restore the catalysts capability. For example, MnO_2 catalyst used for FDCA production from HMF was able to be recycled for five times without significant decrease in catalytic performance by simple filtration (Hayashi et al., 2017a). In addition, research has been done on incorporation of Fe_2O_3 with noble metal catalysts, in order to achieve magnetic separation. For instance in FDCA preparation, a Pd based catalyst γ-Fe_2O_3@HAP-Pd(0) was introduced to achieve 93 % yield and more importantly, the catalyst was readily recycled by applying an external magnetic field (Zhang et al., 2015).

5. Catalytic carbon number upgrading reactions of biofurans

Further upgrade of biofurans or their derivates also plays an important role in the utilization of biofurans. With 5 or 6 carbon atoms can be upgraded to fuel intermediates and polymer feedstocks with more than 6 carbons by condensation with other small molecules or by self-condensations. The use of reactive small molecules with renewable resources based routes such as acetone can lead to an all renewable carbon based product. A number of catalytic carbon-carbon bond making techniques such as aldol condensation and benzoin condensation have been tested for this approach of upgrading biofurans. Aldol condensation between ketones and aldehyde group of biofurans is an ideal upgrade process for biofuel production, which leads to long chain molecules that can undergo further hydrodeoxygenation to produce high quality fuels or fuel additives. Acetone and related 2-butanone are common starting materials for aldol condensation with furans due to their wide availability. Acetone can be produced by acetone–butanol–ethanol (ABE) fermentation process (Liao et al., 2015; Sreekumar et al., 2015; Kheyrandish et al., 2015) and 2-butanone can also be obtained by microbial production methods (Bramucci et al., 2008). The first aldol condensation with acetone (**19**) gives the C8 product, furfuryldeneacetone (**20**), which can further condense with furfural to produce C13 compound, 1,5-bis(2-furanyl)-1,4-pentadien-3-one (**21**) as shown in the reaction scheme in Fig. 5. Subsequent hydrodeoxygenation of the C═O, C—O, and furan ring reduction can be achieved with hydrogenation in the presence of Pd or Pt catalysts, producing alkanes compatible to alkanes in petroleum hydrocarbon fuels. Faba et al. (Faba et al., 2012) have demonstrated the use of Mg and Zr mixed-metal oxide Lewis acid catalysts for the aldol condensation, achieving C13 product in over 60 % yield. A number of other inexpensive solid Lewis acids such as active dolomite (O'Neill et al., 2014), calcined hydrotalcites (Guida et al., 1997), Mg/Al layered double hydroxides (Hora et al., 2014; Liu et al., 2010), have also been used as

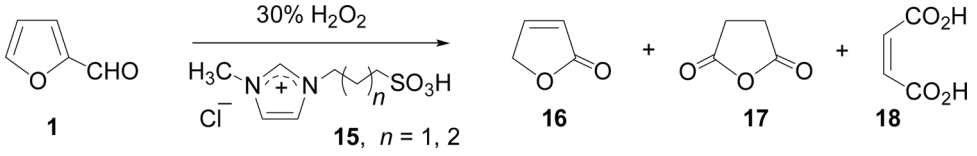

Fig. 4. 1-(3-Alkylsulfonic)-3-methylimidazolium chloride (**15**) catalyzed hydrogen peroxide oxidation of furfural (**1**).

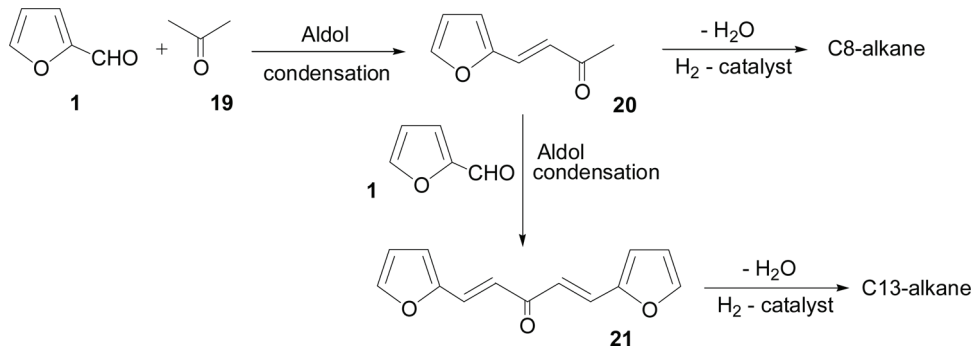

Fig. 5. Reaction pathways for the conversion of furfural (**1**) to higher carbon number alkanes through aldol condensations.

effective catalysts for the furfural-acetone aldol condensations under similar conditions. Meanwhile, Pt/Al_2O_3 was found to be an effective catalyst for the hydrodeoxygenation of both C8 and C13 aldol condensation products, yielding n-octane and n-tridecane in 25 % and 22 % yields respectively, under H_2 at 5.5 MPa and 493 K (Faba et al., 2014, 2016).

Similar to furfural, HMF (**2**) and acetone (**19**) can form the C9 compound (**22**) via aldol condensation, which could further react to give the C15 adduct (**23**) with another equivalent of HMF as shown in Fig. 6. In addition, C═C bonds in HMF can be hydrogenated as it was shown under the reductive upgrading of HMF, thus providing 5-hydroxymethyl tetrahydro furfural (**24**). This aldehyde is known to undergo self-condensation to give the C12 compound (**25**) as shown in the second reaction scheme in Fig. 6. These C9-C15 range aldol upgraded compounds can be hydrodeoxygenated into C9-C15 alkanes, hence providing hydrocarbon products similar to petroleum derived alkanes. The mixed metal oxide catalysts such as $MgO\text{-}ZrO_2$ (Barrett et al., 2006), $Cu/MgAl_2O_4$ (Pupovac and Palkovits, 2013) and $Pt/SiO_2\text{-}Al_2O_3$ (Kong et al., 2018) are suitable for the aldol condensation between HMF and acetone as well as hydrodeoxygenation under a hydrogen atmosphere; consequently providing a one-pot combined process for producing synthetic fuel grade hydrocarbons from biofurans.

Since the aldol condensations of furfural and HMF have similar reaction conditions, direct conversions of biomass-derived biofurans is achievable in mixtures as well. Barrett et al. (Barrett et al., 2006) have demonstrated the use of a novel bifunctional $Pd/MgO\text{-}ZrO_2$ catalyst, which is capable of achieving the one-pot aldol condensation - hydrodeoxygenation of furfural, HMF mixture in aqueous phase; the dimer (C13–C15) selectivity reached over 60 % yield at the optimum temperatures around 326−353 K, and the catalyst could be reused after restoring the activity after calcination at 873 K. The application of Brønsted acidic ionic liquids (BAIL) as catalysts has further advanced the approach by allowing the use of cellulose or raw cellulosic biomass as the feedstock. In this case BAILs were used as multi-tasking catalysts for cellulose depolymerization, dehydration of sugars to biofurans and aldol condensation with acetone to directly produce furanic bio-crude oils from cellulose and biomass (Amarasekara and Gutierrez Reyes, 2019; Amarasekara and Wiredu, 2014). In a more recent development of using BAIL catalysts for upgrading biofurans, Amarasekara and Reyes have produced furanic bio-crude with biofuran aldol products in over 40 % yield from corn cobs and switchgrass (Amarasekara and Gutierrez Reyes, 2020). In the second step, this product was catalytically hydrogenated in aqueous methanol at room-temperature and atmospheric pressure using 5% Pd-C catalyst to further upgrade the aldol products to a complex mixture of C4 - C17 products (Amarasekara and Gutierrez Reyes, 2020).

One of the major drawbacks of biofuran aldol condensation is the formation of significant amounts of humins via polymerization, which could hinder the activity of catalysts and reduce carbon yields (Li et al., 2020). However, cyclopentanone, the product from furfural ring rearrangement as described earlier in the review under reduction products is more stable under aldol reaction conditions; which makes it more suitable for both self and cross-condensation with furans (Cueto et al., 2017). The possible pathways of CPO (**7**) aldol condensation with furfural (**1**) and HMF (**2**) are shown in Fig. 7. In the self-condensation, α-carbons in CPO can react with one or two other CPO molecules to form C10 or C15 molecules: 2-cyclopentylidene-cyclopentan-1-one (**26**)

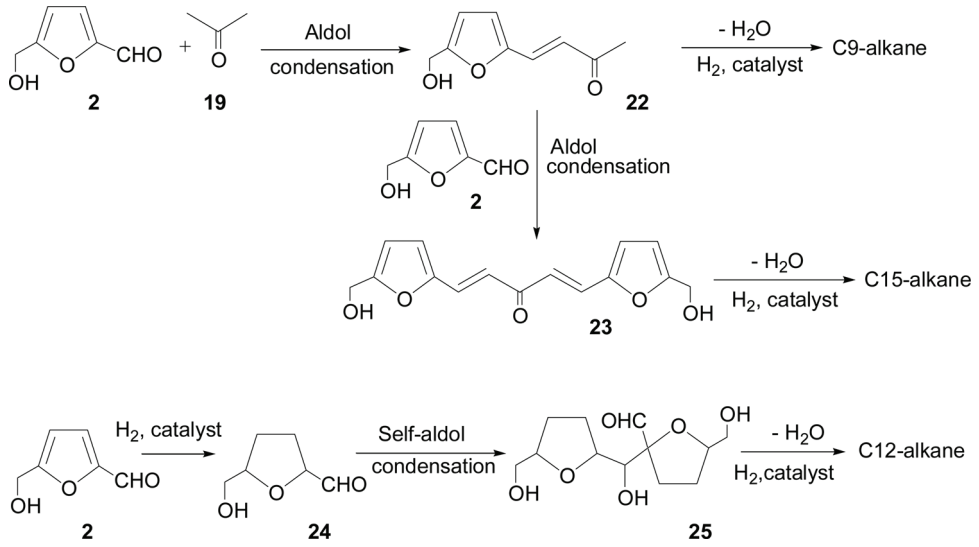

Fig. 6. Reaction pathways for the conversion of HMF (**2**) to higher carbon number alkanes through aldol condensations.

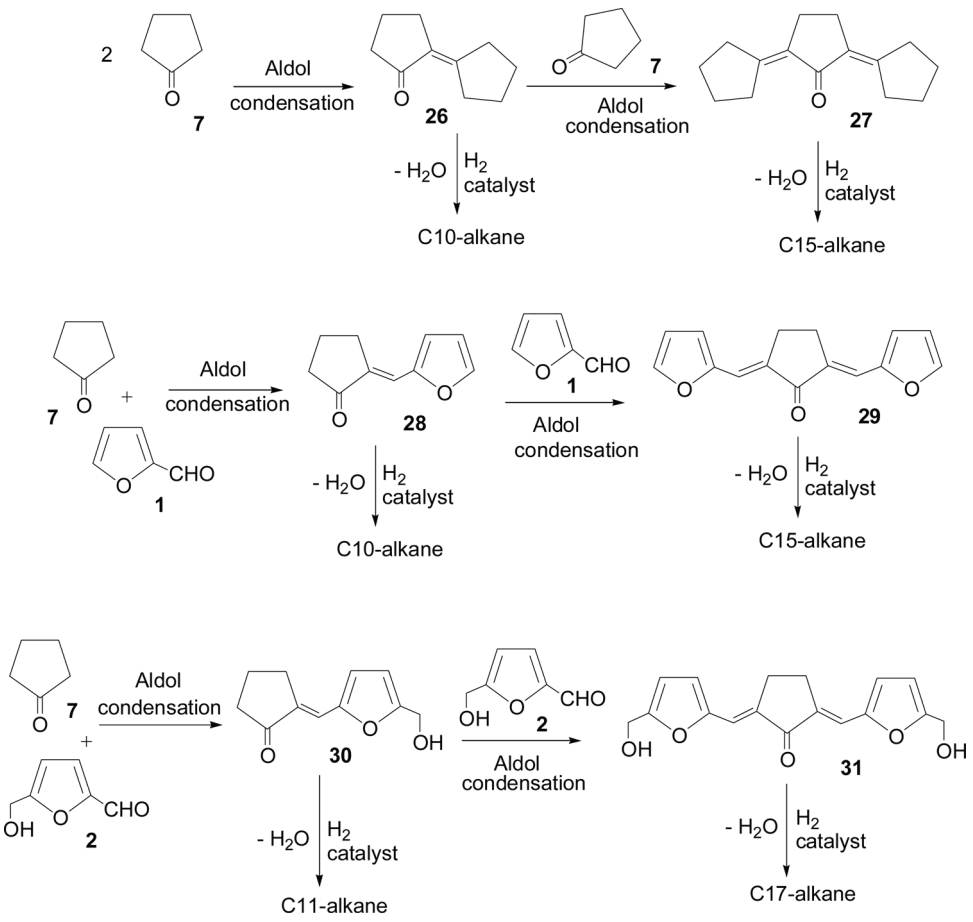

Fig. 7. Reaction pathways for the catalytic conversion of cyclopentanone (CPO, **7**) to higher carbon feedstocks by self-aldol and cross-aldol with furfural (**1**) and HMF (**2**).

and 2,5-bis-cyclopentylidene-cyclopentan-1-one (**27**). These products could be further upgraded to corresponding cycloalkanes by hydrodeoxygenations. Similarly, in cross-aldol condensation with furfural and HMF, α-carbons in CPO may react with aldehyde groups in furfural or HMF resulting the C10 to C17 aldol condensation products: 2-(2-furylmethylidene) cyclopentan-1-one (**28**), 2,5-bis (2-furylmethylidene) cyclopentan-1-one (**29**), 2-(5-hydroxymethyl-2-furylmethylidene) cyclopentan-1-one (**30**), and 2,5-bis (5-hydroxymethyl-2-furylmethylidene) cyclopentan-1-one (**31**). These aldol products can also be further upgraded to C10-C17 cycloalkanes by the subsequent hydrodeoxygenations as shown in Fig. 7.

The Lewis acid ZrO_2 have been used as a catalyst for self-aldol condensation of CPO achieving a 47 %, conversion at 200 °C after 1.5 h; where the CPO dimer to trimer ratio was found to be 10:1 (Li et al., 2020). In another example, Liang et al. (Liang et al., 2016) reported the use of Mg/ZrO_2 as the catalyst at 403 K; self-aldol condensation of CPO could be achieved at a conversion rate of 100 % with 84.6 % selectivity towards CPO dimer. Furthermore, Hronec et al. (Hronec et al., 2014a) have demonstrated the cross-aldol condensation between furfural/HMF and CPO, using sodium hydroxide as a homogeneous catalyst at 40 °C for 3 h. In this case they have achieved an impressive 95 % yield of C15 compound: 2,5-bis (2-furylmethylidene) cyclopentan-1-one and 98 % yield of C17 compound: 2,5-bis (5-hydroxymethyl-2-furylmethylidene) cyclopentan-1-one (Hronec et al., 2014a).

The aldol condensation between biofurans and other renewable feedstocks such as levulinic acid is also known (Amarasekara et al., 2015). The NaOH catalyzed condensation reaction between HMF (**2**) and levulinic acid (**32**) in water is reported to give a 2.5: 1 mixture of aldol products: (*E*)-6-[5-(hydroxymethyl)furan-2-yl]-hex-4-oxo-5-enoic acid (**33**) and (*E*)-3-[5-(hydroxymethyl)furan-2-yl]methylene-4-oxo-pentanoic acid (**34**) in 82 % combined yield as shown in Fig. 8 (Amarasekara et al., 2015).

Benzoin type condensation is another C—C bond making technique used to build C10 and C12 compounds from biofurans. A variety of catalysts such as: polymer supported N-heterocyclic carbenes (Cywar et al., 2018; Wang and Chen, 2015; Zang and Chen, 2015) montmorillonite supported thiazolium ionic liquids (Yan et al., 2016), and 1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene (Liu and Chen, 2013) have shown promise in dimerization of furfural and HMF through this coupling method. The dimerization of HMF (**2**) to a C12 furoin compound (**35**) via benzoin condensation is shown in Fig. 9. The acid catalyzed dimerization to an ether is another approach for the conversion of HMF to relatively more stable C12 dialdehyde-ether 5,5′-[oxybis (methylene)]bis[2-furaldehyde] (Mliki and Trabelsi, 2015; Amarasekara et al., 2017; Amarasekara et al., 2019). This etherification can be carried out after isolation of HMF or as an in-situ reaction at the dehydration of monosaccharide. Furthermore, this upgraded HMF dimer has been used in the preparation of a dicarboxylic acid monomer for the preparation of renewable polyesters (Amarasekara et al., 2017).

Carbon number upgrade of biofurans or their derivates is particularly important in biofuel industry since C8-C17 alkanes are well suited as fuels or fuel additives. However, the major challenges in currently available processes are high energy consumption, catalyst reuse and efficient product purification. Further research on reusable, inexpensive catalyst systems and reaction condition optimizations could be potential solutions to these current challenges.

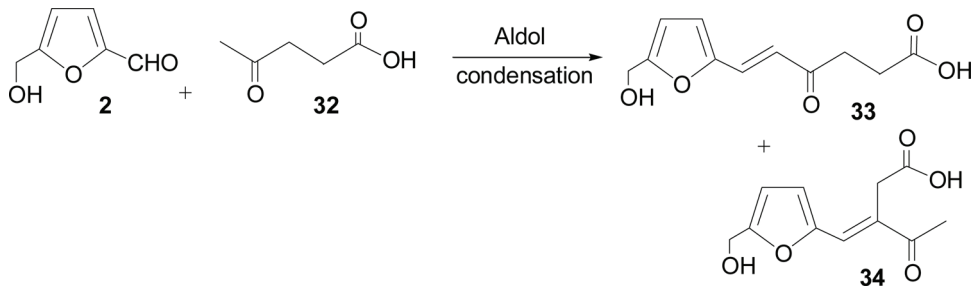

Fig. 8. The NaOH catalyzed condensation reaction between HMF and levulinic acid in water.

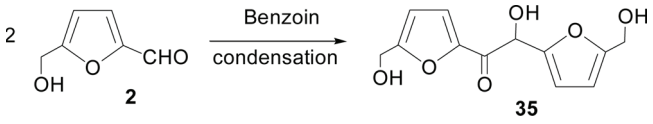

Fig. 9. The Benzoin type condensation reaction as a carbon number upgrading method for 5-hydroxymethylfurfural (**2**).

6. Concluding remarks

The biomass derived furans, furfural and 5-hydroxymethylfurfural have emerged as two leading feedstock chemicals for a sustainable carbon-based future. However, there are a number of hurdles associated with these biofurans such as efficient production from the cellulosic faction of biomass, instabilities of these aldehydes under storage and the tendency for polymerization to humins. The most widely accepted solution for the instability problem is upgrading to more stable value added chemicals. The central theme of this review is to show the recent advances and the range of catalytic methods available for upgrading biofurans into next generation feedstock for renewable fuels and chemicals. The cost of the catalysts used is particularly relevant in the context of fuels as we are looking for cost competitive renewable alternatives to fossil resources in a massive scale. Therefore, catalysis processes based on non-noble metal abundant elements are very attractive in upgrading biofurans.

The future of catalytic upgrading of biomass derived furans is promising, since there are a number of biofuran derived feedstocks such as 2,5-dimethylfuran, cyclopentanone and 2,5-furandicarboxylic acid (FDCA) showing commercial production prospects. 2,5-Furandicarboxylic acid stands out in this respect as this symmetrical aromatic diacid has been considered as a potential replacement and the renewable resources based equivalent of terephthalic acid, which is a monomer in polyethylene terephthalate (PET) plastics (Werpy et al., 2004). The market for terephthalic acid exceeds 50,000 ktons/year, demonstrating the large potential for FDCA for the preparation of polyethylene furanoate (PEF) as a replacement for PET (Eerhart et al., 2012). With presumptive use of 2,5-furandicarboxylic acid as a substitute for terephthalic acid together with biomass based diols allows the preparation of completely renewable polyesters, leading to a significant reduction of greenhouse gas emissions (Eerhart et al., 2012). In addition, potential applications of this diacid monomer include its use in the manufacture of polyamides and polyureas as well (Benecke et al., 2007; King et al., 2008; Mitiakoudis and Gandini, 1991; Moreau et al., 2004; van Es, 2013). However, improvements in catalyst recycling methods are essential in development of profitable commercial processes from the reactions discussed in this review. Oxidative transformations of biofurans to produce well established feedstocks such as succinic and maleic acids are also industrially feasible; however the carbon loss in the reaction may have a negative impact on the overall process. In addition, acid or base catalyzed aldol condensation of biofurans with ketones like acetone and cyclopentanone has emerged as an active field in development of 100 % renewable resources based synthetic hydrocarbon fuels. The next generation of breakthroughs in catalytic biofuran upgrading can be expected in the application of inexpensive Fe, Ni, Cu based catalytic systems, and scaling up of these processes for future biorefinery. Overall the catalytic upgrading of biofurans has grown into an active research discipline with a promising future.

Declaration of Competing Interest

Authors declare that they have no financial or personnel conflicts of interest.

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